

A THERMODYNAMIC STUDY OF THE SILICON-OXYGEN
EQUILIBRIUM IN LIQUID IRON.

THESIS

presented for

The Diploma of Imperial College

by

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ABSTRACT.

The reaction



does not express adequately the ferrous oxide equilibrium with silicon in liquid iron. The total silicon concentration measured by analysis is larger than the amount required to satisfy the equilibrium constant relationship $K = (\text{FeO})^2(\text{Si})$. This discrepancy in the silicon content increases as the oxygen pressure of the system increases.

The product $(\text{FeO})^2(\Sigma \text{Si})$ was determined over the range of ferrous oxide activity, 2.0 to 40×10^{-3} wt.%, for temperatures from 1550°C. to 1700°C., at 25° intervals. This product was found to increase linearly with increase of ferrous oxide activity at constant temperature.

The discrepancy in the silicon content is interpreted in terms of the presence of dissolved silicon monoxide in the liquid iron phase. The total silicon analysed is regarded as the sum of the dissolved silicon and silicon present as silicon monoxide. The reactions expressing the equilibria are represented by the equations:



The experimental data obtained allow the equilibrium constants of the above reactions to be determined, and also their variation with temperature.

The standard free energy changes for the two reactions are derived and compared with the data obtained by other workers.

C O N T E N T S

Pages

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SECTION I. INTRODUCTION

General Survey	1 - 2
Indirect Method for determining ΔG° .	2 - 3
Direct Method for determining ΔG° .	3 - 5
The Fe - O - Si - H System	5 - 7
A Survey of Previous Investigations	7 -16
A Survey of the Work of Zapffe and Sims	16 -26

SECTION II. APPARATUS

Molybdenum-wound Furnace	27 -31
The Optical Pyrometer	31 -33
The Ratharometer	33 -37
The Hydrogen Flow Apparatus	37 -39
The Oxalic Acid Saturator	39
Saturation using Calcium Chloride Solution	39-40
The Reflux Saturator	40 -41
The Dew Point Apparatus	42 -43
The Interior of the Furnace	43 -44
The Argon Purification Apparatus	44 -45

SECTION III. EXPERIMENTAL TECHNIQUE

The Analysis of Total Silicon Content	46 -50
Preliminary Experiments to show the Presence of an Equilibrium	50 -54
The Reduction of the System	54 -56
The Oxidation of the System	56 -59
Some Preliminary Equilibrium Measurements	59 -63
Procedure adopted for Investigating the Equilibrium	63 -69
Thermal Diffusion	69 -72
Ordinary Gas Diffusion	72 -73
Quenching in Argon	73 -74
Technique adopted for Measurements at high Oxygen Pressures	75 -78

SECTION IV. RESULTS

The Ferrous Oxide Activity in Liquid Iron	79 - 82
Results from Direct Experiment	82 - 84
Interpolation of the Isotherms	84 - 91
The Interpretation of the plots (FeO) ² (Σ Si) against (FeO)	92 - 95
The Statistical Analysis	95 - 97
The Thermodynamic Properties of the System	97 - 99
Results from Runs at High Oxygen Pressures	99 - 101

SECTION V. THE PHOTOMICROGRAPHIC EXAMINATION OF MELTS	102 - 106
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SECTION VI. DISCUSSION	107 - 115
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SECTION I

INTRODUCTION.

It is desirable that in the process of steelmaking the quantity of each constituent present should be controlled so that the steel produced has the desired properties. To achieve this end it is necessary to have a knowledge of the thermodynamic properties of each of the reactions involved by the constituents.

Many problems exist in steelmaking on a plant scale such as unequal distribution of one of the components in the liquid or slag phase. These problems may be overcome by conducting experiments on a laboratory scale and thereby reducing the size of the melt to more manageable proportions. Also, when such experiments are carried out in the laboratory, each of the variables may be controlled much more closely.

One of the most important factors controlling the process of steelmaking is the oxygen content of the steel in each of its stages of production. The oxygen content can be, and is, reduced by the various constituents, carbon, manganese, silicon, phosphorus, etc., the degree of deoxidation depending on the relative deoxidising power of the constituent. This relative deoxidising power is best assessed by comparing the standard free-energy

change for the general reaction involving the reduction of ferrous oxide by each of the substances.



In general the standard free energy change for a reaction may be determined in either of two ways: directly, from an experimental determination of the equilibrium constant or electrical measurements, or indirectly by calculation from heats of reaction and entropy and specific-heat data.

The Indirect Method.

The Van't Hoff Isochore relates the variation of the equilibrium constant with temperature to the heat of reaction:

$$d \ln K / dt = \Delta H / RT^2$$

ΔH is the heat of reaction, which may be expressed in terms of the specific heats of the products and reactants by the Kirchoff equation.

$$d(\Delta H) / dt = \Delta C_p$$

where $\Delta C_p = \sum C_p (\text{products}) - \sum C_p (\text{reactants})$

ΔC_p is usually expressed in the form of the equation:

$$\Delta C_p = \Delta \alpha + \Delta \beta T + \Delta \gamma T^2 \dots\dots$$

the constants $\Delta \alpha$, $\Delta \beta$, and $\Delta \gamma$ being derived

from corresponding equations that best fit the plots of C_p

against temperature for each of the reactants and products.

Integration of the Kirchhoff equation gives

$$\Delta H = \Delta H_0 + \int \Delta C_p \cdot dT$$

and the isochore may be rewritten

$$d(\log K)/dT = \frac{H_0}{RT^2} + \frac{\Delta\alpha}{RT} + \frac{\Delta\beta}{2R} + \frac{\Delta\gamma}{3R}$$

which when integrated gives

$$\ln K = -\Delta H_0/RT + \frac{\Delta\alpha}{R} \times \ln T + \Delta\beta T/2R + \Delta\gamma T^2/6R \dots k$$

$$\text{or } -\Delta G^0 = RT \ln K = -\Delta H_0 + \Delta\alpha T \ln T + \Delta\beta T^2/2 + \Delta\gamma T^3/6 + IT$$

Sometimes this equation is better expressed in other forms, each of which is governed by the form of the specific heat equation used for the participating materials.

Substitution of the constants in the above equation will give the standard free energy change for the reaction considered.

The Direct Methods.

For special types of reactions involving electrolytes, the free energy of reaction may be determined by measuring the E.M.F. of a reversible cell.

If the equilibrium constant of a reaction is determined experimentally at some temperature, then from it may be

calculated the free energy of reaction for that temperature. A study of the equilibrium constant over a temperature range will provide the heat of reaction for that range and the entropy change.

The relation between the standard free energy of reaction, the absolute temperature and the equilibrium constant is given by the reaction isotherm. The values of the standard free energies of reaction calculated from the equilibrium constants are plotted against the absolute temperature. From the gradient and intercept of the straight line plot obtained, the heat of reaction and entropy change may be estimated according to the relationship

$$\Delta G = \Delta H - T \Delta S$$

The equilibrium constant is usually expressed in terms of the activities of the products divided by the activities of the reactants, the activities being raised to the ^{wer}point indicated by the reaction equation. The activities are usually expressed as partial pressures in gas reactions and as mol fractions in reactions in solution. Often it is convenient to express concentrations in terms of weight percentages and, providing the units of concentration are carefully specified, this leads to no serious error.

Weight percentages are proportional to mol fractions only if the density of the phase in which measurements are made does not alter when the concentration of one or other of the constituents is altered. This assumption may be made only for relatively small concentration ranges. Throughout this work, concentrations will be expressed in terms of weight percentages.

The Fe-O-Si-H. System.

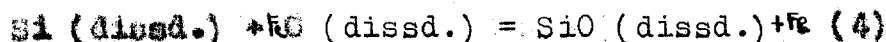
The melting point of pure iron is $1535^{\circ}\text{C}.$, and it is equilibrium in the liquid iron phase above this temperature that is to be studied. The crucible will always saturate the iron with the substance of which it is formed, even though the saturation concentration may be vanishingly small. Silica crucibles, in general, were used as they did not introduce any substance in the liquid iron phase, other than silica, which was already a participant in the equilibrium. The three phases present were the metallic liquid phase, the solid crucible phase and the gas phase which forms the atmosphere surrounding the melt.

The partial oxygen pressure in the furnace atmosphere may be used to calculate the ^{ferrous oxide} oxygen activity in the liquid iron. For the appropriate range of ^{ferrous oxide} oxygen activities the

partial oxygen pressures in the gas phase are too small to be controlled by the direct introduction of oxygen at low pressures, but suitable pressures may be obtained from the dissociation of water vapour. The oxygen pressure of the system was controlled accurately by using an atmosphere of hydrogen with small amounts of water vapour; the oxygen pressures used were always high enough to prevent the reduction of the silica crucible to free silicon.

The equilibrium between the three phases will now be considered from the standpoint of the phase rule. The number of degrees of freedom for a chemical equilibrium is not determined by the number of components solely but rather by the number of independent components. This term is defined as "the minimum number of components the presence of which is necessary and sufficient for building up the system without restricting the proportions of the phases." (H. Schenck. The Physical Chemistry of steelmaking, 1932, 1, Berlin).

The following are the reactions involved:





The number of independent components is clearly four.

By application of the phase rule, these phases always being present, the number of degrees of freedom must be three. These may be temperature, pressure, and the concentration of one of the components. Fixing of these variables defines the system completely from the phase rule viewpoint.

A Survey of Previous Investigations.

In the past the silicon content of molten iron in equilibrium with ferrous oxide has been represented by the following reaction:



A. I. Field (Trans. Faraday Soc., 1925, 21, 295) was the first investigator to try to obtain the equilibrium constant for the above reaction. From the analyses obtained by B. Stoughton ("Metallurgy of Iron and Steel", 1932, p.146, New York) during the course of one basic open-hearth heat, Field derived the product $(\text{FeO})^2(\text{Si})$, where (Si) was the total silicon analysis and (FeO) was the ferrous oxide concentration derived from the solubility product of the manganese reaction.



This solubility product was derived from the total Mn content and (FeO) obtained from the data of Tritton and Hanson (J. Iron & Steel Inst., 1924, 110, 90). The measurement of temperature was not accurate, ~~only~~ the estimated value being 1530°C . The value of $(\text{FeO})^2(\text{Si})$ is given as 0.17×10^{-4} when the (FeO) is 0.0115%, all values being expressed as weight percentages.

At the same time A. McCance calculated the equilibrium constant for the reaction from early thermochemical data (Trans. Faraday Soc., 1925, 21, 176). He obtained a value of 0.56×10^{-4} at 1600°C .

C. H. Herty and G. R. Fitterer (U.S. Bur.Min., Min. & Met. Invest., Coop. Bull. No.36, 1928) investigated the deoxidation of liquid steel on a laboratory scale. Small ingots were made at a temperature somewhere near 1600°C and the ferrous oxide was determined by a modification of the Ledebur method previously used by the same authors and their co-workers (Carnegie Inst. Technol., 1927, Bull. No.34). The silicon content was determined by the Dickenson extraction method, which gave a total silicon analysis less the amount of silicon present as inclusions. In terms of weight percentages the constant was found to be

1.49×10^{-4} .

C. H. Herty, G. F. Christopher and R. W. Stewart (Carnegie Inst. Technol., 1930, Bull. No.38) obtained another value for this equilibrium constant using the same method of analysis as did Herty and Pitterer (loc. cit.), but the samples were taken from experiments carried out on a plant scale. The constant was now found to be 2.07×10^{-4} for a temperature in the region of 1600°C .

C. H. Herty, G. R. Pitterer and G. F. Christopher (U.S. Bur. Min., 1931, Tech. Paper No.492) claimed that the average of the laboratory result and the plant-scale result for the equilibrium constant would give an accurate estimate of the value of the constant for the reaction. They suggested that their result was higher than that of A. L. Field (loc. cit.) because he did not take the precaution of saturating his iron with silica. The average result of the two constants was given as 1.65×10^{-4} in the range (FeO) between 0.05 and 0.4%.

H. Schenck (Archiv. Eisenhüttenw., 1930-31, 4, 319; Stahl u. Eisen, Düsseldorf, 1931, 51, 292) investigated the equilibrium of the two reactions:



The equilibrium constants for each reaction were calculated from experimental data on the assumption that the Mn and Si were contained in the slag mainly as the orthosilicate Mn_2SiO_4 . Samples were taken from acid Siemens-Martin fusions and Bessemer Converter fusions, at temperatures between 1500°C . and 1675°C . The oxygen and silicon were determined by analysis and expressed in terms of weight percentages, giving an equilibrium constant of 0.28 and 0.044×10^{-4} , at temperatures of 1600°C . and 1527°C ., respectively.

The same worker later (The Physical Chemistry of Steelmaking, 1932, 1, Berlin) derived this constant from thermodynamic data. The three phases silica, metallic solution, and a gaseous phase. The oxygen pressure due to oxygen in the iron phase must adjust itself to the value fixed by the presence of free silica.

$$K_{\text{Si}} = (\text{FeO})^2(\text{Si}) = \frac{P^1(\text{Si})_{\text{max.}}}{D_{\text{FeO}}}$$

where P^1 is the dissociation of pure silica, D_{FeO} is the dissociation constant of ferrous oxide in metallic solution and $(\text{Si})_{\text{max.}}$ is taken as the maximum silicon concentration, which must be 100% as silicon is soluble in all proportions in liquid iron. The value derived by this method was

2.5×10^{-4} at a temperature of 1600°C .

F. Korben and W. Oelsen (Mitt. Kaiser-Wilhelm-Institut für Eisenforschung, 1933, 15, 271) made a study of the relative deoxidising powers of elemental manganese and silicon in liquid iron. The equilibrium measurements were derived from the analyses of small ingots contained in specially prepared silica crucibles and covered with a slag phase.

The equilibrium constant of the reaction involving the reduction of silica with iron to dissolved silicon was expressed in terms of the square of the concentration of ferrous oxide in the slag phase and the silicon content of the liquid iron phase. The constant so obtained was modified to express the reaction in the liquid phase by including the partition coefficient of the ferrous oxide between the slag phase and the liquid phase. The modified constant obtained at the temperature 1600°C . was 7.1×10^{-4} .

The oxygen content of the iron was determined by the vacuum fusion technique and the silicon by direct analysis. No attempt was made in this investigation to control the furnace atmosphere or to ensure that equilibrium was obtained with the atmosphere.

A. M. Portevin and R. Perrin (J. Iron Steel Inst., 1933, 27, 153) made an extensive examination into the cause of inclusions in steel. In this work the silicon content of a sample was reported as 0.29% for a ferrous oxide activity of 0.05% in the region of 1600°C. These results produced an equilibrium constant of 6×10^{-4} at this temperature.

The next attempt made was that of J. Chipman (Trans. Amer. Soc. Metals, 1934, 22, 420) who calculated the value of the equilibrium constant from the thermodynamic data of K. K. Kelley (U.S. Bur. Min., 1932, Bull. No. 350) and of W. A. Roth (Naturwissenschaften, 1931, 19, 860) for the reaction:



From these data the standard free energy of reaction was obtained:

$$\Delta G^\circ = -142,440 + 56.25 T$$

which at a temperature of 1600°C. gives an equilibrium constant of 0.48×10^{-4} . Chipman did not claim great accuracy and suggested that Herty's values of 1.49 - 1.65 $\times 10^{-4}$ were better estimates.

W. Gelsen and G. Kremer (Mitt. Kaiser-Wilhelm-Institut

"fur Eisenforschung, 1936, 18, 89) recalculated the equilibrium constant from selected data in the work of Körber and Oelsen (loc. cit.). The value of the constant arrived at was 11×10^{-4} at 1600°C .

H. Schenck and O. Bruggemann in a survey of reactions of interest in steelmaking entitled "Investigations of open-hearth practice" (Archiv. Eisenhüttenw. 1936, 9, 543) reported on some test samples taken from an acid open-hearth furnace. No indication is given of the technique used and the value given for the constant is given as 3.55×10^{-4} , at a temperature of 1600°C .

A. McCance (J. Iron & Steel Inst., London, Special Report No. 22, 1938, p.348) showed that from Körber and Oelsen's results the heat of reaction for the equation considered was 148 kg.-cal per g.-mol. However, the heat of formation of silica and ferrous oxide would lead to a heat of reaction of only 78.5 kg.-cal per g.-mol., and this difference was attributed by McCance to the heat of solution of ferrous oxide in liquid iron. When a correction was made from the equation for the heat of solution determined by Körber and Oelsen, a heat of reaction of 138 kg.-cal. per g.-mol. was obtained, which is in

satisfactory agreement with the value obtained by direct determination.

P. Harasymenko (Trans. Faraday Soc., 1938, 34, 1245) made an investigation of this reaction by taking samples with a ladle from the hearth of an acid open-hearth furnace. Temperature corrections were made for the emissivity of the iron and for the cooling that inevitably took place as the sample was withdrawn, an accuracy of $\pm 10^{\circ}\text{C.}$ being claimed. The equilibrium constant for the reduction of ferrous oxide by dissolved silicon was expressed in terms of the silicon content of the liquid phase and the ferrous oxide content of the slag phase. Correction was then made using Korber and Oelsen's partition function so that the constant could be expressed in terms of the ferrous oxide concentration of the liquid phase. The constant was calculated to be 11×10^{-4} at a temperature of 1600°C. , for a ferrous oxide concentration of 0.08% in the liquid phase.

L. S. Darken (Trans. Inst. Min. Metall., London, 1940, 140, 204) made an attempt at calculating the equilibrium constant from a knowledge of the standard free energy of reaction for the following reactions:

$$\underline{Si'} = Si (l) \quad \Delta G^\circ = -14,400 + 23.98 T$$

$$Si (l) + O_2 = SiO_2 (solid) \quad \Delta G^\circ = -213,650 + 46.61 T$$

$$\underline{2 FeO} = \underline{2 Fe} + O_2 \quad \Delta G^\circ = -27,080 + 22.40 T$$

where Si' refers to silicon at unit activity in liquid iron.

From these three equations may be derived the reaction:



where $\Delta G^\circ = -200,970 + 92.59 T$.

These calculations produced a constant of 6.1×10^{-4} at a temperature of $1600^\circ C$. Darken also found that when the isotherms derived by calculations were compared with the experimental results of other workers very little agreement could be found.

The next significant contribution was that made by Zepffe and Sims.

A Survey of the Work and Results of Zapffe and Sims.

C. A. Zapffe and C. E. Sims (Trans. Inst. Min. Metall. London. Tech. Paper 1498, 1942) were the first workers to make a systematic investigation of the silicon-oxygen equilibrium in liquid iron by direct measurement. Their results were based on concentration measurements of small ingots contained in silica crucibles and surrounded by an atmosphere of water vapour and hydrogen.

As has already been shown, previous investigators have not attempted an investigation of the isolated system, but have based their conclusions on data derived from one or other of the following sources. One of these methods may be described as the evaluation of the heat content change by application of the Harnst law and subsequent substitution in the integrated form of the Van't Hoff isochore. The other method was that of determining the equilibrium constant by measurement of the concentrations of silicon and ferrous oxide in samples which contained at least one or more other constituents such as manganese, carbon, etc.

Zapffe and Sims controlled the ferrous oxide in the liquid iron by using an atmosphere of hydrogen and water

vapour. Such gas mixtures enabled the very small oxygen partial pressures to be obtained and controlled with comparative ease. The water vapour content of the hydrogen was maintained by passing the gas through a saturator similar to that described in section (2) of this thesis.

Reliable temperature measurements were made by focussing a calibrated pyrometer through a prism and on the surface of the molten iron. Furthermore, accurate analysis of the ingot for silicon was obtained by cleaning its surface free from adhesions.

When the standard free energy of reaction is to be found by measuring the equilibrium constant of the reaction, it is of paramount importance that the concentrations measured shall be equilibrium values. Although such a statement may be considered obvious, many workers on similar systems have tended in the past to assure that equilibrium conditions are reached with comparative ease. Zepffe and Sims made an attempt to obtain equilibrium conditions in their measurements, but it seems unlikely from their results that they were altogether successful.

The method used by these workers to show that equilibrium was reached was that of measuring the total silicon content

before and after melting in the controlled atmosphere. If the silicon content was found to increase during the course of the run then it was assumed that equilibrium was not reached for that particular ferrous oxide activity, and a further run would be carried out with the same ferrous oxide activity but with an increased amount of silicon in the initial charge. This process of silicon additions was continued until no further increase took place during the course of a run.

The reverse reaction was detected by the silicon content of the melt decreasing during the course of reaction. By suitably adjusting the silicon of the charge the equilibrium was approached from the other direction. The error Zepffe and Sims made was that they never showed that equilibrium was reached with sufficient accuracy. The melts were only heated for a period of three hours at temperature and sometimes much less, but no attempt was made to show that this period was sufficient to ensure that, from the approximate approach made by the additions of silicon, the equilibrium was finally reached. Such an assumption that equilibrium was reached can be made only when the rates of reaction are known to be relatively

high, and in this investigation no attempt was made to measure these reaction rates. On such a premise the results may be examined further.

The relationship between the water vapour content of the hydrogen and the ferrous oxide activity of the melt was obtained from a knowledge of the equilibrium constant for the reaction:



The values used were those obtained by J. Chipman and M. G. Fontana (Trans. Amer. Soc. Metals., 1936, 24, 313) by carefully conducted laboratory experiments.

The results of Zepffe and Sims' investigations are shown in tabular form on p. 9 of their paper. From these results can be observed the lack of reproducibility of silicon concentrations for fixed values of the ferrous oxide activity. However, from these results Zepffe and Sims were able to show that the product of the square of the ferrous oxide activity and that of the total silicon concentration was not a constant but varied with the ferrous oxide activity. This product was meant to be the equilibrium constant the reaction



The concentration of iron was regarded as unity as it

formed over 99% of the melt, while the concentration of silica could also be regarded as unity since free silica was present in the crucible. This made the equilibrium constant a function of the ferrous oxide activity and the silicon activity only.

The actual value of this "equilibrium constant" was found to increase with increase of oxygen pressure and this was attributed to the presence of some form of silicon in the iron other than dissolved silicon. As the oxygen pressure of the system increased, so the unaccounted for part of the silicon concentration was found to increase in magnitude. This led Zapffe and Sims to believe that the excess silica was present in an oxidised form of the element.

This oxidised form was considered to be silicon monoxide in the liquid iron. The possibility of the increment being the consequence of dissolved silica had to be discarded, as the silica concentration was kept constant at its saturation value by the presence of the silica crucible. The presence of silicon monoxide being accepted, the reduction of the ferrous oxide was suggested to take place by the two stages:



Furthermore the total silicon analysis, (ΣSi) now had to be differentiated from the silicon present as dissolved silicon, (Si), and that due to silicon monoxide, (Si_{SiO}).

$$(\Sigma \text{Si}) = (\text{Si}) + (\text{Si}_{\text{SiO}}) \dots\dots\dots (3)$$

The portion of silicon present as dissolved silica was shown to be negligibly small.

The equilibrium constants were defined as:

$$K_{\text{Si}} = (\text{FeO})^2(\text{Si}) \quad \text{and} \quad K_{\text{SiO}} = (\text{FeO})(\text{SiO})$$

From these and equation (3) the following identity was derived:

$$(\text{FeO})^2 \left\{ (\Sigma \text{Si}) - (\text{Si}_{\text{SiO}}) \right\} = K_{\text{Si}} \dots\dots\dots (4)$$

$$\text{also from } K_{\text{SiO}} \quad (\text{FeO})_a (\text{SiO})_a = (\text{FeO})_b (\text{SiO})_b \dots\dots (5)$$

By substituting the values of $(\text{FeO})_a$ and $(\text{SiO})_a$ etc., in equation (4) the equilibrium constants were solved by the simultaneous equations produced, and in conjunction with equation (5).

The results from two experimental runs were used to calculate the silicon monoxide concentration appropriate to one of these points and "from that basic value for (SiO) all other values of (SiO) immediately follow from equation (5)" (Zapffe and Sims, op. cit., p.21).

It is certainly true that from one value of (SiO) all other values may be calculated, but Zapffe and Sims give no reason why such great significance should be attributed to one result; nor do they say which value it is from which all others are derived. This method of interpretation was clearly to be regarded as unsatisfactory when no indication was given of the relative reliability of the data given for the ferrous oxide and total silicon concentrations.

Accordingly an analysis of their results has now been made, based on the following reasoning.

From equations (1) and (2) representing the reduction of ferrous oxide by either of two reactions, the equilibrium constants may be defined as:

$$\text{for reaction (1), } K_1 = \frac{(SiO)}{(FeO)(Si)} \dots\dots\dots (6)$$

$$\text{for reaction (2), } K_2 = \frac{L}{(FeO)(SiO)} \dots\dots\dots (7)$$

and from equation (3) may be derived

$$(\Sigma Si) = (Si) + (SiO).k. \dots\dots\dots (8)$$

where k is the proportionality factor to convert wt. % of silicon as silicon monoxide to that of silicon monoxide.

$$k = \frac{\text{Mol.wt. of } SiO}{\text{Mol.wt. of } Si} = 1.57 \dots\dots\dots (9)$$

From equations (6) and (7),

$$\frac{1}{K_1 \cdot K_2} = (\text{FeO})^2(\text{Si}) \dots\dots\dots (10)$$

and combining this with equation (8)

$$\frac{1}{K_1 \cdot K_2} = (\% \text{FeO})^2 \left\{ (\Sigma \text{Si}) - k \cdot (\text{SiO}) \right\} \dots\dots\dots (11)$$

Substituting (SiO) from equation (7)

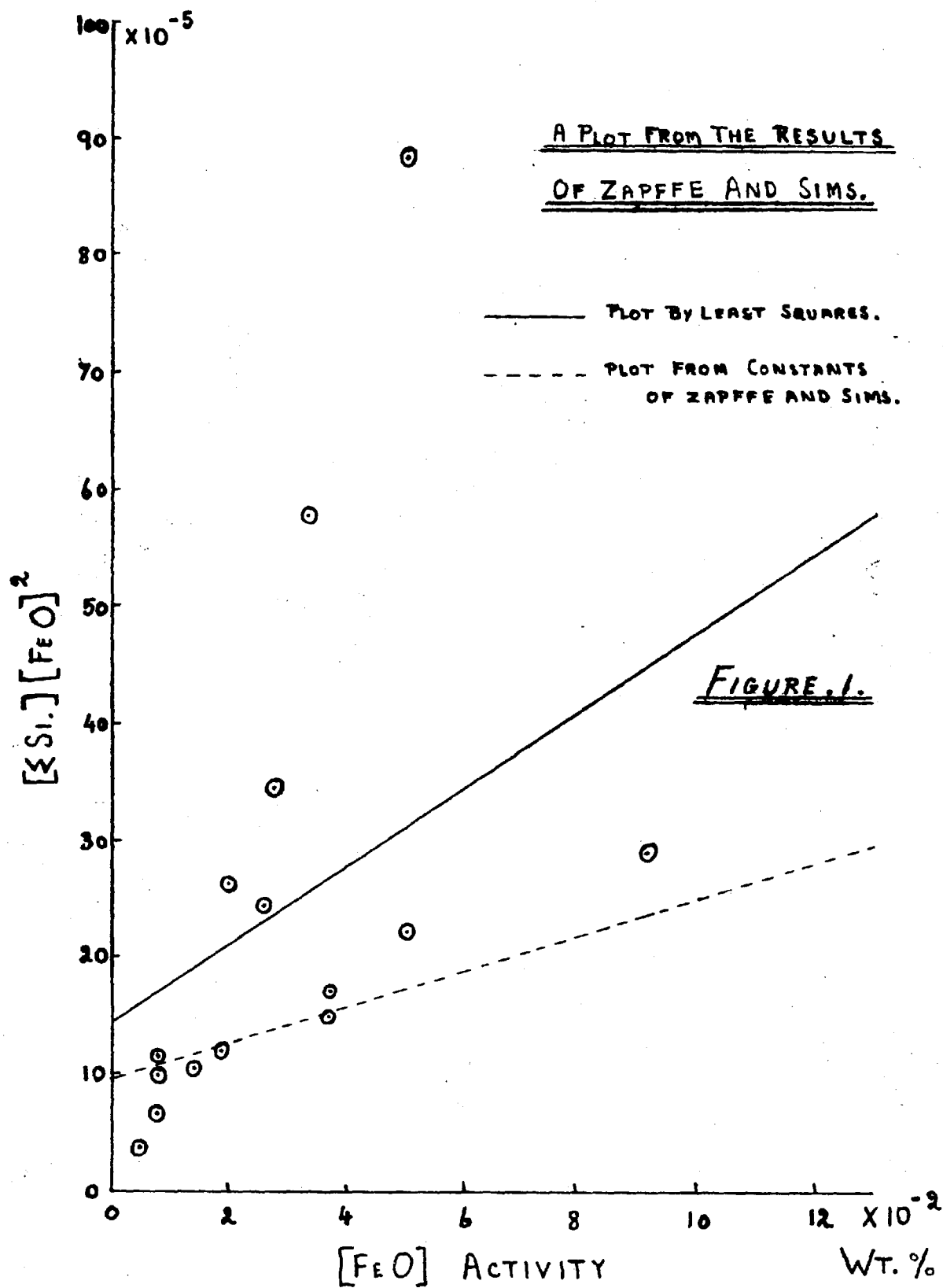
$$\frac{1}{K_1 \cdot K_2} = (\text{FeO})^2 \left\{ (\Sigma \text{Si}) - \frac{k}{K_2(\text{FeO})} \right\}$$

which gives the identity

$$(\text{FeO})^2(\Sigma \text{Si}) = \frac{k}{K_2} (\text{FeO}) + \frac{1}{K_1 \cdot K_2} \dots\dots\dots (12)$$

If equations (6) and (7) represent the reactions that occur in the melt then it is clear from equation (12) that a plot of $(\text{FeO})^2(\Sigma \text{Si})$ against (FeO) should produce a straight line, from the slope and intercept of which K_1 and K_2 may be calculated.

Plots were made from the results given, for each of the temperatures 1550°C., 1600°C. and 1650°C. in order to verify the significance attached to Zapffe and Sims' results. Fig.1 shows the plot of Zapffe and Sims' results obtained at 1600°C. On this graph two lines are drawn, one of which represents the equilibrium constants of Zapffe and Sims, the other representing the best straight



lines to fit the points plotted. The method used to derive the best straight line was that of least squares, the term known with greater accuracy being assumed to be the ferrous oxide concentration. From the graph it may be seen that as the ferrous oxide concentration is increased so the product $(\text{FeO})^2(\Sigma \text{Si})$ tends to increase.

The marked difference between these two lines, representing Zapffe and Sims' constants and those obtained by treatment shown in this survey, is also found to exist to a similar degree with the isotherms at 1550°C . and 1650°C . Table I shows a comparison of these equilibrium constants.

TABLE I.

	TEMPERATURE		
	1550°C .	1600°C .	1650°C .
K_{Si} (Zapffe & Sims) $\times 10^{-4}$	0.42	0.95	2.15
K_{Si} (From this survey) $\times 10^{-4}$		1.45	0.605
K_{SiO} (Zapffe & Sims) $\times 10^{-4}$	13	25	48
K_{SiO} (From this survey) $\times 10^{-4}$	37	53	109

The equilibrium constant K_{Si} is a function of the intercept and as such was found to be subjected to a very high degree of error owing to the fact that small variations in the gradient can alter the intercept by as much as two

to three hundred per cent. Such considerations leave the constant without any real significance at all.

Fig. 2 shows the plot of the respective equilibrium constants against the reciprocal of the absolute temperature. By assuming these curves are linear over the temperature range investigated, equations representing the free energy change as a function of the temperature may be derived from the gradient and the intercept of these plots.

The thermodynamic data of the results of Zepffe and Sims may now be compared with the results obtained by the statistical treatment applied in this survey for the reaction:



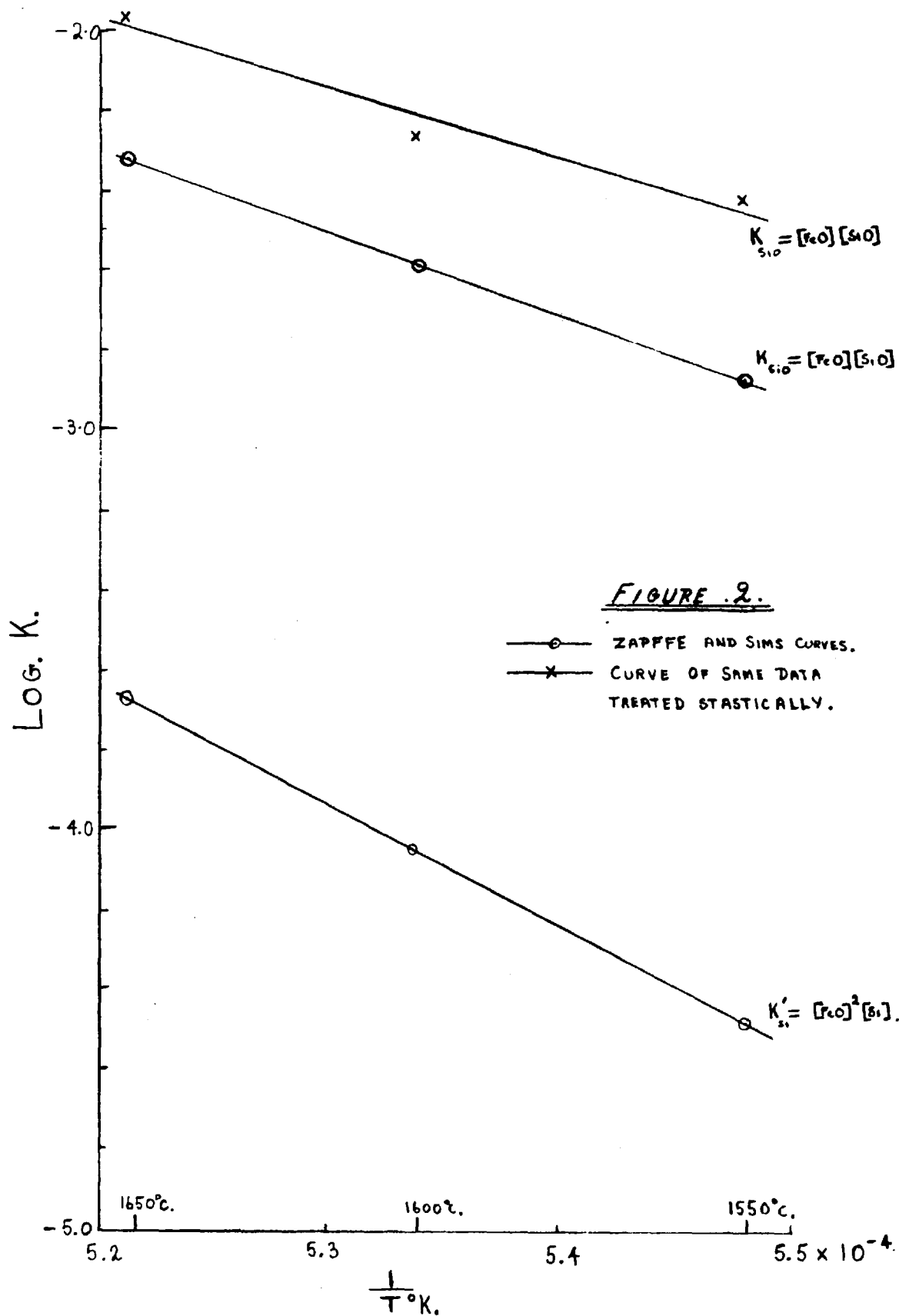
$$\text{where } K_{\text{SiO}} = (\text{SiO})(\text{FeO})$$

This comparison is shown in Table 2.

TABLE 2.

Thermodynamic prop.	Zepffe & Sims	From this survey
Expression for ΔG°	- 94650 + 38.7 T	- 82500 + 33.8 T
ΔG° @ 1600°C.	- 22000 g.-cal.	- 19100 g.-cal.
ΔH°	- 94650 g.-cal.	- 82500 g.-cal.
ΔS°	- 38.7 g.-cal./°K	- 33.8 g.-cal./°K

An interesting consequence of Zepffe and Sims' results



was their prediction of the total oxygen content of the iron. They suggested that the oxygen content decreased with decrease in ferrous oxide activity until a minimum was reached. At this minimum value the oxygen present as silicon monoxide was equal to that present as ferrous oxide and further reduction of the ferrous oxide activity produced an increase of the total oxygen content. Such a postulate involves indiscriminate use of concentrations in place of activities when dealing with silicon and silicon monoxide.

SECTION II

APPARATUS.

In order to investigate the silicon-oxygen equilibrium in liquid iron it is necessary to obtain some accurate form of control and measurement of each of the three variables, temperature, gas composition and silicon content of the liquid iron.

The required temperatures were obtained by using a molybdenum-wound furnace, the temperature being measured with an optical pyrometer. The atmosphere surrounding the ingot inside the furnace was controlled by saturating oxygen-free hydrogen with adjustable amounts of water vapour; measurement of the water vapour pressure in the hydrogen was effected by using either katharometers or a dew-point apparatus. The third variable, the silicon concentration, was adjusted (but not controlled) by the addition of small amounts of silicon to the charge.

The Molybdenum-Wound Furnace.

The two types of furnaces generally used for such investigations are the molybdenum-wound furnace and the high frequency induction furnace. In this investigation the molybdenum-wound furnace was used.

A cross-sectional diagram of such a furnace, together with adjacent fittings, is shown in Fig.3. The furnace

THE MOLYBDENUM FURNACE.

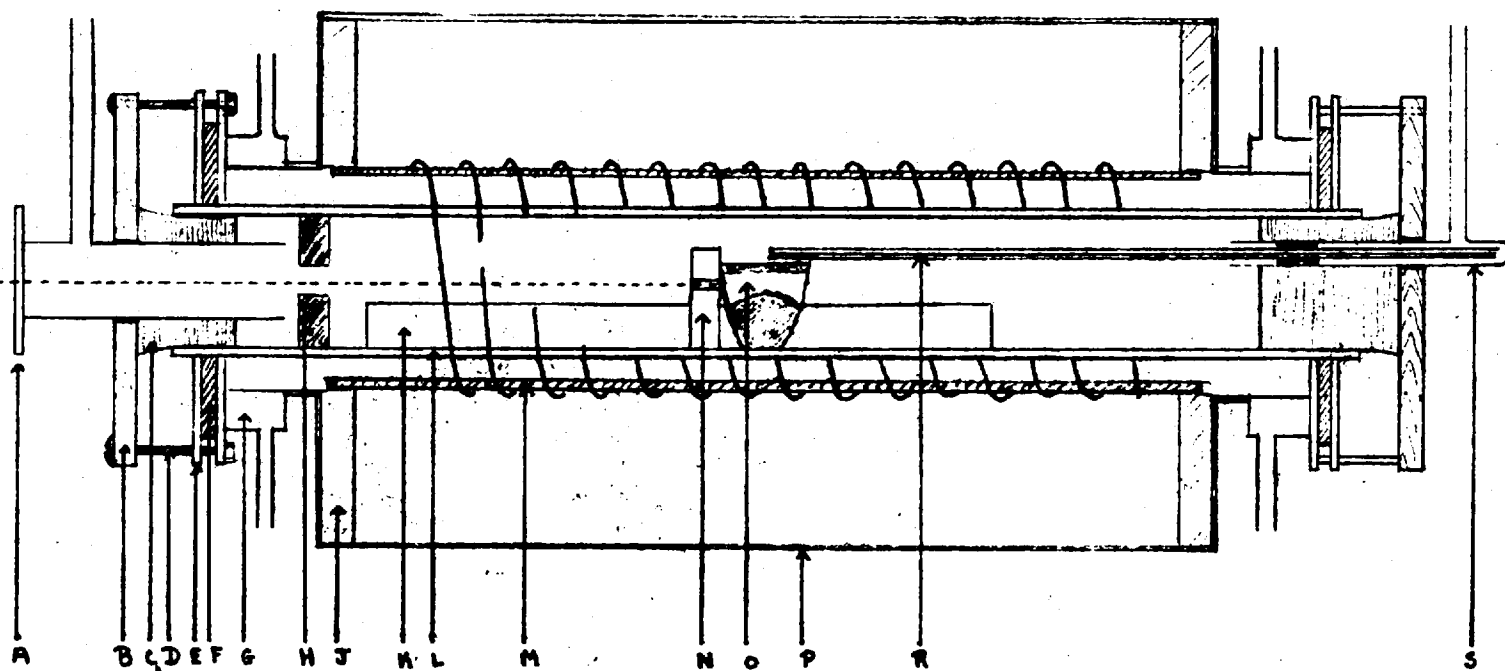


FIGURE 3.

consists of an outer case of sheet steel the corners of which are brazed. The top is removable, being secured in position by bolting to the main case. Excessive leakage of hydrogen at the join is prevented by placing a silicone rubber gasket between the top and the main case.

In the middle of each end of the case is welded a 4" diam. tube about 6" long, and to the ends of each of the protruding tubes are welded 8" diam. flange plates with six suitably placed bolt holes therein.

The furnace tube is sealed from the surrounding atmosphere by a rubber gasket (F) which is compressed against the fixed flange by a further flange (E), the two flange plates being bolted together. Cooling of these ends is necessary in order to prevent pyrolysis of the rubber gasket, and this is achieved by two cooling chambers (G) fixed between the flanges and the furnace casing.

The furnace tube may be wound with either molybdenum tape or wire. Although both have been used, the tape winding was found to give a more satisfactory all-round performance. The tape used was 0.03" thick and one-eighth of an inch wide. It was wound on an 18" length of 'Triangle R' alumina tubing (H), external diameter $3\frac{1}{2}$ ". The tape was wound on this tube at $\frac{1}{4}$ " intervals, i.e., with an eighth-

inch space between each turn, and the total length of tube wound was 14". The tape was secured at each end of the tube by binding with heavy gauge molybdenum wire and any movement of the wire due to expansion of the tape on heating was prevented by covering the windings with a $\frac{1}{4}$ " layer of alundum cement. The tube was then held in position inside the furnace by means of suitably placed firebricks, and the free space between the windings and the case was filled with fine alumina powder.

Oxidation of the molybdenum tape at the high temperatures reached by the interior of the furnace was prevented by passing a stream of hydrogen through the casing. A flow of about half a litre an hour was found sufficient but this was increased to two litres an hour for temperatures above 1400°C . This gas stream was passed in through two tubes welded to the side of the case, and excess gas escaped through the cracks and leaks inevitable in such a furnace.

The tape ends were passed through the furnace casing by insulating with porcelain ferrules plugged with asbestos wool and covered with alundum cement. The current was supplied to the windings from a "Vari-volt" transformer made by the Gresham Transformer Company. The current

passing through the furnace could be conveniently adjusted by variation of the voltage obtained from the transformer, the secondary of which was tapped at two-volt intervals. The current passed was always in the region of 25 amps., the maximum never being allowed to go above 35 amps.

The furnace tube (L) which contained the charge and through which was passed the controlled atmosphere, was made of recrystallised alumina as supplied by Thermal Syndicate Ltd. At each end of this tube were fitted rubber bungs (C) held firmly in position by wooden saddles (B) which in turn were held by two long bolts (D).

Through the bung at one end of the furnace was passed a "Pyrex" glass tube 1" diam., and to the end of this tube a microscope slide was sealed with picein wax, so forming an observation window through which the optical pyrometer could be focussed. On one side of the glass tube was sealed a side arm, forming an inlet for the furnace atmosphere.

The bung at the other end of the main furnace tube was fitted with a short length of "Pyrex" glass tubing in order to provide a support for the anti-thermal diffusion tube (R). This tube was made of mullite and extended to

the middle of the furnace, it being supported in its "Pyrex" tube by a small rubber ring.

The current passing through the furnace windings was measured by a 'tong test' ammeter, and was never allowed to exceed 35 amps, which, although safe for "running up" the furnace to $1000^{\circ}\text{C}.$, was dangerously high at higher temperatures. In consequence the furnace had to be heated above $1500^{\circ}\text{C}.$ rather slowly, the maximum current of 35 amps being only two to three amps above the holding current for the furnace at $1600^{\circ}\text{C}.$

During the "running up" the voltage drop across the furnace windings was increased intermittently so that the current passing was maintained at the maximum of 35 amps. $500^{\circ}\text{C}.$ was reached in 3 to 4 hours and $1300^{\circ}\text{C}.$ after a similar period. At this stage the run was usually interrupted and the furnace left at $1300^{\circ}\text{C}.$ overnight.

The Optical Pyrometer.

Accurate measurements of temperature were required in the range $1500^{\circ}\text{C}.$ to $1700^{\circ}\text{C}.$, and these were carried out by using the disappearing-filament type of optical pyrometer. Such measurements assumed that the temperature of the liquid iron was uniform within the limits of accuracy of the determination.

The pyrometer was sighted so that the side of the crucible (O), Fig.3, was observed through both the glass window at the end of the furnace, and the hole in the radiation shield (H) placed against the side of the crucible.

Fig.4 is a clearer and larger picture of the way in which the pyrometer was set up. From it may also be seen the way in which the current to the filament was supplied and measured.

The filament current was supplied by a battery of three 2-volt accumulators and varied by a resistance box connected in series. From a knowledge of the voltage drop across a fixed resistance, connected in series with the circuit, the current passing through the filament could be obtained. This voltage drop was measured either directly by means of a voltmeter or more accurately with a potentiometer. Utilising the potentiometer, variations of 2°C . were readily observable.

Calibration of the pyrometer was carried out by plotting the cooling curves of both iron and nickel. In the region below 1450°C . a platinum-platinum-rhodium thermocouple was used. The cooling curves of iron and nickel were obtained by plotting measurements of the filament current, taken at half minute intervals, against time. The

THE OPTICAL PYROMETER.

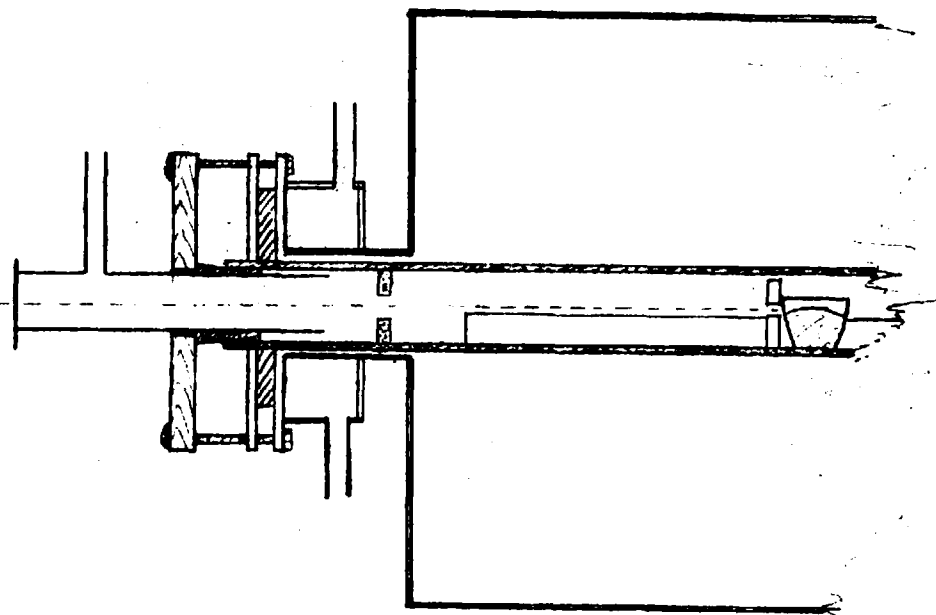
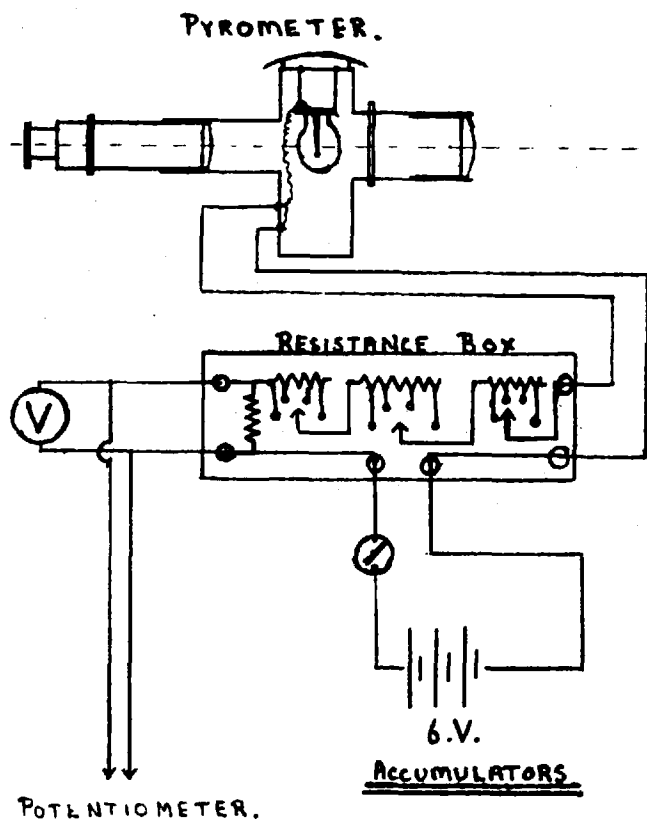


FIGURE. 4.

melting points so obtained were found to bear a close relation to the extrapolation of the calibration curve obtained at lower temperatures using the thermocouple.

Any departure from black-body conditions of the radiator will not produce error providing the departure is constant for each measurement. Such error was avoided, as the calibration was made directly to the temperature of the melt. The radiation shield placed against the crucible prevented radiation from other parts of the furnace being reflected off the side of the crucible. Observation of the melting point using transparent crucibles produced a calibration differing from that obtained from cooling curves, but the cooling-curve points were those considered to be more reliable and so were used in the final calibration curve.

The Katharometer.

The analysis of a gas mixture may be made by comparing its thermal conductivity with that of some standard gas. The katharometer is an instrument capable of detecting a difference in thermal conductivity in two gas streams instantaneously. An analysis by this method can be carried out only if there is sufficient difference in thermal conductivity between the constituent gases. The

conductivities of water vapour and hydrogen differ considerably, so that a determination of small quantities of water vapour in hydrogen may be carried out using katharometers.

The diagram of a katharometer is shown in Fig.5. The analyser compares the thermal conductivity of the "wet" hydrogen with that of pure dry hydrogen by passing a stream of each of the gases through an H-tube in the manner shown in the diagram. The sealed ends of each of the H-tubes contain elements connected so that each forms an arm of a Wheatstone bridge circuit. These elements consist of platinum spirals coated with a thin layer of glass and are heated by a current of 350 milliamps. This current was supplied by a battery of three 2 V. accumulators trickle-charged from the D.C. mains supply (see Fig.7). The current taken from the accumulators was never allowed to exceed 50 milliamps.

Analysis of the gas composition was made by measuring the extent to which the balance of the Wheatstone bridge circuit was disturbed when the gas of greater conductivity lowered the temperature of the appropriate spirals and hence decreased their resistance. Deviations from balance of the electrical circuit were measured with a "Type B" Cambridge recorder. This recorder is capable of showing

the deflection, and also recording it, in the form of a trace made up of points taken at one-minute intervals. Two katharometers were used for these investigations, and each of them was calibrated for the partial water-vapour pressure in the "wet" side of the analyser.

Before any accurate tests could be made the accumulators had to be left running for at least a week, hydrogen being circulated through both sides of the Katharometers. The current passing through the elements was then adjusted by switching the recorder on "test" and varying the resistance S (see Fig.7), until the galvanometer showed zero deflection. In this way the filament current was standardised to some arbitrary fixed value by comparing the voltage drop across a resistance against the voltage of a standard cell.

The filament current having been set, it was then necessary to balance the Wheatstone bridge circuit. This was achieved by passing dry hydrogen through both sides of the analyser and then, with the galvanometer switch on "record", the resistance C (Fig.6) was altered until the galvanometer showed zero deflection. After these adjustments had been made the katharometers were ready for measurements of the thermal conductivity variance from

that of the standard gas.

Hydrogen containing water vapour picked up from a saturator containing a saturated solution of calcium chloride was passed through the "wet" side of the katharometers and then through an analysis train. The water vapour was absorbed from the gas stream by two weighed tubes containing "Anhydron". The dried hydrogen was then passed through a standard gas-meter which measured the total volume, at room temperature, of gas passed. The total volume of hydrogen, corrected to conditions of standard temperature and pressure, was used to find the number of gram-mols of the gas present and this value together with the number of gram-mols of water vapour allowed the ratio of the partial pressures of water vapour and hydrogen to be calculated. The gas flow for each calibration point was run for several hours, during which time a continuous trace of the galvanometer deflection was made. From calibration points obtained in this way the plots shown in Fig. 8 were constructed.

The katharometers were used to measure partial pressures in the range 0 to 15 mm. The error never exceeded 0.1 mm, and this error in the range most frequently used (5 to 15 mm.) constitutes an error not exceeding 0.2%.

THE KATHAROMETER ANALYSER.

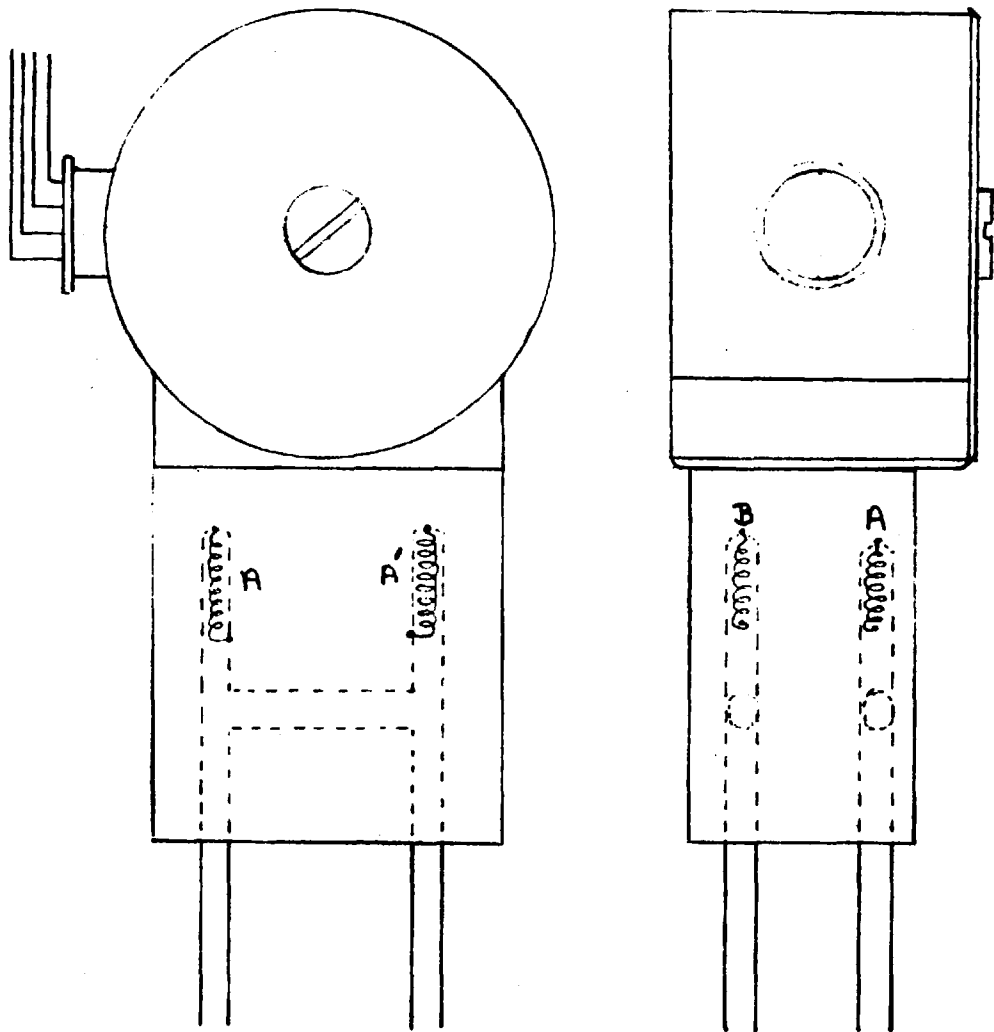


FIGURE. 5.

ELECTRICAL CIRCUIT OF THE ANALYSER.

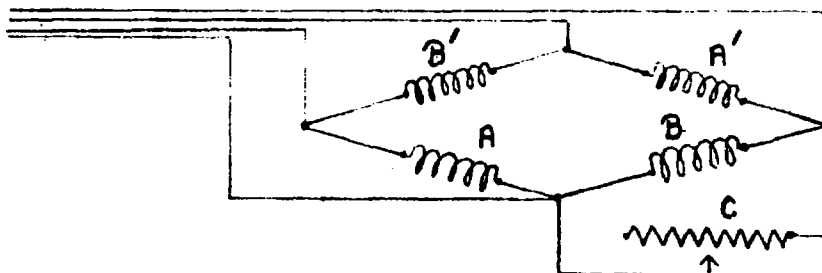
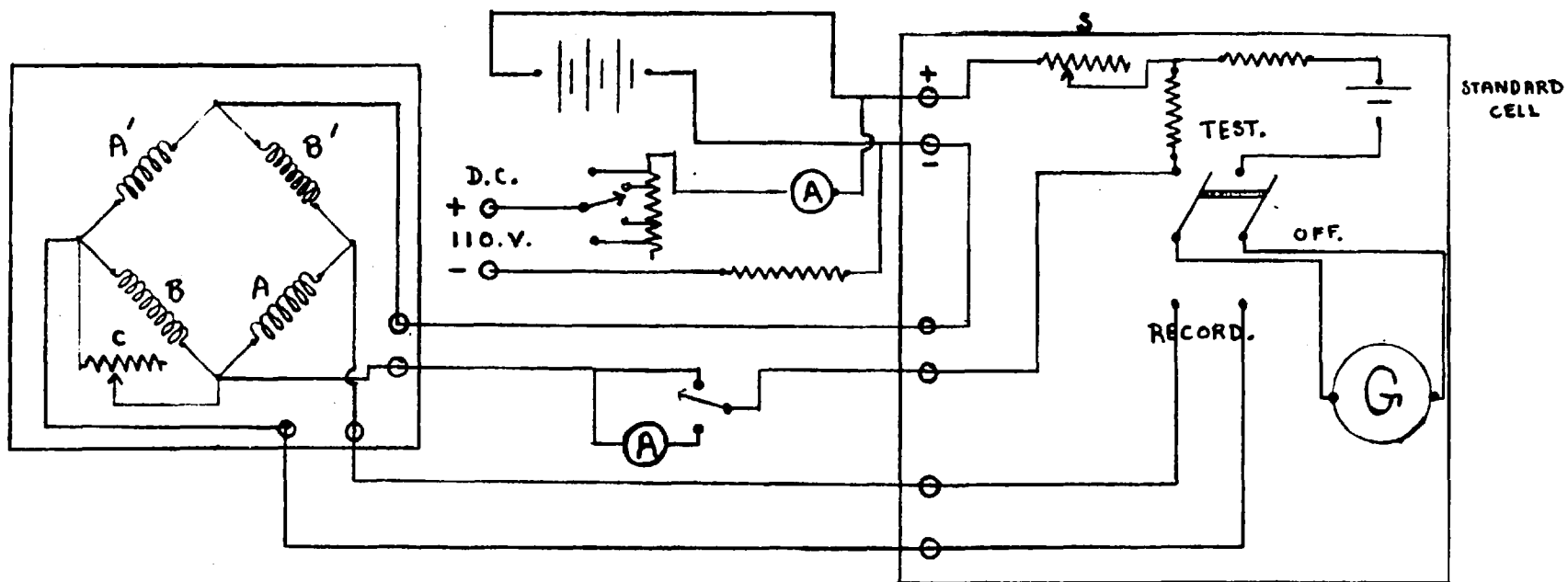


FIGURE. 6.

CIRCUIT DIAGRAM OF THE KATHAROMETER

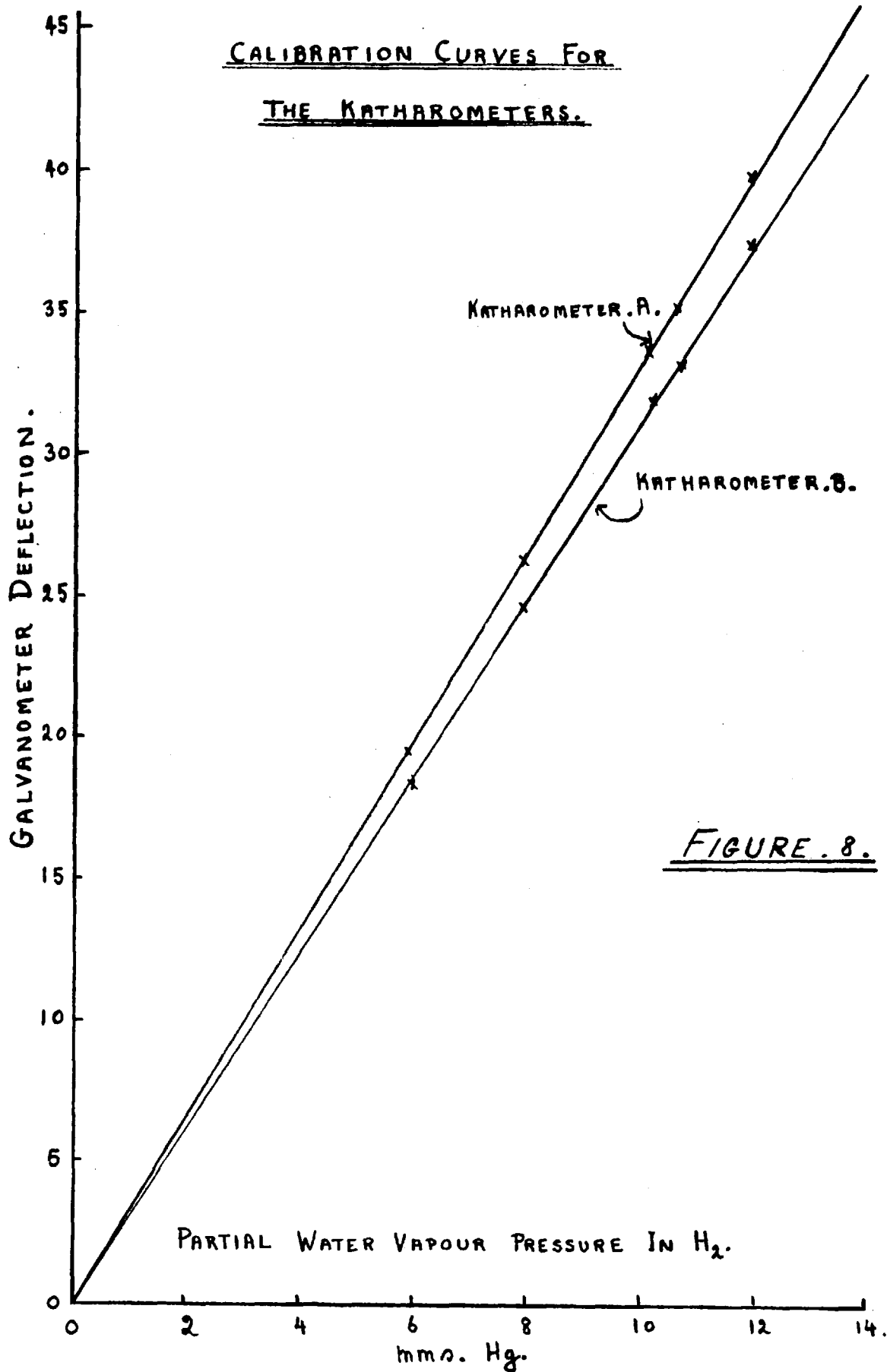


THE ANALYSER.

THE CONTROL BOX AND RECORDER.

FIGURE. 7.

CALIBRATION CURVES FOR
THE KATHAROMETERS.



Two sources of error were experienced when using katharometers in the manner shown. For flow rates exceeding 4 litres/hr. consistently low results were obtained. Correction for such errors was made by passing dry hydrogen through both sides of the katharometer at the required flow rate and then readjusting the zero of the galvanometer. This operation, although tedious, was necessary for any measurements made at each of the flow rates exceeding 4 litres/hr.

A further source of error was introduced by variations in temperature of the body and surroundings of the katharometers. Both analysers had to be in close proximity to the molybdenum-wound furnace in order that the dead space of the connecting tubes should be a minimum. Although the katharometers were placed below the level of the furnace, sufficient heating of the analysers took place to produce errors. Such errors were avoided by adjusting the zero of the galvanometer when the furnace was at temperature.

The Hydrogen Flow Apparatus.

Fig.9 shows the apparatus used for producing a stream of pure hydrogen to a portion of which controlled amounts

of water were added to produce a convenient furnace atmosphere.

A supply of hydrogen was obtained from a cylinder of the "oxygen-free" gas. This supply entered the system at a flask the pressure of which was stabilised by a manostat. The manostat operated by adjustment of the height of a long column of water up which surplus hydrogen from the flask bubbled.

The pressure-stabilised hydrogen leaving the flask was passed through a furnace containing palladised asbestos and heated to a temperature of 360°C . Any oxygen present in the gas was thus converted into water, which was removed by passing the gas through a bubbler containing concentrated sulphuric acid. Acid spray was then removed by passing the gas through solid potassium hydroxide pellets; finally the gas was passed over 'Anhydron'.

The stream of dry hydrogen was divided into two parts at this stage, one going directly to the dry side of the katharometers to act as standard gas, the other going through a flow meter to one or other of the saturators.

Three types of saturators were used for admitting fixed quantities of water vapour into the hydrogen stream. They were either the oxalic acid saturator, the saturated calcium chloride solution saturator, or the reflux water

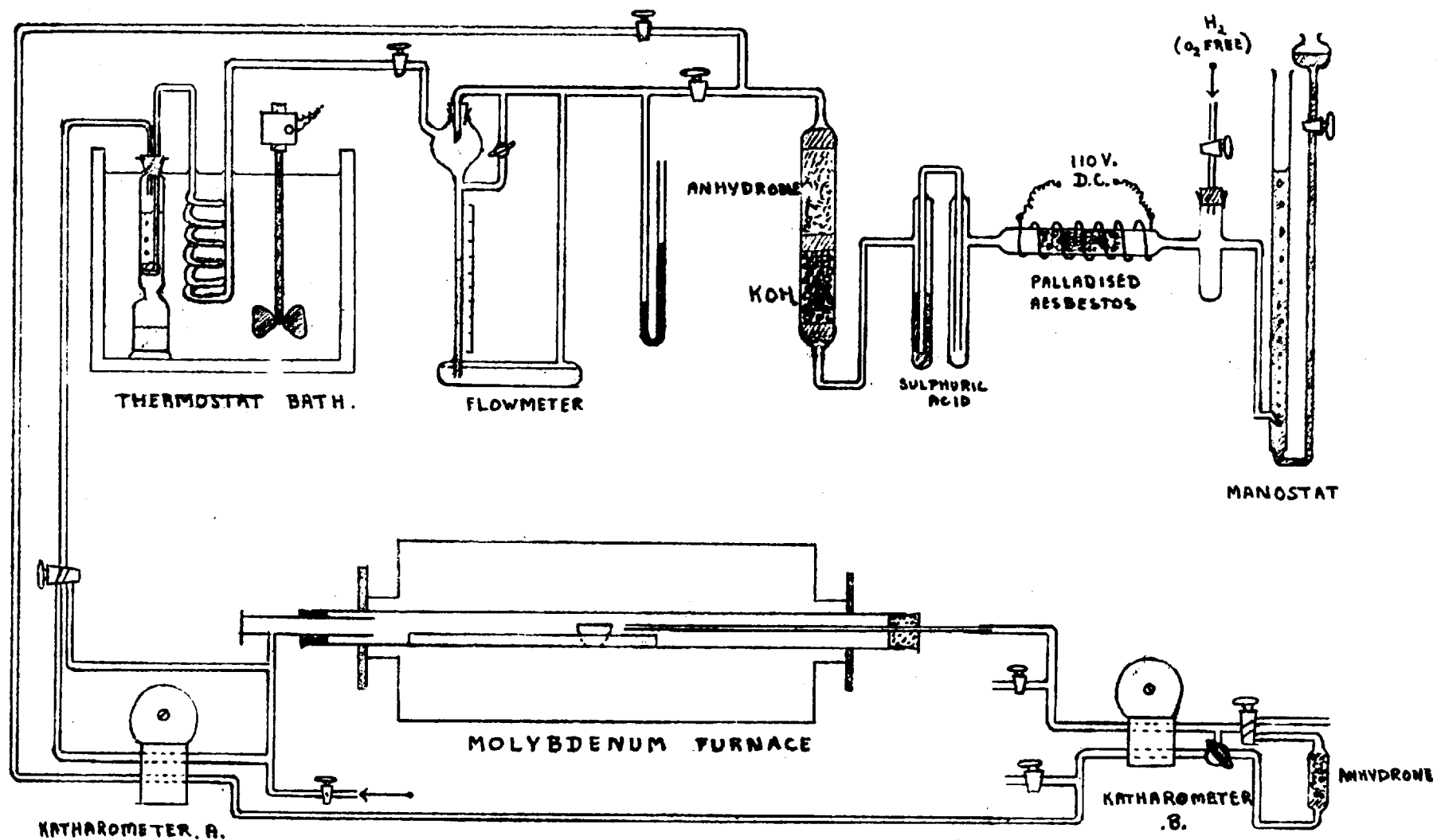
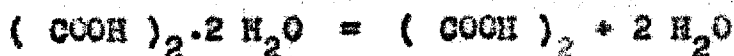


FIGURE. 9.

saturator.

Oxalic Acid Saturator:

In order to produce easily controlled amounts of water vapour in the hydrogen below a partial pressure of 4 mm. the hydrogen was passed over crystals of oxalic acid dihydrate. Water is given off by the decomposition of the dihydrate in the following way:



The acid dihydrate with 10% of the anhydrous acid was placed in a large U-tube, the temperature of which was controlled by immersing it in a thermostat bath. By adjusting the temperature, within the limits of the thermostat, the hydrogen could be saturated with water vapour in the pressure range 0.5 to 7.0 mm.

Saturation with Calcium Chloride Solution:

By passing the hydrogen gas through a saturated solution of calcium chloride, water vapour pressures in the range 3 mm. to 5 mm. could be obtained. Although a solution of this salt tended to be unreliable, it was chosen in preference to solutions of other possible salts because of the relatively large range of water vapour-pressures obtained for reasonable variations of temperature.

Hydrogen was bubbled through this saturated solution by blowing the gas through a porous plate of sintered glass. The porous plate was placed well below the surface of the solution which was contained in a "drying" tower, the bottom of which was filled with crystals of calcium chloride hexahydrate to maintain complete saturation.

The Reflux Saturator:

A diagram of this apparatus is shown in Fig.10. The hydrogen entrains an excess of water vapour by passing through a flask of boiling water. The wet hydrogen rises through a lagged column, from which it passes through a side arm to a glass spiral contained in a thermostat. By suitably adjusting the temperature of the thermostat bath, the amount of water in the hydrogen may be controlled. Excess water is condensed out in the spiral, and this water drains to the bottom of the spiral and thence via a U-tube back to the flask containing the boiling water.

The saturated hydrogen was led off to the furnace through heated tubes. All such tubes were heated by winding them with Nichrome wire and passing a suitable small current through the winding; the condensation of water vapour was thus prevented. Glass taps had to be avoided, and where necessary taps were constructed of heated lengths of

WATER SATURATOR.

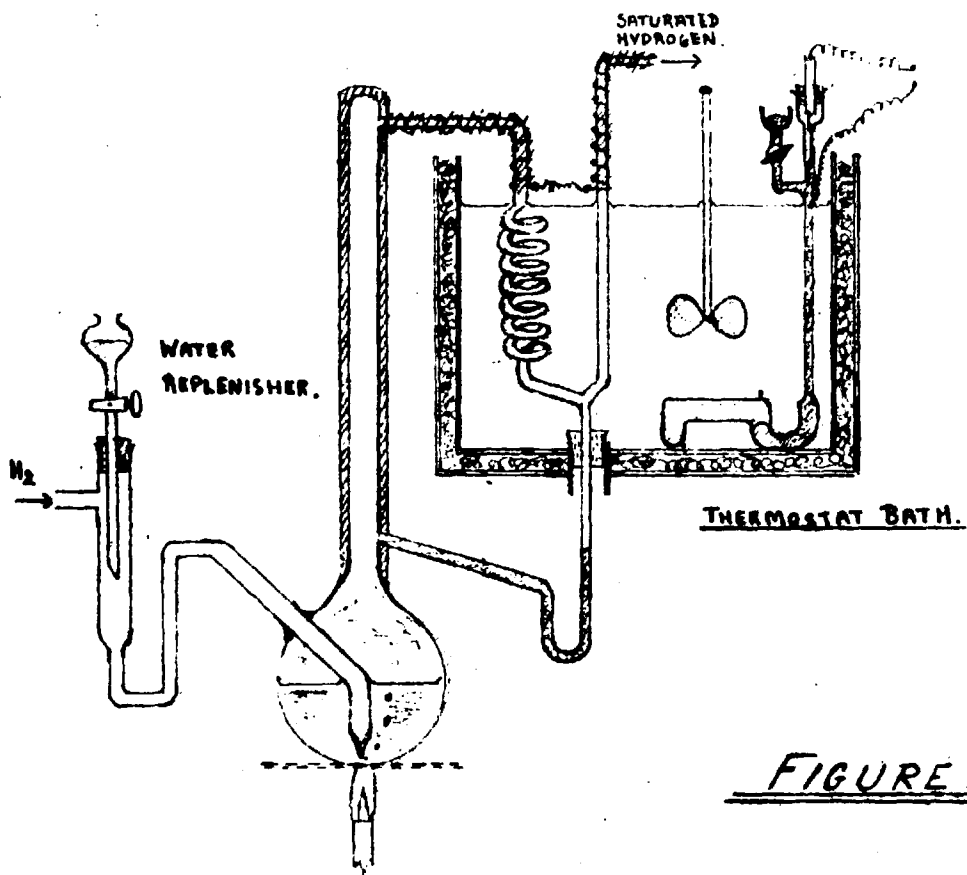


FIGURE. 10.

DEW POINT APPARATUS.

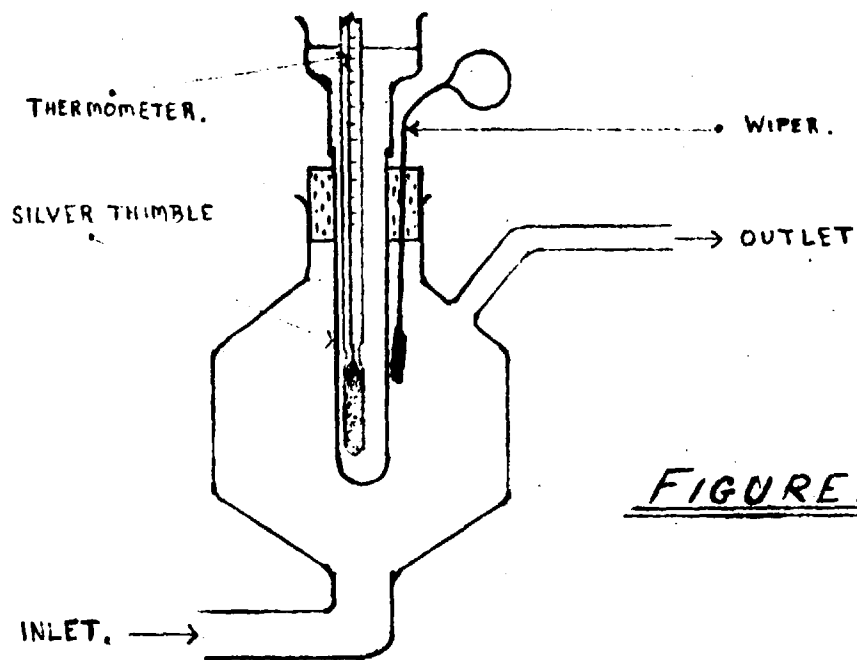


FIGURE. 11.

silicone rubber tubing compressed by means of a screw clip. Katharometers could not be used for the measurement of the water vapour contents of the hydrogen at these higher values as the heating of the analysers, a precaution necessary to prevent the deposition of dew, was impracticable.

The katharometers were connected to the ends of the furnace and the hydrogen flow system by narrow-bore glass tubing, leaks being prevented by glass-blowing all joints. Each of the katharometers was provided with a by-pass, as was also the furnace. Taps were suitably placed in the system so that the furnace could be flushed with argon without passing this gas through the katharometers.

In order that the katharometer analysing the gases leaving the furnace should detect water vapour only, the gas leaving the "wet" side of the katharometer was dried with "Anhydrene" and passed back through the "dry" side; the dried gas from the furnace was thus used as a standard of reference, instead of pure hydrogen.

The back-diffusion of air into the system was found to be quite appreciable at points where hydrogen left the system. This was avoided by interposing bubblers, containing dibutyl phthalate, in all such positions.

The Dew-Point Apparatus.

A method was required whereby partial water vapour pressures greater than 15 mm. could be measured. Of the various forms of hygrometers, the dew-point apparatus was considered the only one that would give the required results.

A diagram of this apparatus is shown in Fig.11. It consists of a glass vessel to which are sealed two tubes, one at the bottom and the other on the upper side. At the top is a neck which contains a rubber bung to hold a thin silver thimble in place. This silver thimble, on which the "dew" deposits is a tube about $\frac{1}{2}$ " wide and 4" long, sealed at the lower end. The detection of the "dew" is facilitated by wiping the surface of the thimble with a rubber pad fixed to the end of a piece of iron wire. This wiper is held in position by the rubber bung through which it passes. To the upper end of the thimble is fixed a glass funnel held to the thimble with picien wax. A thermometer rests on the bottom of the thimble and the thimble and funnel are filled with a 20% solution of alcohol in water. Cooling of the liquid is effected by placing small lumps of solid carbon dioxide in the upper part of the funnel and stirring the liquid by

elevating and lowering the thermometer. The surface of the thimble was strongly illuminated so that the deposition of dew could be observed through a magnifying glass.

Greater accuracy was obtained if the dew-point was taken at that temperature at which the dew disappeared rather than that at which the dew appeared. Calibration to investigate the accuracy of the method was made by comparison with the katherometers and also by comparison with known atmosphere of saturated hydrogen produced by the reflux saturator. The errors in measurement were somewhat great, in the region of $\pm 8\%$, so results obtained can be little more than qualitative.

The Interior of the Furnace.

Silica crucibles were used to contain the liquid iron, as this ensured complete saturation of the liquid phase with silica.

Translucent "Vitreosil" silica crucibles were those generally used for the equilibrium measurements, but transparent "Vitreosil" silica and zircon crucibles were also tried.

Reaction between the silica crucible and the furnace tube had to be prevented, as the glass produced by such fluxing would, on cooling, inevitably crack the furnace

tube as well as making the removal of the crucible impossible. Such a state of affairs was avoided by resting the crucible on a Mullite trough which was slid into the furnace. No fluxing was found to take place between the trough and the furnace tube, but slight fluxing did occur between the trough and the crucible.

Silice crucibles could be used once only as, on heating above $1400^{\circ}\text{C}.$, they were found to become very brittle and fall to pieces on removal from the furnace. Zircon crucibles were found to be more satisfactory in this respect and could be used repeatedly.

At each end of the furnace tube were placed large radiation shields made of alundum cement so that the bungs at each end were protected from the radiation.

The Argon Purification Apparatus:

The argon was purified by passing it through an absorption train to remove oxygen and nitrogen. The entrainment was effected by passing the argon first through a sulphuric acid bubbler, followed by a tube containing potassium hydroxide pellets and then a further tube containing "Anhydrone". All traces of moisture having been removed residual oxygen was removed by passing the

argon stream through copper gauze heated to 480°C . The nitrogen was removed by passing the argon through a further tube of "Pyrex" glass containing a mixture of calcium oxide and magnesium powder and maintained at a temperature of 610°C .

PLATE I:

THE HYDROGEN ENTRAINMENT APPARATUS.

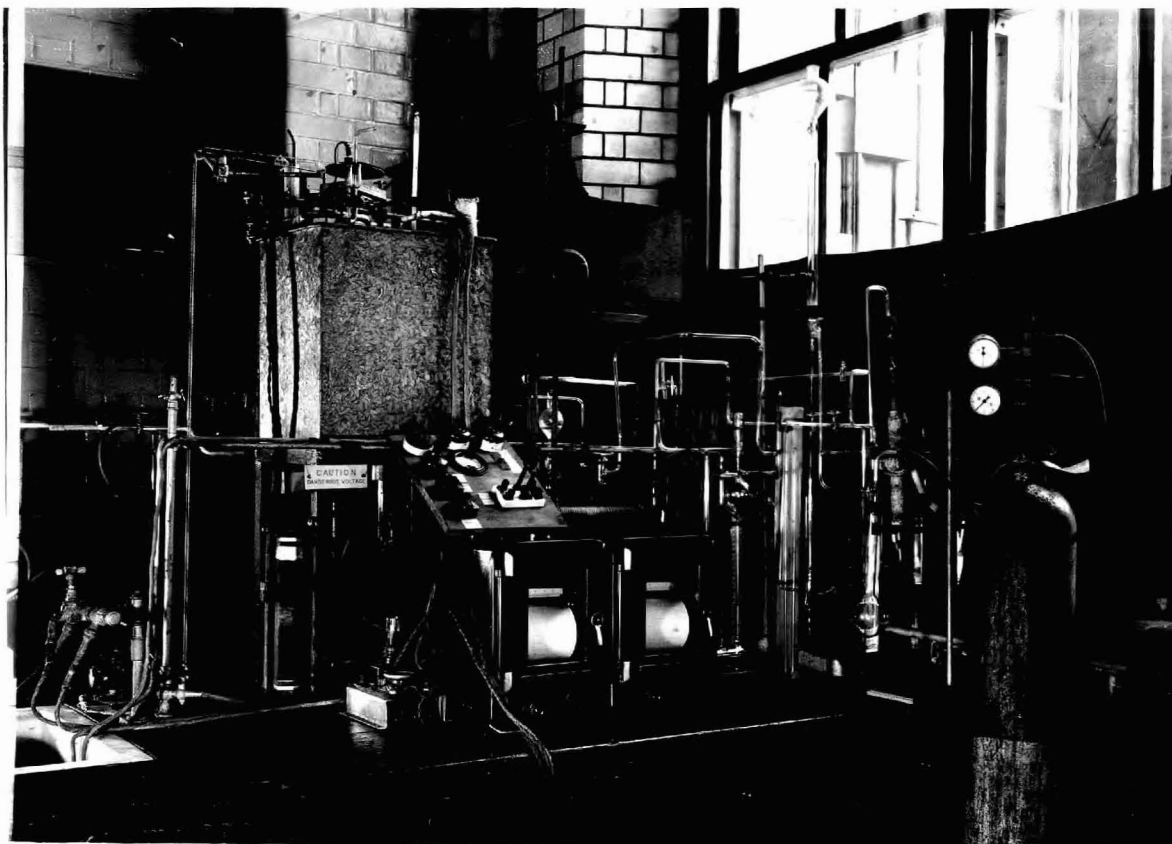


PLATE II.

THE FURNACE SET UP AND THE POTENTIOMETER:

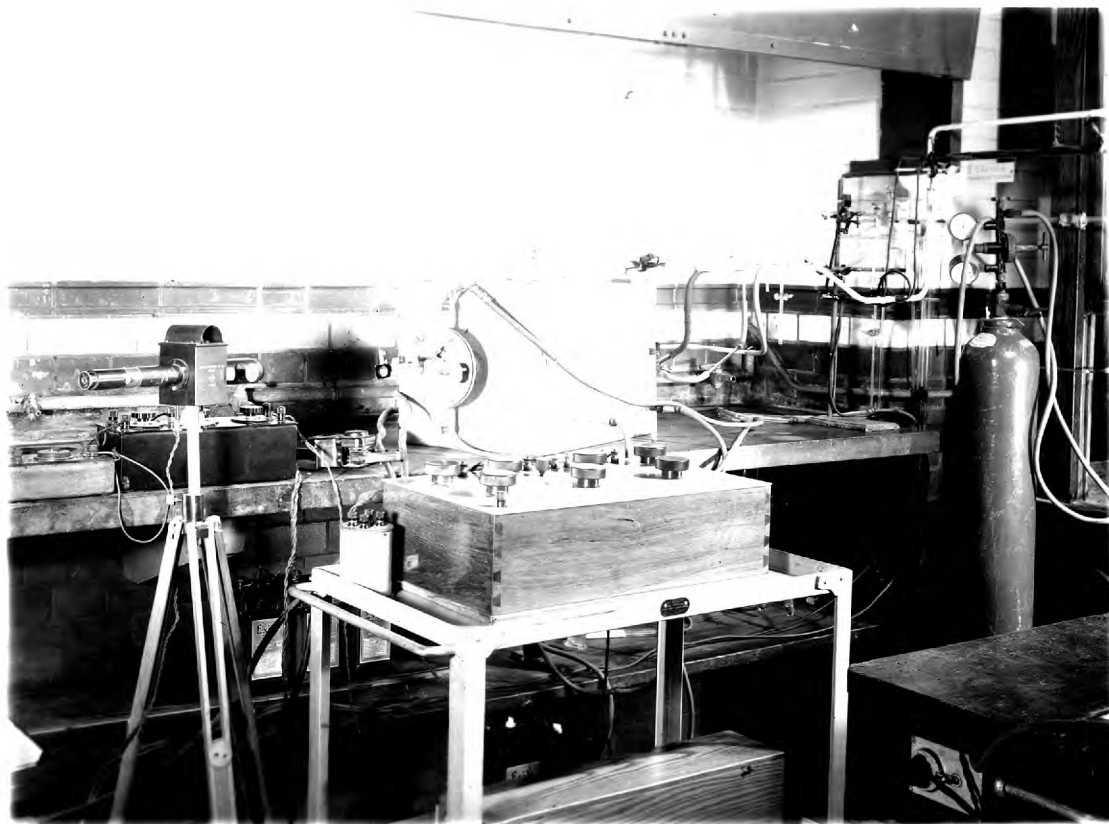


PLATE III.

CRUCIBLES, INGOTS AND REFRACTORIES.

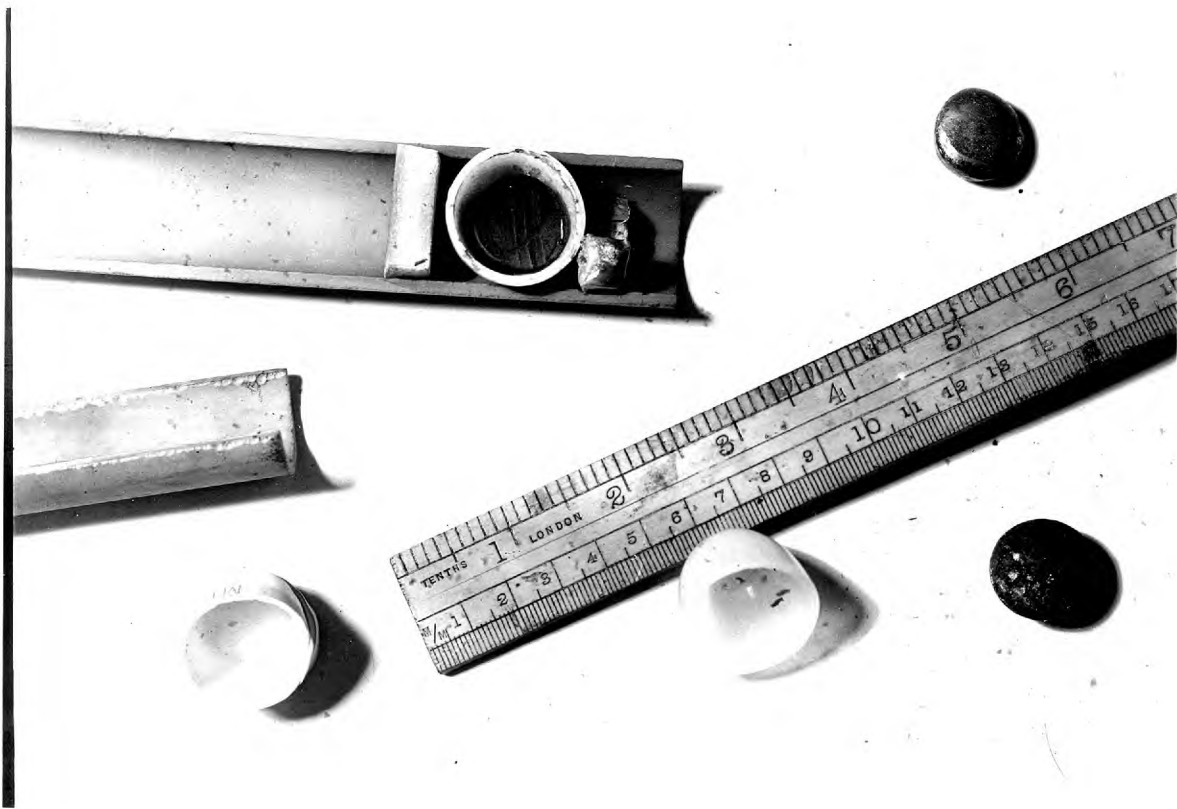
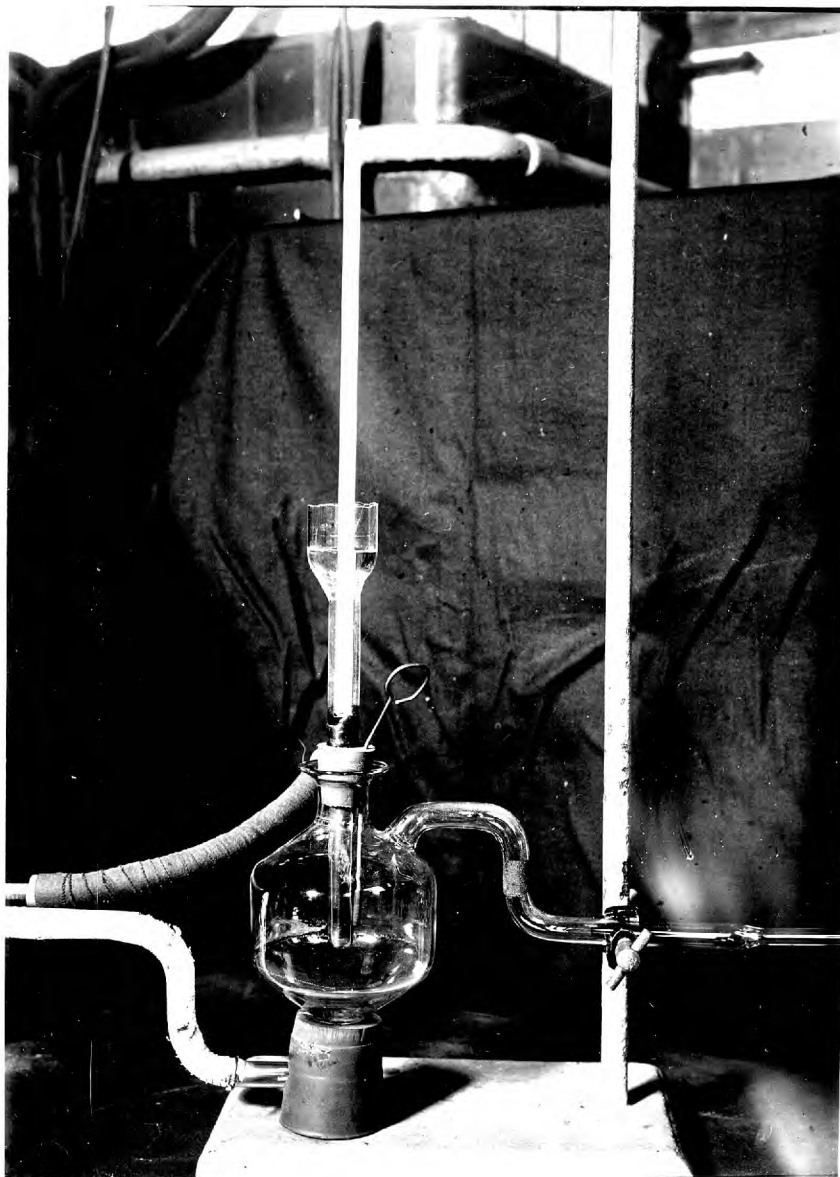


PLATE IV.

THE DEW POINT APPARATUS.



SECTION III

EXPERIMENTAL TECHNIQUE

The Analysis of Total Silicon Content.

The silicon content of the ingot was determined by precipitating the silicon as silica. To do this, three requirements must be satisfied: first that all silicon must be oxidised to silica, secondly that the precipitate must be freed as completely as possible from impurities, and thirdly that the precipitate must be of manageable proportions. The actual size of the ingot was kept constant so that temperature measurements were made under similar conditions, the final weight of the ingot usually being about 10 to 15 grams, circular in shape and about half an inch deep. The silicon content of the ingot was, generally, between 0.3% and 2%, but measurements outside this range were made extending the range from 0.1% to 10% silicon. The whole ingot was analysed when the expected silicon was less than 1.0%, but for silicon contents higher than this value only a "pie" shaped segment of the ingot was used for each analysis. In this way the bulk of the precipitate was kept down to manageable proportions. The procedure adopted was as described below.

The cold ingot was taken from the furnace and freed from all surface adhesions. The inevitable presence of these adhesions was caused by particles of the silica crucible, which become extremely fragile on being heated to 1600°C. and then being cooled, sticking to the ingot. Ingots with low silicon concentrations were found to have few or no adhesions on their surfaces, but ingots containing 2% or more silicon were found to have many small particles of silica attached to the surface of the ingot. The complete removal of these adhesions was necessary as their presence would vitiate the subsequent analysis carried out on the ingot. The silica adhesions were removed by scraping the sides and bottom of the ingot with a clean file. The particles of the crucible did not stick hard to the sides of the ingot and scraping brought about their almost complete removal, which was revealed when the surface was inspected with a magnifier. Some ingots were treated with 40% hydrofluoric acid for periods of up to three hours to effect removal of adhesions, but this method was abandoned as the scraping operation was found to be much quicker and more complete. When the surface of the ingot was pitted complete removal of adhesions was

achieved first by scraping away as much of the silica as possible and then treating the ingot with 40% hydrofluoric acid for a period of several hours.

The cleaned ingot or a portion thereof was weighed and then dissolved in 150 ml. of concentrated hydrochloric acid, to which were added 50 ml. of concentrated nitric acid. This operation was carried out in a large porcelain evaporating basin, which was kept covered; it took about five hours for the ingot to dissolve completely. Ingots containing more than 5% silicon were not readily attacked and further additions of nitric acid were made during the dissolving-up process. 17 ml. of 60% perchloric were added to the solution in the evaporating basin, which was then heated on a steam bath in a fume cupboard until the perchloric acid began to fume. At this point a large clock glass was placed over the basin and the precipitates of silica and crystalline ferric chloride allowed to digest for one hour. This period of digestion was necessary to coagulate colloidal silica set free in the dissolving-up process. 100 ml. of hydrochloric acid diluted with an equal volume of water were added to redissolve the ferric chloride, the silica precipitate being left in a form

readily filterable. When the ferric chloride had redissolved the solution was filtered through a Whatman No.42 filter paper. The precipitate was washed free of ferric chloride with repeated applications of first 10% and finally 1% hydrochloric acid, until the silica appeared quite white. The filtrate was washed into the original evaporating basin and a further addition of perchloric acid made, followed by a similar process of evaporation and filtration. The second precipitate was washed free of impurities and added to the first, which was contained in a clean platinum crucible. The combined precipitates, when bulky, as in the case of the higher silicon contents, were heated for two hours in a steam oven before ignition to constant weight. The first stage of the ignition was conducted with more than usual care to prevent divided silica from being carried away with the volatile matter of the filter paper.

When constant weight (within ± 0.2 mg.) had been reached the silica was treated with 20 ml. of 40% hydrofluoric acid, the solution evaporated to dryness, and the small residue (0.08 gram) ignited to constant weight. The difference between the weights before and after treatment with hydrofluoric acid, less the "blank", was taken as

the weight of the silica precipitate. This figure, in conjunction with a knowledge of the weight of the sample, gave the total silicon content of the ingot.

The accuracy of this method was verified by analysing a steel the composition of which was known. The total silicon content of this steel was given as 3.30% Si.

	Analysis A.	Analysis B.
Wt. of sample	2.2312 g.	2.2373 g.
Wt. of ppt. less blank	0.1574 g.	0.1586 g.
% silicon	3.296%	3.308 %

Wherever possible the ingot was analysed in duplicate; the difference between the duplicate analyses was never greater than 0.02% Si and usually much less than this value.

Preliminary Experiments to show the Presence of an Equilibrium.

During the course of an experimental run the only quantities instantaneously measurable were the temperature of the ingot and the composition of the gases entering and leaving the furnace tube. The only way in which the equilibrium could be shown to exist was by studying these gas compositions. When they were equal the system could be shown to be at equilibrium, providing that reaction takes place at a detectable velocity. Katharometers were

used to make the analyses of the gas compositions, but these instruments were sensitive to any impurity in the gas stream, and so before reliable measurements were made it was necessary to show that the gas compositions measured were free from errors derived from such impurities.

The first experimental run was carried out by setting up the furnace in the normal manner and not charging the crucible with iron. By doing this any difference found in gas composition at the "inlet" and "outlet", when the furnace was taken up to temperature, could be attributed to impurities introduced through leaks in the apparatus. Leakage of air into the system was detected and traced to two causes - ineffective sealing of the bungs at each end of the furnace tube and rubber-to-glass joins in the apparatus. The latter defect was remedied by constructing the apparatus as completely as possible with glass-blown joints; where this was impossible short lengths of rubber tubing were used, sealed with acetone collodion. The leaks occurring at the bungs were prevented by smearing the bungs with glycerol and strapping them in position with wooden saddles bolted firmly in position. These saddles had to be loosened while the furnace was being heated, so as to give the furnace tube room to

expand. The apparatus was now found to be completely leak-proof at room temperature, but when the temperature was raised higher than 1400°C . small quantities of hydrogen sulphide were detected. This was traced to pyrolysis of the rubber bungs, and almost completely eliminated by inserting radiation stoppers at each end of the furnace tube. The presence of hydrogen sulphide was, as would be expected, registered by the "outlet" katharometer only, and the effect of the small traces of this gas still present was avoided by passing the gases first through the "wet" side of the katharometer, then through an efficient drying tube containing "Anhydron", and finally through the "dry" side of the katharometer. In this way the effects of gaseous impurities other than water vapour were avoided altogether. After these preliminary investigations, the apparatus was considered ready for reliable measurements.

A run was now carried out by filling the crucible with 15 g. of carbonyl iron, containing 1% silicon intimately mixed therewith. The figure of 1% silicon was chosen as, according to the results of Zapffe and Sims, this should give a water vapour content in the surrounding atmosphere within the range measurable by the katharometers.

Oxidation of the charge during the heating-up of the furnace was prevented by passing dry hydrogen through the furnace tube until the temperature reached 1450°C . Above this temperature hydrogen containing the appropriate amount of water vapour for equilibrium conditions at 1600°C . was admitted. An attempt was made to reach a temperature of 1600°C . by adjusting the current passing through the windings, but this temperature was approached only within 5°C . and never exactly reached, because each step of the transformer tapping-system corresponded to a rise of furnace temperature of about 8°C .

When a steady temperature was reached the water content of the "outlet" gases was found to be constant, as indicated by the katharometer. This being so, the water vapour content of the "inlet" gas was altered by adjusting the temperature of the thermostat bath in which was immersed the calcium chloride saturator, so that its water vapour content was equal to that of the "outlet" gas.

When steady conditions had been reached the flow of hydrogen and water vapour was discontinued and replaced by a rapid stream of argon. After flushing the furnace tube with argon the current passing through the windings was turned off and the ingot allowed to cool inside the

furnace.

When cold, the furnace was opened, the ingot removed, and an analysis of the total silicon made in the manner described earlier in this section. The total silicon content of the ingot was found to be 1.07%, showing that no appreciable change from that charged initially had taken place.

From this experiment it appeared that equilibrium conditions not dissimilar to those of Zapffe and Sims were being produced. However, before further experiments of this nature were conducted it was necessary to show that the equilibrium being measured was real and not governed by some very slow rate-controlling process. Accordingly experiments were devised to show that both oxidation and reduction of the system were possible and that equilibrium may be approached from either direction.

The Reduction Process.

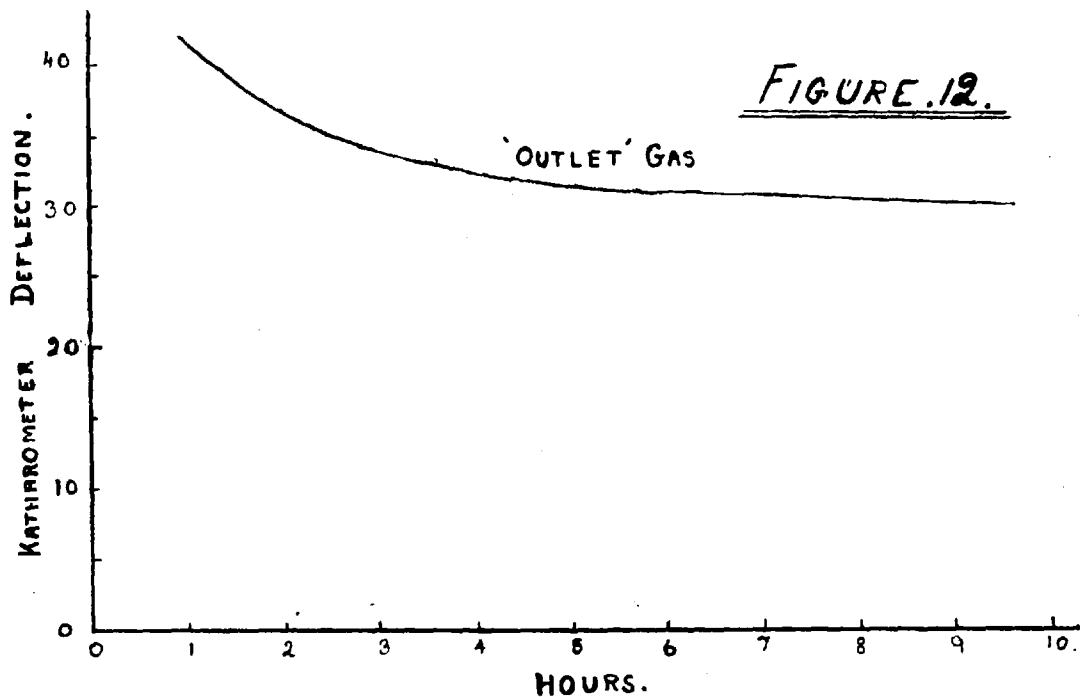
A charge of carbonyl iron containing no silicon was put into a translucent vitreosil silicon crucible and placed in the furnace. This charge was heated in a stream of dry hydrogen, as described for the previous experiment, but instead of changing the gas stream to the "wet" gas at 1450°C., the flow of dry gas was left uninterrupted

throughout the course of the run. The temperature was raised to some arbitrary value as near as possible to 1600°C. , and there allowed to remain.

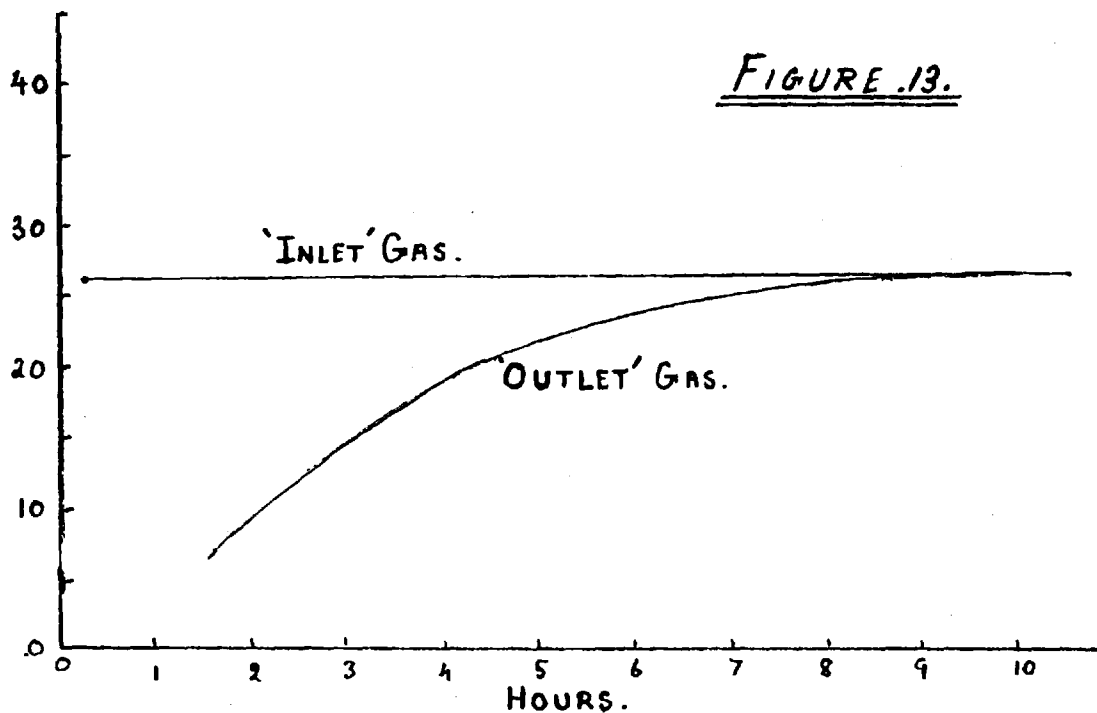
During the heating of the furnace and the subsequent period at a steady temperature, a continuous trace of the deflection of the katharometer provided a record of the gas composition of the "outlet" stream. Examination of this trace showed that during the period of increasing temperature the water vapour content of the "outlet" gas increased continuously to some very high value, off the scale of the katharometer records^{or}. After a period of about half an hour at 1608°C. the water vapour content dropped to a partial pressure of 15 mm., which was measurable by the katharometer. From this point onwards a continuous trace, which is reproduced in Fig.12, was obtained.

From this trace it may be seen that during the first two hours of the period at constant temperature most of the change in water vapour content took place, and after that period only very small changes occurred, even though there was still a difference in gas compositions in the "inlet" and "outlet" streams (the "inlet" being pure hydrogen only).

After a period of 10 hours the tube was flushed with



THE REDUCTION PROCESS.



THE OXIDATION PROCESS.

argon and cooled. Subsequent analysis of the ingot showed the silicon content to be 0.42% by weight, the whole of which must have been found from the crucible by reduction. This rate of pick-up was found to be very slow. Further experiments were carried out in the same manner, but for each successive run increasing amounts of silicon were added to the initial charge. From these further experiments it was found that as the silicon content of the ingot increased it became increasingly difficult to reduce the silica of the crucible and thereby increase the silicon content of the ingot.

Reduction did occur, because after each run the analysis for total silicon in the ingot revealed an increase in silicon content in each case.

This evidence showed that oxygen could be removed from the system, that the silicon content of the iron could be increased by reduction and that a condition which appeared to be that of equilibrium could be reached from the reduction of silica in contact with liquid iron.

The Oxidation of the System.

Satisfactory proof of the existence of a true equilibrium required approach of the same (supposedly equilibrium) concentrations by oxidation of silica in

the liquid iron, as well as by reduction of silica in contact with the metal.

A run was carried out in which the silica crucible was charged with iron containing 2% of silicon. The temperature was raised as quickly as possible to 1600°C . while the furnace tube was pumped out continuously. A vacuum was preferred to an atmosphere of dry hydrogen as hydrogen would almost certainly have increased the silicon content by a comparatively small, yet undesirable, amount. When a steady temperature had been reached the pumping was discontinued and hydrogen, containing water vapour in considerable excess over that expected for "equilibrium" conditions, was admitted. As soon as the furnace tube had been filled with wet hydrogen and a continuous flow established, a record of both "inlet" and "outlet" gas composition was made.

The two traces were examined by superimposing them one on the other, as shown in Fig.13. These two traces show that the "outlet" gas started with a relatively small water vapour content which, after a period of about seven hours, increased to a value equal to that of the "inlet" gas. The oxidation process, it appeared, was very much faster than the reduction and, furthermore, the oxidation

proceeded to equilibrium. A further experiment was carried in the same way but with no iron in the crucible. The "outlet" gas reached the same composition as that of the "inlet" gas without any time lag, showing that no oxygen was taken up from the gas stream. It was thus obvious that the oxygen take-up in the former experiment could only be attributed to oxidation of the liquid iron phase.

The ingot produced from this run was examined and visible signs of oxidation were found to be present on the surface, which was pitted and very rough in comparison with the surface of the ingots obtained by reduction. These latter ingots were smooth and shiny. Any oxidation of silica in the liquid iron phase necessarily produced free silica, which, on precipitation, rose to the surface. However, analysis showed the final silicon content of the ingot to be 1.85%, which shows a loss of only 0.15% from the value initially charged.

The oxidation process was shown to have reached equilibrium from gas composition measurements, but the

amount of silicon eliminated from the melt was only a fraction of that expected from the study of the reduction process. The final silicon content was expected to be very near 1.0%. The high final silicon content, in this experiment, and in others conducted similarly, was attributed to the incomplete separation of precipitated ^{silica} from the liquid iron phase, the silica remaining suspended in the iron in a finely divided form.

Some Preliminary Equilibrium Measurements.

From the above considerations it was considered desirable to approach the equilibrium from the reduction side as, if oxidation was allowed to take place for any length of time, an increasing part of the total silicon content of the ingot would be present as suspended silica, which would be determined by analysis as silica dissolved in the iron phase.

Several experimental runs were made at a temperature as near as possible to $1600^{\circ}\text{C}.$, so that the ferrous oxide activities corresponding to the different total silicon contents used could be measured under equilibrium conditions.

Charges were made with the silicon content 0.1% lower than the expected final value. The "run up" was carried out by passing a stream of dry hydrogen through the furnace

tube until a temperature of 1450°C . was reached. At this point the hydrogen was replaced by "wet" hydrogen. The temperature was raised to the required value and allowed to become steady. During this "run up" period the gas compositions of both "inlet" and "outlet" streams were continuously recorded by the katharometer recorders. When the difference in gas composition dropped to about 0.5 mm., the reaction was so slow that no change of the conditions occurred inside the furnace over periods of time as long as 24 hours.

Covering the charge of carbonyl iron with a layer of powdered quartz considerably increased the rate of take-up of silicon by the liquid phase, and large variations of the silicon concentration occurred in shorter periods of time. However, the difficulty of reaching the equilibrium still existed because the rate of reaction near equilibrium was still slow, and this was overcome finally by adjusting the water-vapour content of the "inlet" gas to the steady value reached by the "outlet" gas. The presence of the powdered quartz accelerated the initial part of the reaction so much that it was possible to bring the difference of gas compositions to within 5% within three to five hours.

Approach of the equilibrium by this method involved

long periods of time during which the furnace could not be kept at a steady temperature. Furthermore, it was only after both the silicon content and the oxygen pressure of the system had been altered that one equilibrium point could be measured.

This technique, although satisfactory for obtaining preliminary data, was inadequate for full investigation of the system over the temperature range desired.

The system has four variables, each of which has to be fixed for any one equilibrium point. These variables are total pressure, temperature, partial oxygen pressure (in this case measured from a knowledge of the water vapour pressure - hydrogen pressure ratio), and total silicon content of the melt. In the preliminary experiments the temperature and total pressure were fixed, and the silicon content and oxygen pressure adjusted until no further reaction took place.

The oxygen pressure was the easiest of the four variables to measure and to alter. If the total silicon content could be kept constant as well as the total pressure, then the oxygen pressure variation could be studied with variations of temperature. The following run showed this to be possible.

A silica crucible was charged with carbonyl iron containing 0.7% of silicon, placed in the furnace, and heated in a current of dry hydrogen. The temperature was increased until some arbitrary value over 1535°C . was reached. When the temperature was steady the gas composition of the "outlet" stream was noted and the water vapour pressure of the "inlet" stream adjusted to a value about 1.0 mm. lower than that of the "outlet" stream from the furnace. The composition of the "inlet" gas stream was then slowly increased by raising the temperature of the thermostat bath surrounding the calcium chloride saturator. In this way the equilibrium point could be reached, as shown by the compositions of "inlet" and "outlet" gas streams being equal; further increase in the water vapour content of the "inlet" gas over the value of that of the "outlet" gas showed that oxidation was now occurring and that the equilibrium point had been passed. The water vapour content of the "inlet" gas stream was lowered to a value about 0.1 mm. lower than that of the "outlet" stream and left steady for half an hour, during which time equilibrium was finally attained.

The measurements now made established one set of equilibrium values of silicon concentration in the melt, oxygen

pressure and temperature. For a further measurement the current passing through the furnace was increased sufficiently to raise the temperature some fifty degrees. The actual temperature of the furnace did not matter so long as it remained constant and was accurately known. As this new temperature was being reached, the water vapour content of the "outlet" gas rose to a new value, so in order to obtain new equilibrium conditions the water vapour content of the "inlet" gas was increased slowly, as before, and further equilibrium concentrations measured. In this way the oxygen pressure of the system could be studied for a number of temperatures during the course of one run, provided the silicon content remained constant from the first measurement until the furnace was flushed with argon. Subsequent analysis of the ingot from this run for total silicon content revealed that the silicon content had not altered measurably.

When the "inlet" and "outlet" gas compositions did not differ by more than 2 mm., the change in the silicon content, produced by such difference, was small. This is better understood by considering the change in silicon content that would occur in 1 hour at a flowrate of 4 litres/hour

in an 18 gram ingot. The change in silicon content is calculated on the assumption that 1 gram-mol of oxygen is required to alter the silicon content by 1 gram atom.

Diff. in gas composition	% wt. of Si changed
0.2 mm. H_2O	0.0037%
0.5 " "	0.0092%
1.0 " "	0.0185%
2.0 " "	0.0370%
5.0 " "	0.0925%
10.0 " "	0.185%
20.0 " "	0.370%

If some increase of the total silicon had occurred it would almost certainly have taken place during the period of the "run-up" when the ingot was subjected to strongly reducing conditions. Evidence from previous runs has shown that when equilibrium was nearly reached the amount of silicon taken up by the reduction of the silica in contact with the ingot was not measurable. The rate of reduction of silica was further reduced by omitting to place the layer of powdered quartz on top of the charge. The small variations of silicon content occurring during a series of runs were accordingly neglected. It was by using this technique of studying the variation of oxygen pressure with temperature that the majority of data were obtained.

Procedure adopted for Investigating the Equilibrium.

A small translucent "Vitrescil" crucible was filled with about 18 g. of carbonyl iron containing some admixed silicon in the form of a fine powder. Carbonyl iron grade C was used as supplied by the Menel Nickel Company. The maximum limits of impurities are given as:

Ni	0.05%
C	0.1 %
O	0.2 %
N ₂	0.02%
S ₂	0.001%
Si, Cu, Co and Cr.	0.2 %

The amount of silicon charged was always slightly less (0.1%) than that desired at equilibrium, as in the runs with small silicon contents the small take-up of silicon, which sometimes occurred during the "run up", increased the total silicon above the desired value.

If the total silicon content produced an unexpectedly large water vapour content in the "outlet" gas stream, the hydrogen flow was continued until sufficient reduction had taken place to reduce the water vapour content of the furnace atmosphere to the value desired. When the water vapour and hydrogen mixture was afterwards admitted, it stopped further reaction and the total silicon content of the melt remained approximately constant for the duration

of the run.

The air inside the tube was pumped out and the system tested for leaks. If the pressure inside the furnace tube did not increase to more than 2 mm. over a period of five minutes after complete evacuation, the apparatus was considered to be leak-proof. Dry hydrogen was now admitted to the tube and when atmospheric pressure had been reached inside the tube the tap controlling the exit of gases from the furnace was opened to allow the passage of a steady stream of hydrogen. The normal rate of flow was a little over 4 litres per hour.

The temperature was raised to about 10°C. above the melting point (1535°C.) of the iron phase and allowed to become steady. The water vapour content of the "outlet" gas, was observed from the katharometer recorder and the temperature of the calcium chloride saturator altered to the desired value. If alteration of the silicon content was to be avoided during the run up wet hydrogen was substituted for the dry gas at a temperature lower than 1450°C.

When the change over from "dry" to "wet" hydrogen was made no appreciable variation in the gas composition at the outlet was observed once the effects of the alteration

of flow rate had passed.

When the required temperature was reached reduction of the system was taking place. The reduction of the system was followed by oxidation which was only allowed to continue for a period of ten minutes - sufficient to show that equilibrium had been passed and that the effect was real. The water vapour content of the "inlet" gas was then reduced so that it was again lower than that of the "outlet" gas. The gas compositions were then left to become steady over a period of twenty minutes, during which time the water-vapour pressure in the "outlet" gas seldom varied by more than 0.2 mm. This final gas composition was taken as the equilibrium value attained by the system.

Before each temperature measurement was made the potentiometer system was standardised. During the course of the run temperature measurements were taken about every fifteen minutes, except during the final stages of the equilibrium, when they were taken every five minutes.

The temperature of the furnace was now increased some fifty degrees and allowed to become steady. The water vapour content of the "outlet" gas stream had increased to some value higher than that previously measured. At this new temperature the whole procedure was repeated and

a further set of measurements made.

After measurements had been taken at three or four temperatures, the flow of hydrogen and water vapour was replaced by a rapid (6 litres per hour) stream of argon. The argon was passed into the furnace through the anti-thermal diffusion tube in order to surround the ingot constantly by the inert atmosphere. After the argon had flowed for about ten minutes the furnace was cooled.

Some experiments were conducted by cooling the furnace to 700° C. only, to save time and strain on the furnace windings. Although the crucible could be removed readily, the thermal strain on mullite trough was usually too great and caused it to fracture. Also, on placing the new charge in the hot furnace excessive oxidation occurred which could only be counteracted by prolonged reduction in a dry hydrogen atmosphere. The cold crucible was taken from the furnace and the ingot removed.

Except in the runs carried out at high silicon concentrations, the upper surface of each ingot was bright, smooth, and free from surface adhesions. The sides and bottom were seldom found to be pitted but small particles of silica from the crucible adhered to the surface.

The ingot was cleaned, if necessary cut up, and

analysed for total silicon as previously described.

The oxygen pressures had been determined at several temperatures at a constant silicon content of the melt. The temperature range over which the investigation was carried out was 1540°C. to 1660°C. In three runs the temperature was taken a few degrees over 1700°C. and the results obtained showed the system in a manner similar to that at lower temperatures.

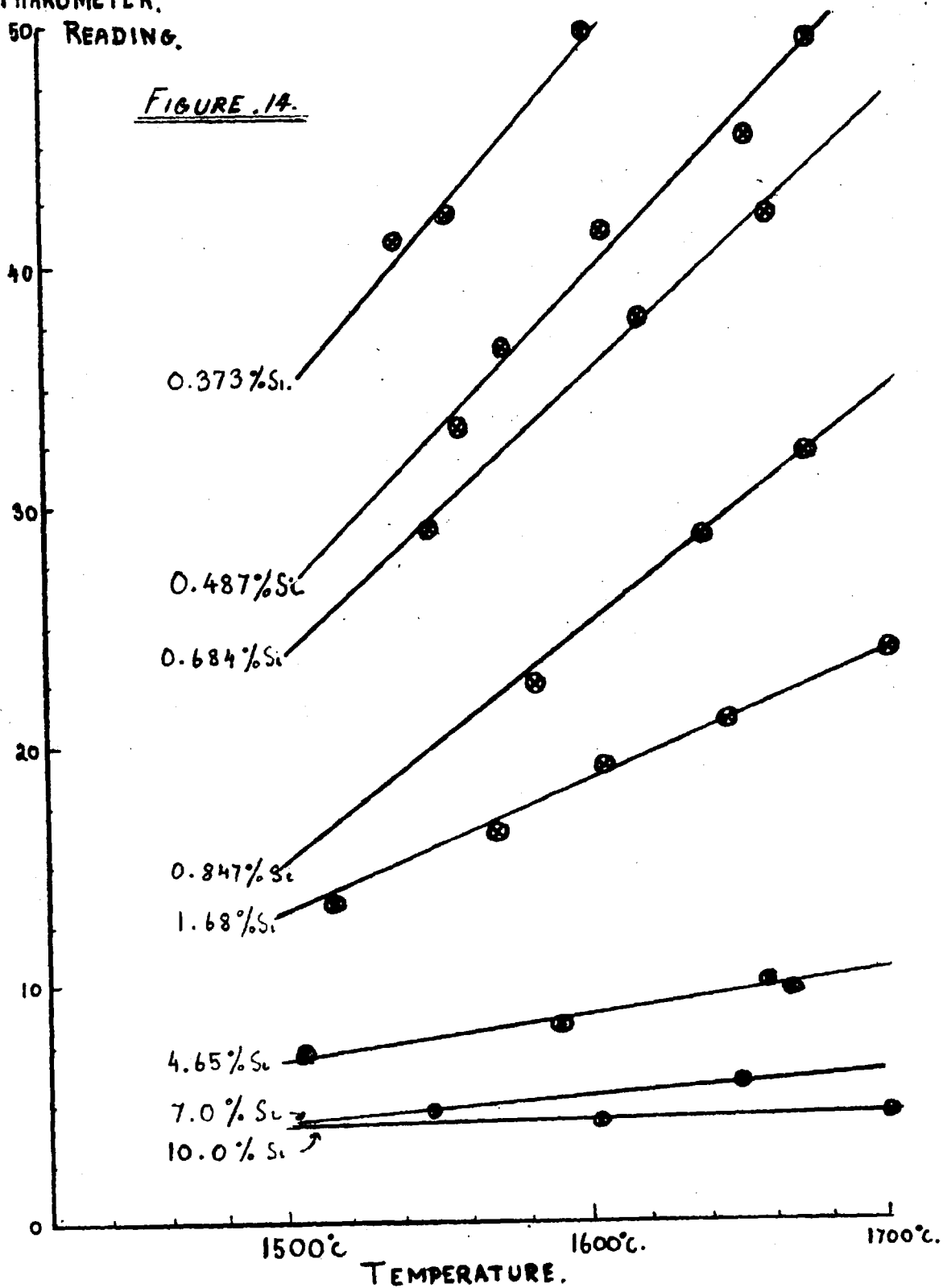
The katharometer records allowed the water vapour - hydrogen ratio in the equilibrium gas atmosphere to be plotted against temperature for each value of the total silicon content. Some of these plots are shown in Fig.14, and from them may be seen that a linear relation exists within experimental error. The three runs carried out at a maximum temperature of 1700°C. showed that this linearity was maintained, and so extrapolation of all plots to 1700°C. was considered justified.

Thermal Diffusion.

When a mixture of two or more gases is contained in a vessel in which a large thermal gradient exists, the gases with the greater molecular weights tend to concentrate at the cooler end of the gradient. This phenomenon is known

50f READING.

FIGURE 14.



as thermal diffusion, and is explained by the kinetic theory of gases. The effect may be lessened considerably by causing the mixture of gases to flow through the vessel at a sufficient rate to procure establishment of the thermal-diffusion equilibrium.

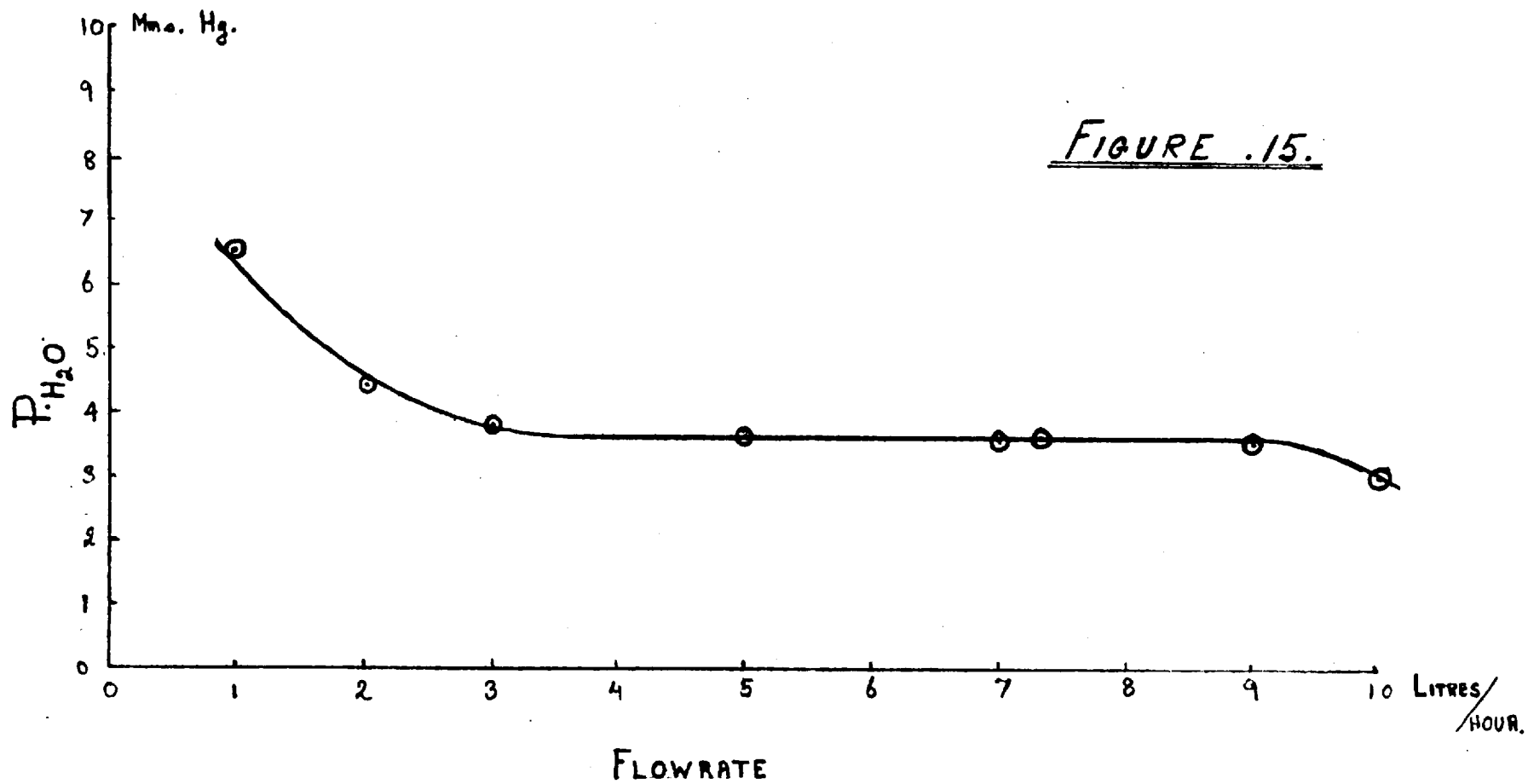
Fontana and Chipman (J. Amer. Chem. Soc., 1934, 56, 2011) showed that when a concentration of one of the reactants in an equilibrium was controlled by a gas mixture, the errors of the equilibrium in consequence of thermal diffusion could be as much as 20%.

Zepffe and Sims (Metals Technology, 1942, 9, No. 6) in their investigation of the silicon-oxygen equilibrium in liquid iron, relied on the preheating of the water vapour-hydrogen gas mixture by the furnace tube only to overcome the effects of thermal diffusion, but no experimental evidence was given to justify the technique. Fontana and Chipman overcame the effect by preheating the gases in a narrow alumina tube, heated by windings of platinum wire, through which the gases were passed rapidly before entering the furnace.

In this research the problems of thermal diffusion were somewhat different from those of previous investigators, as both "inlet" and "outlet" gas streams were analysed

for their water-vapour content. The tube through which the gases left the furnace was, as described in Section 2, of narrow-bore mullite, and extended into the furnace to a position directly over the crucible. The gases, if passed at a sufficient rate, were "quenched" before any thermal diffusion could take place along the thermal gradient. No attempt was made to preheat the incoming gases because when the system was not at equilibrium it was not important that the exact composition reaching the melt be known, providing it was known whether oxidation or reduction was occurring. When equilibrium was reached then the composition of the "inlet" gas measured by the katharometer was the same as that reaching the ingot inside the furnace, otherwise it would imply that water vapour was being lost or gained under "equilibrium" conditions.

The extent to which thermal diffusion took place was controlled by the flow rate. Accordingly, the effect of variations of flow rate on the composition of the effluent gas was investigated. The carbonyl iron in the crucible was charged with 7% silicon, as it was known that at this high concentration both the temperature effect and the effect of increasing the silicon by reduction had negligible



effects on the equilibrium gas composition. The gas composition of the "outlet" gas was measured at each of a number of flow rates between one and ten litres per hour. As each variation of flow rate was made, the katharometer zero had to be readjusted to prevent the effect of the flow rate on the katharometer interfering. Fig.15 shows a plot of katharometer reading against flow rate carried out at a constant temperature of 1605°C . The effects of thermal diffusion are quite pronounced when the flow rate is below 3 litres per hour, but above this value no effect at all was measurable until at 10 litres per hour the effect of turbulence on the katharometer became significant. The flow rate used was usually 4 litres per hour.

Ordinary Gas Diffusion.

The furnace tube isolating the system from the furnace was of an alumina refractory. Such tubes develop a slight porosity above 1600°C ., but it was found that if an excess pressure of 5 mm. was maintained inside the tube, the diffusion of foreign gases into the system was negligible. The furnace tubes developed micro-cracks after prolonged usage, and when this occurred the tube was discarded, as diffusion of foreign gases into the system vitiated

measurements. Such breakdown was immediately detected by the katharometer, the galvanometer deflection of which swung right off the scale.

Quenching in Argon.

The type of furnace used was not suitable for quenching the melt by withdrawing it from the furnace tube. Previous workers have used vertical furnaces and dropped the crucible from the hot zone of the furnace directly into some cooling liquid: water, liquid tin, and carbon tetrachloride have been used for this purpose. Withdrawal of a crucible at 1650°C. from a horizontal furnace in the course of a few seconds was impracticable, especially as the furnace atmosphere was predominantly hydrogen and therefore a potential explosive.

Evidence already obtained showed that precipitation of silica from the melt was very slow. Measurements of the rate of cooling of the furnace once the current had been turned off showed that solidification of the melt took place about 10 minutes after cooling from 1650°C. ; during this time the amount of silicon precipitated as silica would be considerable only if the hydrogen-water vapour atmosphere was maintained. For a melt containing

0.85% silicon in equilibrium with its surroundings at 1650°C., about half the silicon would be oxidised to silica if the temperature was dropped to 1550°C. and the composition of the atmosphere maintained. By replacing the atmosphere of hydrogen and water vapour with argon, the source of oxygen was removed and the high degree of oxidation prevented. However, even if this source of oxygen was not removed previous evidence has shown that the major part of the silica would remain suspended in the melt. That a part of the total silicon content of the ingot was present as suspended silica did not matter so long as it did not rise to the surface, as it was the total silicon content of the ingot that was measured.

Technique used for Measurements at High Oxygen Pressures.

Katharometers could not be used to measure the water vapour content of the hydrogen at the higher values required. Of the methods available for measuring the water vapour pressure of a gas, a modified form of the Regnault dew-point method was used. These methods, including the dew-point technique, are subject to rather large inaccuracies. As in the work carried out at lower oxygen pressures, it was desirable to measure the water-vapour content of both the "inlet" and the "outlet" gas streams.

The amount of water vapour in the hydrogen was closely controlled by the saturating unit described fully in Section 2. This apparatus had the advantage over the calcium chloride saturator of being more reliable in controlling the water vapour content of the gas stream. The hydrogen and water vapour from the saturator were led straight to the furnace through glass tubing heated by a suitable winding of "Nichrome" resistance wire, and it was from the temperature of the thermostat bath of the saturator that the degree of saturation of the "inlet" gas stream was measured.

The gases left the furnace by passing through the anti-thermal-diffusion tube, to which was connected heated

glass tubing leading to the dew-point apparatus. The construction and use of this piece of apparatus is described in Section 2. A further disadvantage of the dew-point apparatus was the time required for each measurement to be made - about four minutes.

The "run up" had to be carefully controlled, as excessive oxidation would have led to formation of a large and undesirable amount of silica, and excessive reduction to too much silicon present in the liquid-iron phase. It was found satisfactory to run the furnace up to a temperature of about 800°C . in a current of pure hydrogen and then pass a stream of hydrogen containing a suitable amount of water vapour. The amount of water vapour chosen was guided by dew-point measurements made during the "run up" to 800°C . This method of controlling the furnace was found to prevent both excessive reduction and excessive oxidation.

Attempts were made in earlier runs to investigate the variation of the oxygen pressure of the system with variation of temperature at constant silicon concentration. This, however, was found impracticable as, when using small amounts of silicon, it was impossible to keep the silicon content constant while measurements were being

made over a temperature range. At the lower silicon concentrations, small increases in total silicon content represent a very much larger proportional increase.

No silicon was put in the initial charge, as sufficient was taken up by reduction of the silica crucible during the initial period of running up in pure hydrogen. When a temperature of 1600°C . was reached, dew-point measurements of the "outlet" gas were made every half hour until a steady value was obtained.

The water-vapour content of the gas stream entering the furnace was kept somewhat lower than that leaving the furnace so that reduction was always occurring. When the temperature of the furnace was steady the water vapour content of the "inlet" gas was increased until it became equal to that of the "outlet" gas. It was not considered wise to increase the water vapour content of the "inlet" gas above that of the "outlet" gas, as the accuracy of measurements in the latter was not sufficient to show when the one composition was only slightly greater than the other. The melt was allowed to equilibrate over a period of one hour, during which time dew-point measurements were taken continually. After the requisite measurements were made the furnace tube was flushed with argon, the

furnace current cut off, and the melt allowed to cool inside the furnace. When cold the ingot was taken from the furnace and analysed in the usual way.

SECTION IV

RESULTS.

The Ferrous Oxide Activity in Liquid Iron.

When small quantities of oxygen (less than 0.9%) dissolve in liquid iron, then from the free-energy considerations of J. Chipman and M. G. Fontana (Trans. Amer. Soc. Metals, 1936, 24, 313) most of the oxygen may be considered to react with the liquid iron to form dissolved ferrous oxide. The partial oxygen pressure of the atmosphere surrounding such a melt at equilibrium would be very small and not directly measurable, so in order to control and measure this small oxygen pressure indirect methods have to be used. Mixtures of small amounts of water vapour in equilibrium with hydrogen will produce oxygen pressures of the right order of magnitude, therefore if the partial water vapour pressure in the surrounding atmosphere is accurately known, the ferrous oxide activity in the melt may be derived. The equations representing the various stages of the reaction are:



which, when combined, give the equation:



$$\text{where } K_{\text{FeO}} = \text{H}_2/\text{H}_2\text{O} \times (\text{FeO})$$

The ratio of the partial pressures of hydrogen and water vapour was measured directly by the katharometers. A knowledge of this ratio, together with the value of the equilibrium constant K_{FeO} at the appropriate temperature allows the ferrous oxide activity to be calculated.

Attempts to obtain values of K_{FeO} in the liquid-iron range 1535°C. to 1700°C. have been made by several workers, but a comparison of the various results shows considerable divergence exists.

F. D. Richardson and J. H. E. Joffe (J.Iron.Steel.Inst. 1948, 160, 268) have made a comprehensive survey of all existing data for the reaction:



The principal results taken for consideration were those of J. Chipman and S. Marshall (J.Amer.Chem.Soc., 1940, 62, 299), P. H. Emmett and J. F. Schultz (J.Amer. Chem.Soc., 1930, 52, 4268), L. S. Darken and R. W. Gurry (J.Amer.Chem.Soc., 1945, 67, 1398), and V. Cirilli (Gazetta Chimica Italiana, 1947, 76, 331). Of these results, only those of Chipman and Marshall were given for the liquid iron range, 1535°C. to 1700°C. , but these did not produce a straight line when ΔG° was plotted against the reciprocal of the absolute temperature.

Richardson and Jeffes arrived at their final values by extrapolating the data known to be reliable below the melting point of iron, and making appropriate corrections for the entropy change at the melting points of ferrous oxide and iron. In that way they arrived at the following expression representing the variation of free energy with temperature for reaction (5).

$$\Delta G^{\circ} (1808^{\circ} - 2000^{\circ}\text{K.}) = -111,250 + 21.67 T \dots (6)$$

The equation for reaction (1) was obtained from Richardson and Jeffes' survey (*ibid.*, p.267) of existing data, the principal works considered being those of F. D. Rossini (*Res. Nat. Bur. Stds.*, 1939, 22, 407) and A. R. Gordon (*J. Chem. Physics*, 1934, 2, 65). The equation derived was:

$$\Delta G^{\circ} (373^{\circ} - 2500^{\circ}\text{K.}) = -118,000 + 26.75 T \dots (7)$$

Combining equations (6) and (7) the equation representing reaction (4) is obtained:

$$\Delta G^{\circ} (1808^{\circ} - 2000^{\circ}\text{K.}) = 3,380 - 2.54 T \dots (8)$$

From this expression the values of K_{FeO} shown in Table 3 were calculated.

TABLE 3.

T [°] C.	T [°] K	Log.K.	K _{FeO}
1550 [°] C.	1823 [°] K.	1.850	0.708
1575 [°] C.	1848 [°] K.	1.844	0.698
1600 [°] C.	1873 [°] K.	1.839	0.690
1625 [°] C.	1898 [°] K.	1.834	0.682
1650 [°] C.	1923 [°] K.	1.829	0.675
1675 [°] C.	1948 [°] K.	1.825	0.668
1700 [°] C.	1973 [°] K.	1.820	0.661

Results from Direct Experiment.

Each "run" provided oxygen pressures corresponding to a set of fixed temperatures at a constant silicon concentration. The oxygen pressures were interpreted from the katharometer deflections, a continuous record of which was obtained from the trace of the recorder. The data obtained are shown in the table below.

Data Obtained Directly from Experiments.

TOTAL SILICON					
No.	Init.	Final	Temperature	Kato. Defl.	P _{H₂O}
	% wt.	% wt.	[°] C.	Divisions	mm.
1.	1.0	1.68	1560 [°] C.	15.8	4.70
			1601 [°] C.	18.5	5.52
			1631 [°] C.	20.0	5.97
			1703 [°] C.	24.5	7.20

TOTAL SILICON					
No.	Init.	Final	Temperature	Kato. Defl.	P _{H2O}
	% wt.	% wt.	°C.	Divisions	mm.
2.	0.6	0.785	1559°C.	24.0	7.13
			1645°C.	32.2	9.62
			1661°C.	34.7	10.38
3.	0.3	0.684	1535°C.	24.5	7.31
			1559°C.	30.0	8.97
			1679°C.	41.0	12.24
4.	1.0	0.847	1589°C.	23.1	6.90
			1640°C.	29.0	8.66
			1668°C.	31.7	9.47
5.	0.4	0.487	1551°C.	32.0	9.60
			1562°C.	32.7	9.79
			1610°C.	41.0	12.25
			1648°C.	45.5	13.65
			1669°C.	43.0	14.28
6.	0.4	0.373	1539°C.	40.9	12.20
			1554°C.	42.1	12.57
			1590°C.	48.2	14.36
7.	0.5	0.568	1592°C.	32.0	9.60
			1610°C.	36.3	10.84
			1679°C.	44.6	13.37
			1590°C.	30.6	9.15
8.	0.4	0.388	1537°C.	40.7	12.13
			1561°C.	44.0	13.15
			1597°C.	48.5	14.46
9.	1.0	1.387	1636°C.	21.8	6.52
			1665°C.	24.5	7.20
			1705°C.	25.9	7.71
10.	5.0	4.65	1541°C.	7.5	2.21
			1596°C.	8.2	2.41
			1665°C.	10.1	3.00
			1658°C.	9.8	2.89
11.	10.0	9.9	1701°C.	4.5	1.31
			1604°C.	4.2	1.22
12.	7.0	7.1	1636°C.	4.2	1.22
			1601°C.	5.1	1.51
			1653°C.	5.5	1.63

TOTAL SILICON			Temperature	Kato Defl.	P_{H_2O}
No.	Init.	Final			
	% wt.	% wt.	°C.	Divisions	mm.
13.	0.9	0.825	1542°C.	21.0	6.24
			1605°C.	26.5	7.91
			1691°C.	35.4	10.57
14.	0.0	0.48	1571°C.	33.2	9.92
			1627°C.	40.9	12.20
			1694°C.	44.7	13.39

The Interpolation of the Isotherms.

Direct interpretation of the data in the preceding table is impossible as each point represents equilibrium concentrations determined at some arbitrary temperature in the range 1550°C. - 1700°C.

From the plot of oxygen pressure against temperature at constant silicon concentration, the oxygen pressure was interpolated at each temperature between 1550°C. and 1700°C. at 25°C. intervals. The interpolated data are shown in Tables 4 - 10, each table representing the isothermal variation of $(FeO)^2 (\Sigma Si)$ with (FeO) .

The oxygen in the liquid iron phase was considered by previous workers to be present as dissolved ferrous oxide, rather than dissolved oxygen. For the purposes of uniformity and comparison, the oxygen present is regarded here as being due to ferrous oxide dissolved in the iron.

TABLE 4.

TEMPERATURE 1550°C.

	Final Si	P _{H₂O}	P _{H₂O} /P _{H₂}	(FeO)	(FeO) ² (Σ Si)
	% wt.	mm.	x 10 ⁻³	x 10 ⁻³	x 10 ⁻⁵
1	1.68	4.62	6.07	8.58	12.35
2	0.785	6.85	9.00	12.75	12.63
3	0.684	8.32	10.92	15.47	16.26
4	0.847	5.95	7.82	11.08	10.35
5	0.487	9.71	12.77	18.02	15.72
6	0.373	13.80	18.15	25.63	25.71
7	0.568	8.74	11.50	16.25	15.03
8	0.388	12.47	16.41	23.20	20.90
9	1.387	4.88	6.42	9.07	11.4
10	4.65	2.26	2.97	4.19	8.20
11	9.9	1.20	1.58	2.23	4.96
12	7.1	1.30	1.71	2.41	4.07
13	0.825	6.30	8.28	11.72	11.01
14	0.48	9.40	12.40	17.53	14.78

A plot of (FeO)²(Σ Si) against (FeO) is shown in Fig.16. The equation representing the best straight line passing through these points is given by

$$(FeO)^2(\Sigma Si) = 0.818 \times 10^{-2} (FeO) + 2.43 \times 10^{-5}$$

TABLE 5.

TEMPERATURE 1575°C.

	Final Si	P _{H₂O}	P _{H₂O} /P _{H₂}	(FeO)	(FeO) ² (Σ Si)
	% wt.	mm.	x 10 ⁻³	x 10 ⁻³	x 10 ⁻⁵
1	1.68	5.05	6.65	9.51	15.1
2	0.785	7.68	10.09	14.45	16.3
3	0.684	9.13	12.05	17.25	20.4
4	0.847	6.67	8.78	12.60	13.4
5	0.487	10.71	14.12	20.2	19.9
6	0.373	14.80	19.48	27.9	29.0
7	0.568	9.63	12.65	18.1	18.7
8	0.388	13.30	17.50	25.1	24.7
9	1.387	5.30	6.97	9.98	13.87
10	4.65	2.41	3.17	4.53	9.60
11	9.9	1.20	1.58	2.26	5.10
12	7.1	1.42	1.87	2.68	5.04
13	0.825	7.08	9.32	13.36	14.76
14	0.480	10.34	13.65	19.52	18.31

A plot of (FeO)²(Σ Si) against (FeO) is shown in Fig.17. The equation representing the best straight line passing through these points is given by

$$(FeO)^2(\Sigma Si) = 0.846 \times 10^{-2}(FeO) + 3.94 \times 10^{-5}$$

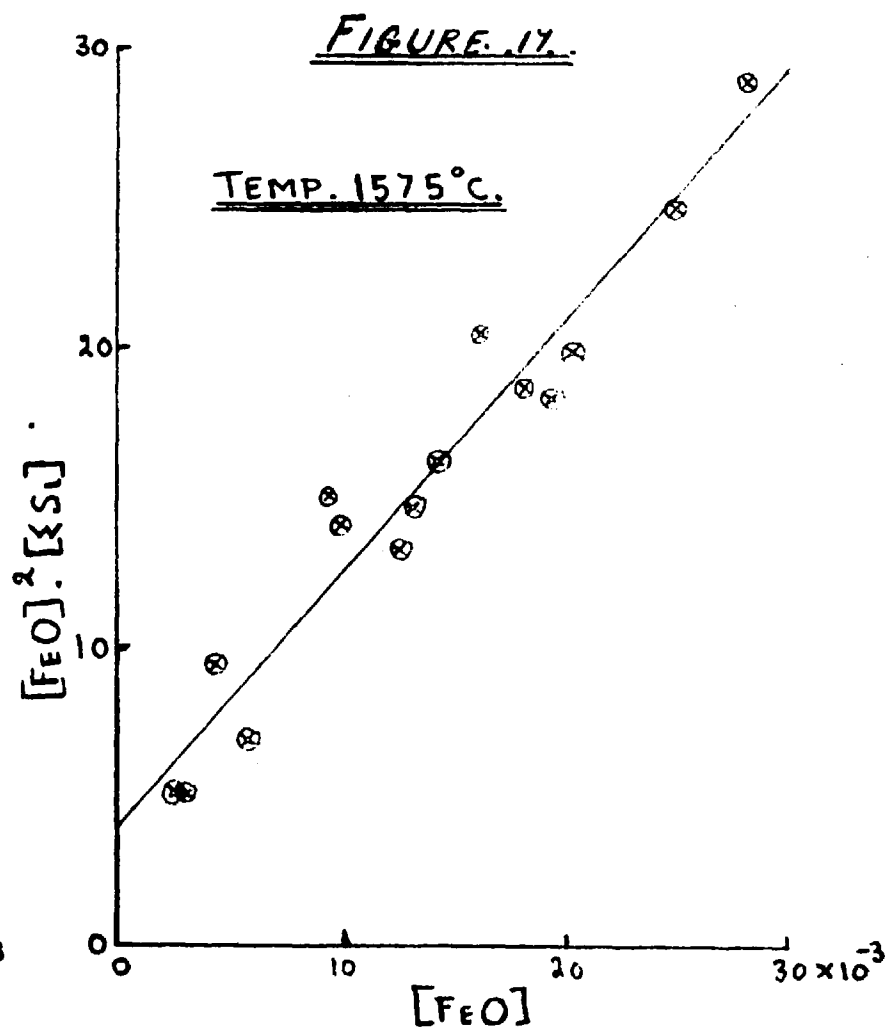
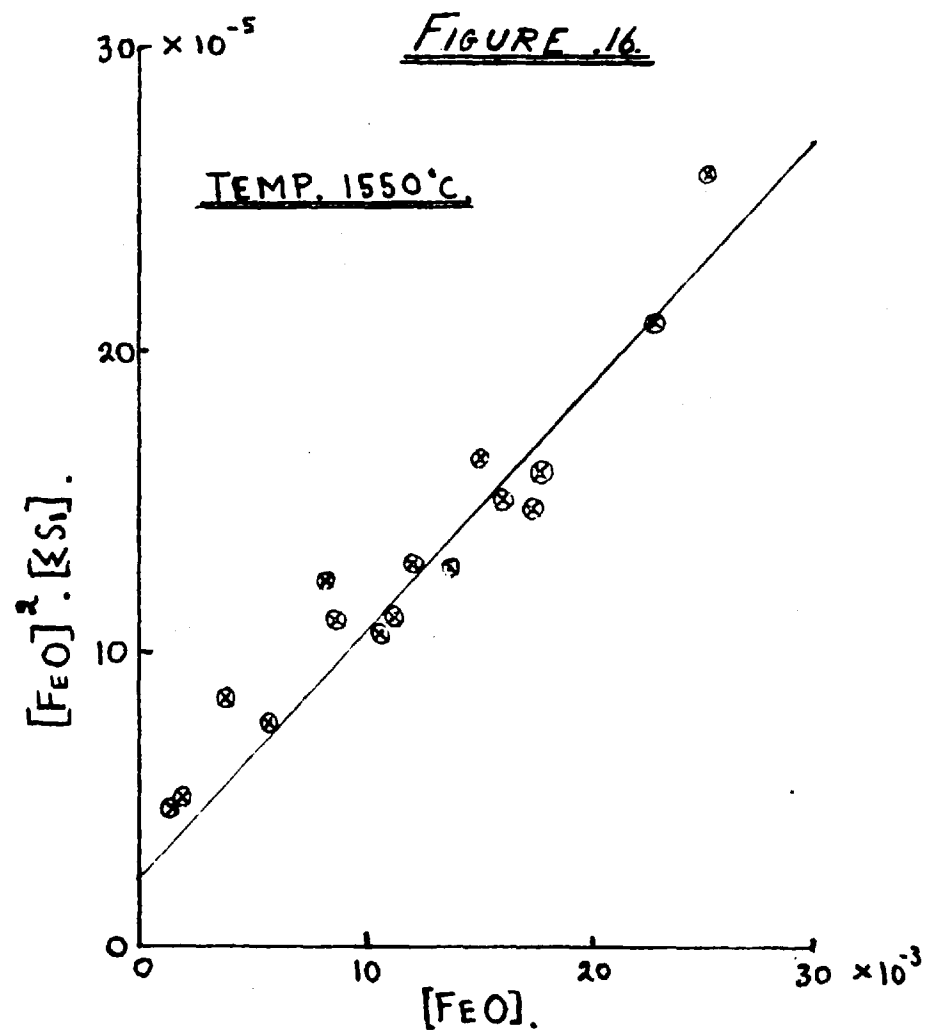


TABLE 6.

TEMPERATURE 1600° C.

	Final Si	P _{H₂O}	P _{H₂O} /P _{H₂}	(FeO)	(FeO) ² (Σ Si)
	% wt.	mm.	x 10 ⁻³	x 10 ⁻³	x 10 ⁻⁵
1	1.68	5.45	7.17	10.40	18.1
2	0.785	8.45	11.10	16.10	20.4
3	0.684	10.00	13.12	19.05	24.8
4	0.847	7.38	9.73	14.10	16.8
5	0.487	11.72	15.42	22.17	24.3
6	0.373	16.00	21.08	30.50	34.6
7	0.568	10.52	13.80	20.02	22.8
8	0.388	14.60	19.2	27.8	30.1
9	1.387	5.80	7.63	11.02	16.9
10	4.65	2.56	3.37	4.88	11.0
11	9.9	1.21	1.59	2.31	5.3
12	7.1	1.47	1.94	2.81	5.5
13	0.825	7.87	10.38	15.05	18.6
14	0.480	11.36	14.95	21.7	22.5

A plot of (FeO)²(Σ Si) against (FeO) is shown in Fig. 18. The equation representing the best straight line passing through these points is given by:

$$(FeO)^2(\Sigma Si) = 0.912 \times 10^{-2} (FeO) + 5.21 \times 10^{-5}$$

TABLE 7.

TEMPERATURE 1625°C.

	Final Si	P_{H_2O}	P_{H_2O}/P_{H_2}	(FeO)	$(FeO)^2(\Sigma Si)$
	% wt.	mm.	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-5}$
1	1.68	5.90	7.77	11.36	21.8
2	0.785	8.12	10.6	15.64	19.2
3	0.684	10.83	12.7	20.9	29.8
4	0.847	8.20	10.8	15.8	21.0
5	0.487	12.78	16.9	24.65	30.1
6	0.373	16.98	22.3	32.8	39.9
7	0.568	11.40	15.0	22.0	27.5
8	0.388	15.71	20.7	30.3	35.6
9	1.387	6.24	8.2	12.02	19.9
10	4.65	2.72	3.58	5.26	12.7
11	9.9	1.25	1.64	2.41	5.8
12	7.1	1.55	2.04	2.99	6.2
13	0.825	8.62	11.34	16.6	22.7
14	0.480	12.23	16.1	23.6	26.8

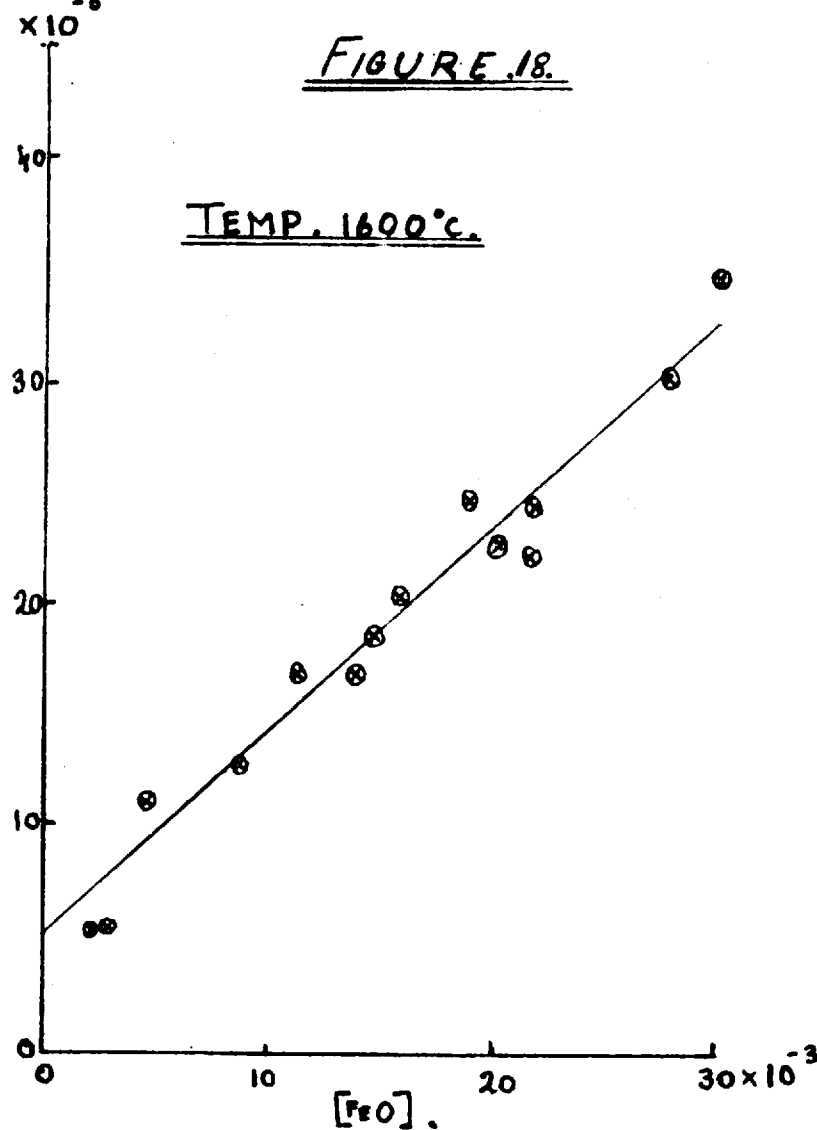
A plot of $(FeO)^2(\Sigma Si)$ against (FeO) is shown in Fig.19. The equation representing the best straight line passing through these points is given by:

$$(FeO)^2(\Sigma Si) = 1.012 \times 10^{-2} (FeO) + 5.84 \times 10^{-5}$$

$[\text{FeO}]^2 \cdot [\text{KSl}] \cdot 10^{-5}$

FIGURE 18.

TEMP. 1600°C.



$[\text{FeO}]^2 \cdot [\text{KSl}] \cdot 10^{-5}$

FIGURE 19.

TEMP. 1625

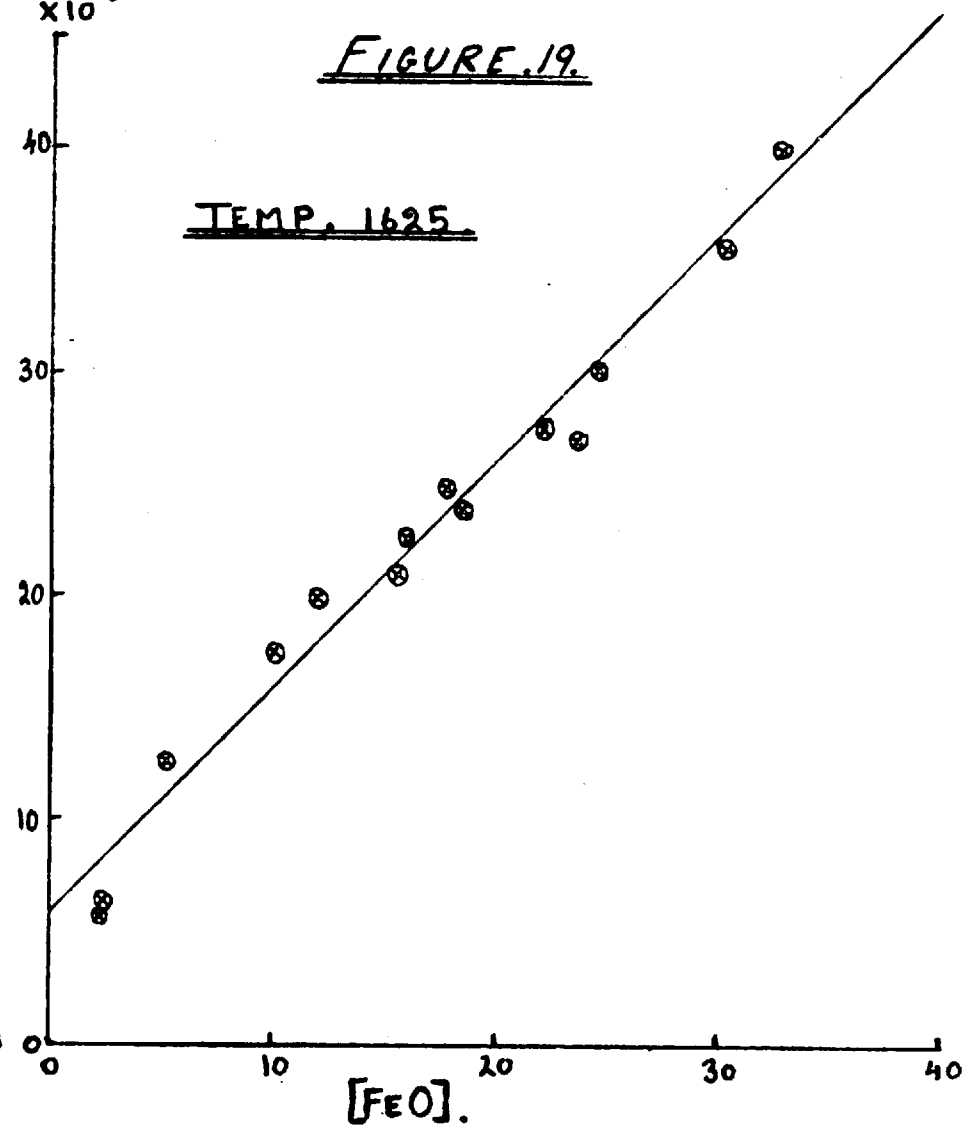


TABLE 8.
TEMPERATURE 1650°C.

	Final Si	P_{H_2O}	P_{H_2O}/P_{H_2}	(FeO)	$(FeO)^2(\Sigma Si)$
	wt.	mm.	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-5}$
1	1.68	6.30	8.29	12.3	25.2
2	0.785	10.05	13.22	19.6	30.2
3	0.684	11.65	15.31	22.7	35.3
4	0.847	8.93	11.72	17.4	25.6
5	0.487	13.80	18.15	27.0	35.4
6	0.373	18.03	23.70	35.1	46.1
7	0.568	12.30	16.20	24.0	32.8
8	0.388	16.75	22.1	32.6	40.2
9	1.387	6.72	8.85	13.1	23.7
10	4.65	2.83	3.72	5.5	14.2
11	9.9	1.26	1.66	2.5	6.02
12	7.1	1.63	2.15	3.2	7.07
13	0.825	9.36	12.34	18.3	27.7
14	0.480	13.20	17.35	25.7	31.6

A plot of $(FeO)^2(\Sigma Si)$ against (FeO) is shown in Fig. 20. The equation representing the best straight line passing through these points is given by:

$$(FeO)^2(\Sigma Si) = 1.101 \times 10^{-2} (FeO) + 6.22 \times 10^{-5}$$

TABLE 9.

TEMPERATURE 1675° C.

	Final Si	P_{H_2O}	P_{H_2O}/P_{H_2}	(FeO)	$(FeO)^2(\Sigma Si)$
	wt.	mm.	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-5}$
1	1.68	6.68	8.78	13.2	28.8
2	0.785	10.82	14.25	21.3	35.6
3	0.684	12.15	16.00	23.9	39.2
4	0.847	9.67	12.75	19.1	30.8
5	0.487	14.68	19.30	28.9	40.7
6	0.373	19.14	25.2	37.7	53.0
7	0.568	13.21	17.4	26.0	38.4
8	0.388	17.81	23.5	35.1	47.2
9	1.387	7.13	9.38	13.9	26.7
10	4.65	3.00	3.95	5.9	16.6
11	9.9	1.29	1.70	2.5	6.0
12	7.1	1.70	2.24	3.4	7.7
13	0.825	10.10	13.3	19.9	32.7
14	0.480	14.10	18.55	27.7	37.0

A plot of $(FeO)^2(\Sigma Si)$ against (FeO) is shown in Fig. 21. The equation representing the best straight line through these points is given by:

$$(FeO)^2(\Sigma Si) = 1.217 \times 10^{-2} (FeO) + 6.58 \times 10^{-5}$$

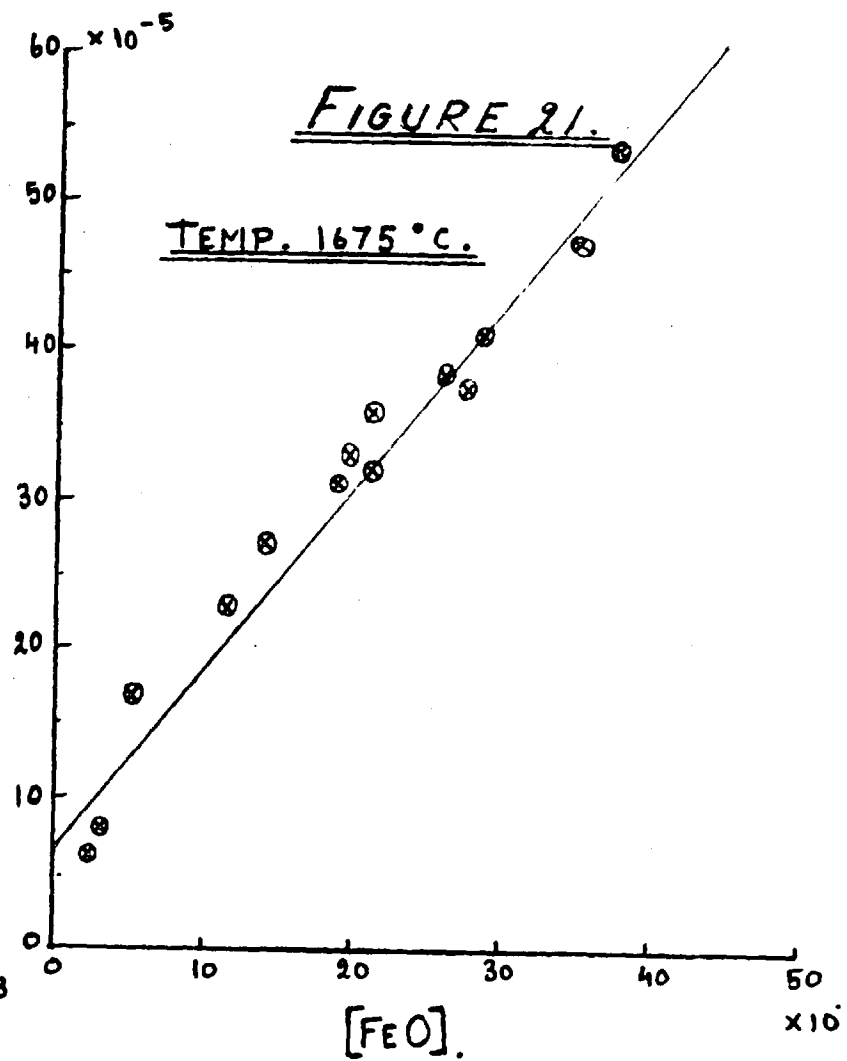
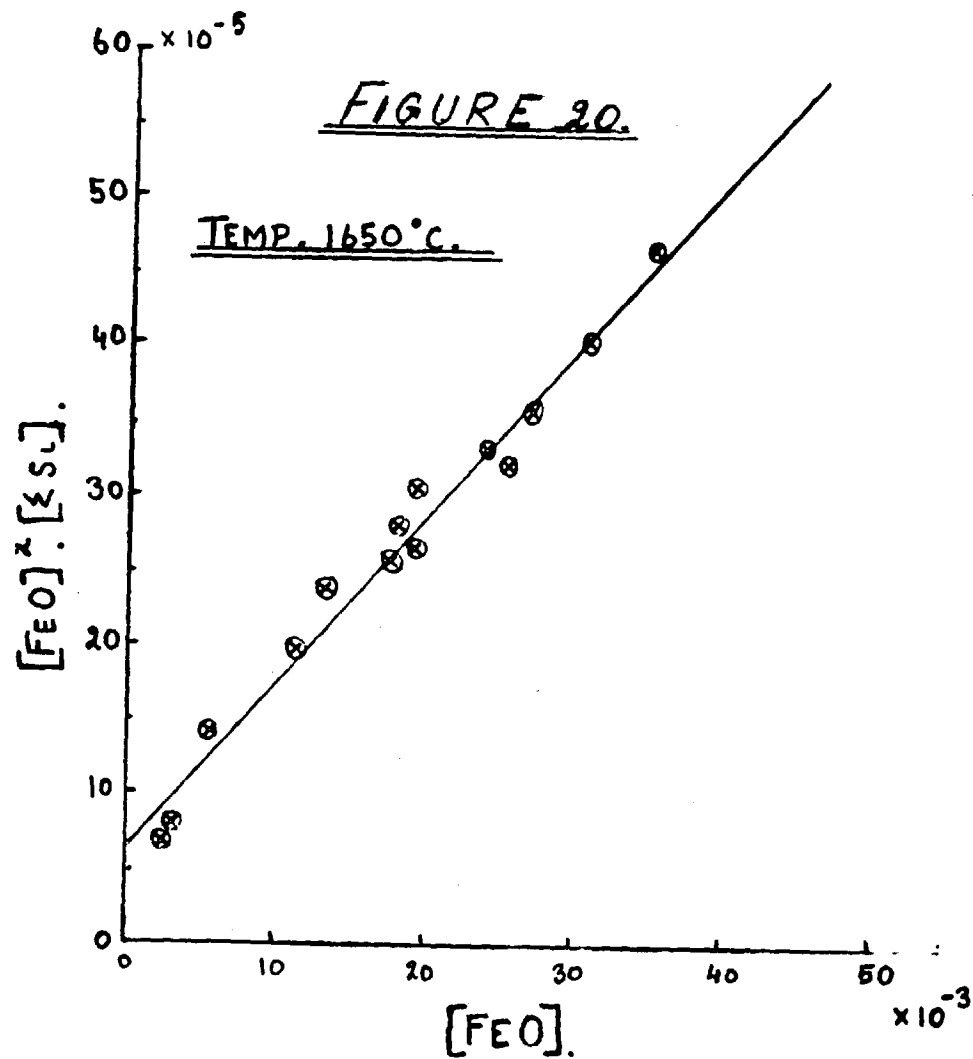
TABLE 10

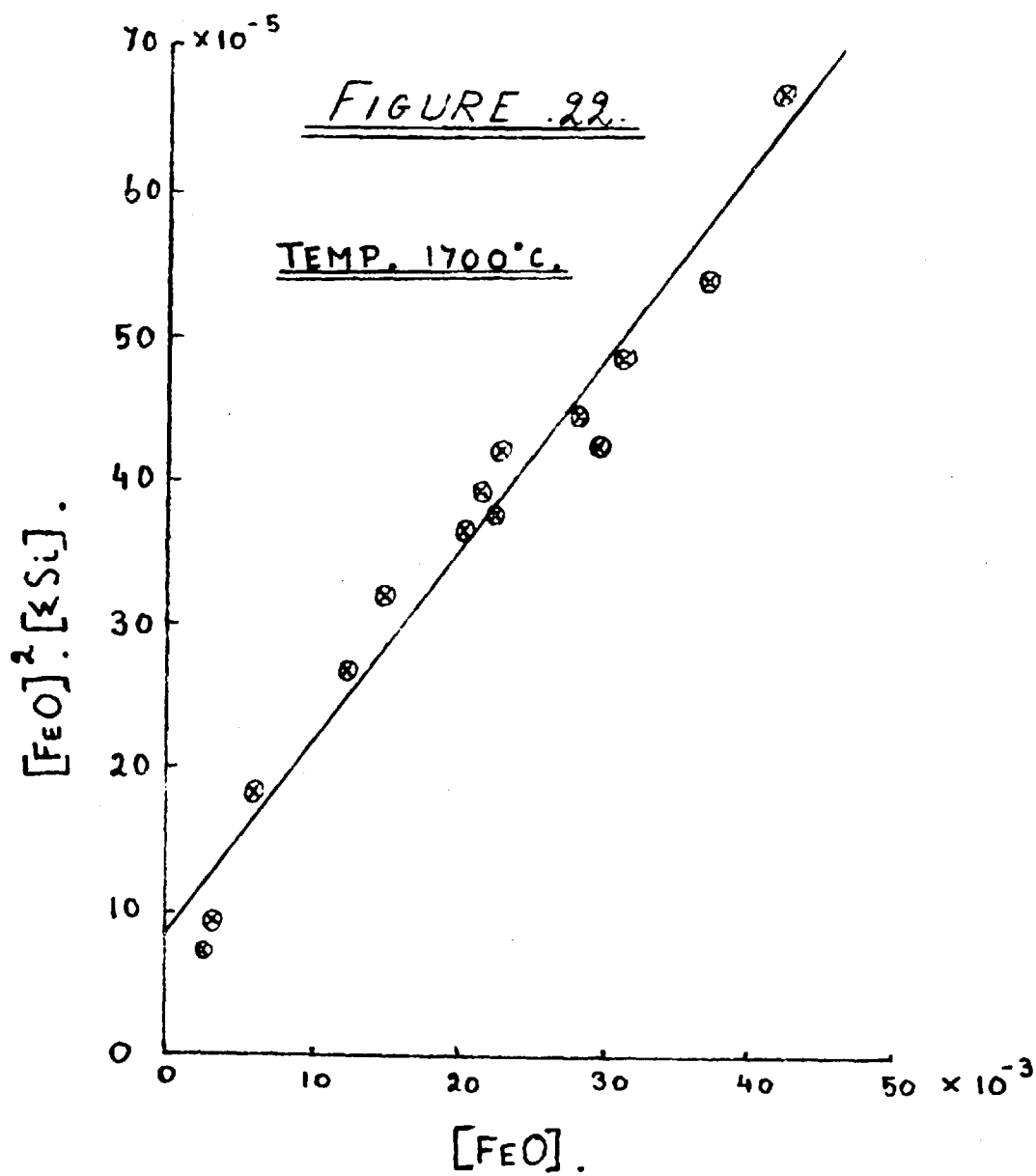
TEMPERATURE 1700°C.

	Final Si	P_{H_2O}	P_{H_2O}/P_{H_2}	(FeO)	$(FeO)^2(\Sigma Si)$
	% wt.	mm.	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-5}$
1	1.68	7.08	9.30	14.1	33.2
2	0.785	11.59	15.25	23.1	41.7
3	0.684	13.36	17.60	26.6	48.4
4	0.847	10.37	13.68	20.7	36.2
5	0.487	15.78	20.8	31.5	48.2
6	0.373	20.16	27.9	42.2	66.5
7	0.568	14.00	18.4	27.9	44.3
8	0.388	18.8	24.75	37.4	53.6
9	1.387	7.64	10.02	15.2	31.9
10	4.65	3.1	4.08	6.2	17.6
11	9.9	1.30	1.71	2.6	6.7
12	7.1	1.78	2.34	3.5	8.7
13	0.825	10.88	14.34	21.7	38.8
14	0.480	15.00	19.73	29.9	42.8

A plot of $(FeO)^2(\Sigma Si)$ against (FeO) is shown in Fig. 22. The equation representing the best straight line passing through these points is given by:

$$(FeO)^2(\Sigma Si) = 1.338 \times 10^{-2} (FeO) + 7.95 \times 10^{-5}$$



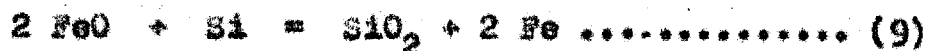


The Interpretation of the Plots of $(\text{FeO})^2(\sum \text{Si})$ against (FeO)

Interpolations from Fig.14 (representing the variation of katharometer reading with temperature at constant silicon concentration) were converted into the appropriate values of ferrous oxide activity by using the calibration curve of the katharometer to obtain the ratio of the partial pressures of the water vapour-hydrogen mixture, and subsequently converting this value to ferrous oxide activity from the data in Table 3. The ferrous oxide activity, expressed in terms of weight percentages, was squared and multiplied by the appropriate final silicon content measured by analysis. In this way the data represented in figures 16 - 22 were computed, the plots being the isotherms at the temperatures 1550°C. , 1575°C. , 1600°C. , 1625°C. , 1650°C. , 1675°C. and 1700°C. respectively.

It is at once obvious that, over the range investigated, these plots are best represented by straight lines with positive gradients. That each of these plots has a gradient and is not parallel to the abscissa axis implies that the product $(\text{FeO})^2(\sum \text{Si})$ is not constant, but increases with the ferrous oxide activity. The only possible explanation of the observed facts is that the total silicon content,

measured by analysis, is, for some reason or other, greater than the amount required to satisfy the equilibrium for equation (9) below, and this discrepancy increases with the degree of oxidation of the melt.



The solubility of silica in liquid iron may be gauged approximately by measuring the silicon content of melts containing large amounts of oxygen. Such measurements have been made by Zapffe and Sims and other workers and in no case was the silicon content found to be more than 0.005% by weight at 1650°C. The effect of determining small quantities of dissolved silica in the total analysis is therefore negligible, and the presence of dissolved silica does not explain the excess portion of silicon.

A further possible explanation might be that the discrepancy in the silicon content is accounted for by the application of an activity correction. Such an explanation seems unlikely because the solutions being dealt with are dilute - the largest ferrous oxide activity met with was 0.042% by weight. Even if the activity correction was appreciable it is unlikely it would bear the observed rather complex (inverse square) relationship

to the ferrous oxide activity.

This discrepancy in the silicon content can best be explained by the presence of silicon in some form dissolved in the liquid phase, other than dissolved silicon and silica. If the presence of some new compound is accepted, compounds of four types must be considered they are:

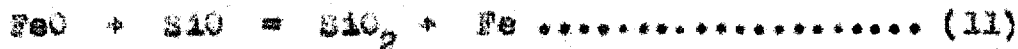
- (1) Iron silicide.
- (2) Silicon hydride.
- (3) Silicates.
- (4) Silicon monoxide.

The first possibility, that of iron silicide, may be dismissed immediately as, on increasing the silicon content, the quantity of iron silicide should increase. However, the discrepancy increases as the silicon content decreases, and so this possibility is excluded. Nothing has been found in this work or in the work by others to justify the presence of large amounts of a silicon hydride. Also it is unlikely that the concentration of hydride would increase with increase of oxygen pressure. The presence of silicates would demand increased solubility of the complexes with increase in oxygen pressure. An explanation on these lines would be reasonable, were it

not for the fact that at very high oxygen pressures the total silicon content is only a few thousandths of 1%.

Silicon monoxide has for several decades been considered to exist at steelmaking temperatures. In recent years its existence has been proved at temperatures above 1000°C. , and its thermodynamic properties have been elucidated. For this reason alone some silicon monoxide, however little, must be present in the melt. That the amount of silicon monoxide present is sufficient to account for the observed discrepancy may be shown in the following way.

In Section 1, dealing with the interpretation of the results of Zapffe and Sims, the two reactions assumed to express the equilibria were regarded as:



The equilibrium constants of these two reactions were:

$$\text{For reaction (10): } K_1 = (\text{SiO})/(\text{Si})(\text{FeO})$$

$$\text{For reaction (11): } K_2 = 1/(\text{FeO})(\text{SiO}).$$

From these two equilibrium constants the following identity was derived, relating them to the total silicon content:

$$1/K_1 \cdot K_2 = (\text{FeO})^2 (\Sigma \text{Si}) + 0.636/K_2 \times (\text{FeO})$$

If the proportion of silicon monoxide present is appreciable, the gradient of the plot of $(\text{FeO})^2(\text{Si})$ against (FeO) will be measurable and the plot will be linear. Such plots were made and are found to be linear. It is for this reason that the presence of silicon monoxide is taken to account for the unexplained portion of silicon in the melt.

From the gradient and intercept of each graph the values of K_1 and K_2 may be calculated. However, in order to obtain an unbiased knowledge of each of these constants, the equation for the best straight line was sought by using the method of least squares.

The Statistical Analysis.

A statistical analysis of the results was carried out with the dual purpose of testing the significance of the linearity of each plot and also of finding the equation of the regression line.

To test the significance of an apparently linear relationship the correlation coefficient is calculated.

It is defined by the expression below where r is the coefficient.

$$r = \frac{(x - \bar{x})(y - \bar{y})}{\sqrt{(x - \bar{x})^2(y - \bar{y})^2}}$$

r has characteristics such that if data can be represented exactly by a straight line then it is equal to ± 1 . As the significance lessens so the value of r drops until no relation exists at all and $r = 0$.

Table 11 shows the correlation coefficients calculated for each temperature. In only one case, that at $1500^{\circ}\text{C}.$, does the value fall below 0.9.

The equation for the best straight line was found by deducing the regression of $(\text{FeO})^2(\Sigma \text{Si})$ upon (FeO) by the method of least squares. This method has the effect of reducing the sum of the squares of the deviations of $(\text{FeO})^2(\Sigma \text{Si})$ to a minimum value. Such a reduction gives the best estimate of values of $(\text{FeO})^2(\Sigma \text{Si})$ from values of (FeO) . The values of K_1 and K_2 are calculated from the constants of the equations. They are shown together with their logarithms in Table 11.

TABLE 11.

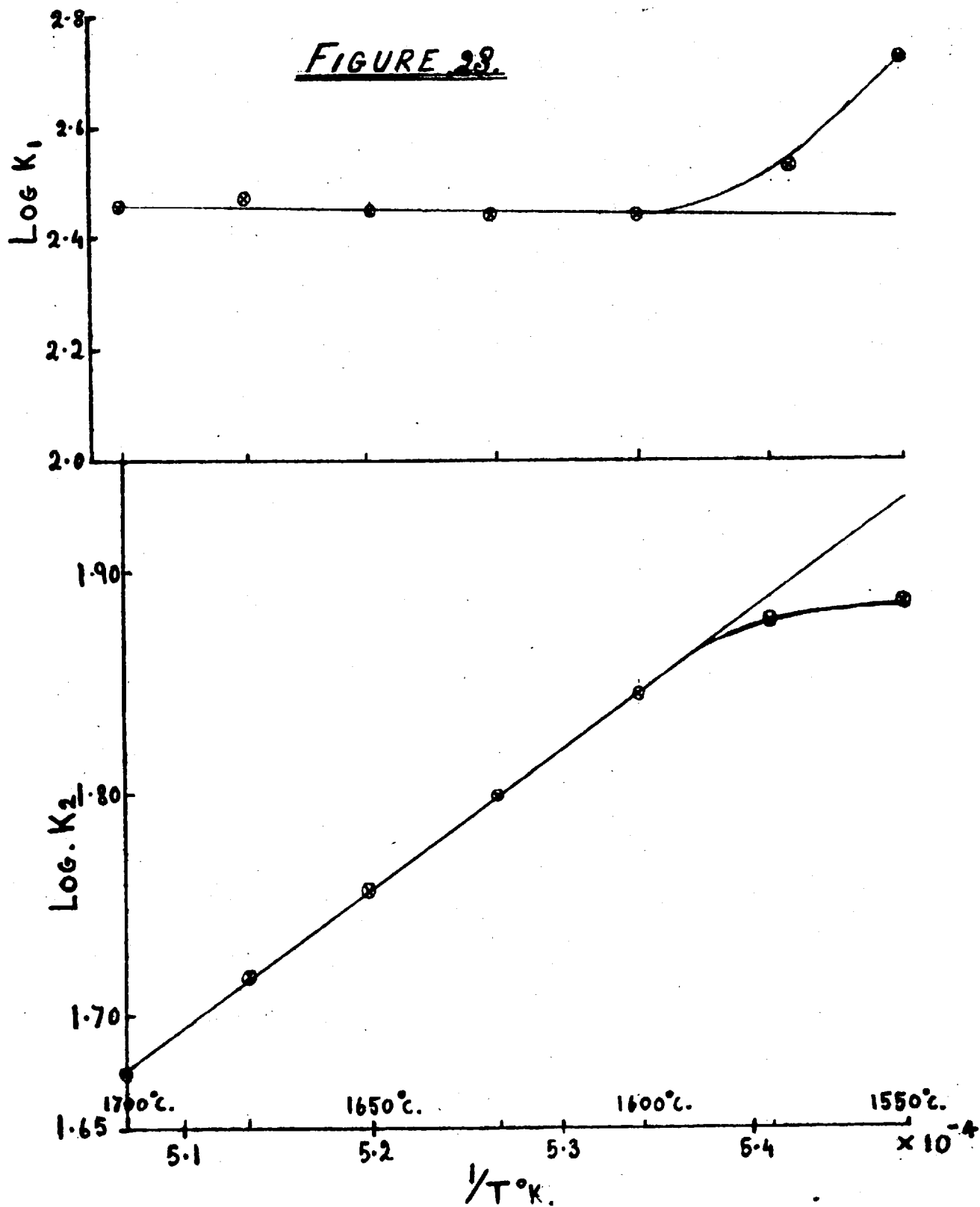
TEMP. °C.	TEMP. °K.	CORRELATION COEFF.	$1/T^{\circ}K$	K_1	$\log K_1$	K_2	$\log K_2$
			$\times 10^{-4}$	$\times 10^2$		$\times 10^2$	
1550°C.	1823°K.	0.890	5.484	5.290	2.7235	0.7779	1.8909
1575°C.	1848°K.	0.943	5.412	3.376	2.5248	0.7519	1.8761
1600°C.	1873°K.	0.963	5.339	2.753	2.4397	0.6975	1.8435
1625°C.	1898°K.	0.974	5.268	2.723	2.4352	0.6286	1.7984
1650°C.	1923°K.	0.983	5.200	2.783	2.4445	0.5777	1.7617
1675°C.	1948°K.	0.991	5.134	2.907	2.4635	0.5227	1.7183
1700°C.	1973°K.	0.922	5.068	2.882	2.4598	0.4752	1.6769

The Thermodynamic Properties of the System.

Fig. 23 shows a plot of the variation of the logarithms of each of the equilibrium constants with the reciprocal of the absolute temperature. The standard free-energy changes are derived from the equations representing the straight-line portion of each plot.

The standard states of the silicon and silicon monoxide are concentration of 1% by weight. The ferrous oxide activity is expressed in terms of weight percentages, and again unit activity refers to a 1% solution of ferrous oxide in liquid iron. The concentration of silica in liquid iron is regarded as constant at the saturation

FIGURE 28.

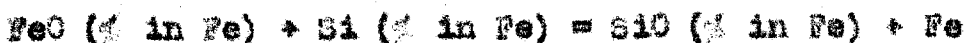


value at any one temperature. This value is automatically incorporated in the equilibrium constant K_2 . The concentration of iron, expressed in terms of weight percentages, may be taken as 100 without serious error, and this constant figure incorporated into the appropriate equilibrium constant.

The standard free-energy change for a reaction is governed by the relationship:

$$\Delta G^\circ = -RT \ln K = -4.575 T \log_{10} K = \Delta H - T\Delta S^\circ.$$

The following equations demonstrate the various reactions involved in the equilibria.



$$K_1 = (\text{SiO})/(\text{Si})(\text{FeO}) \dots\dots\dots (1)$$



$$K_2 = 1/(\text{SiO})(\text{FeO}) \dots\dots\dots (2)$$



$$K_1 K_2 = 1/(\text{Si})(\text{FeO})^2 \dots\dots\dots (3)$$



$$K_2/K_1 = (\text{Si})/(\text{SiO})^2 \dots\dots\dots (4)$$

The equations for the standard free-energy change, the standard entropy change, and the heat of reaction are tabulated below.

TABLE 12

No.	$\Delta G^\circ =$	ΔH g.-cal	ΔS° g.-cal. for $^\circ K.$
1	- 11.17 T	0	11.17
2	- 20,500 + 2.54 T	- 20,500	- 2.54
3	- 20,500 - 8.63 T	- 20,500	- 8.63
4	- 20,500 + 13.71 T	- 20,500	-13.71

The ease with which a reaction will occur at a given temperature is estimated from the standard free energy change accompanying the reaction. At $1650^\circ C.$ the standard free energy changes accompanying each of the above reactions are - 21,500, - 15,600, - 37,100 and - 5,900 cal. A comparison of these figures indicates that the oxidation of silicon to silicon monoxide is more facile than the oxidation of silicon monoxide to silica.

Results from Runs using the Dew-point Apparatus.

The results carried out at these higher oxygen pressures are shown in Table 13.

TABLE 13

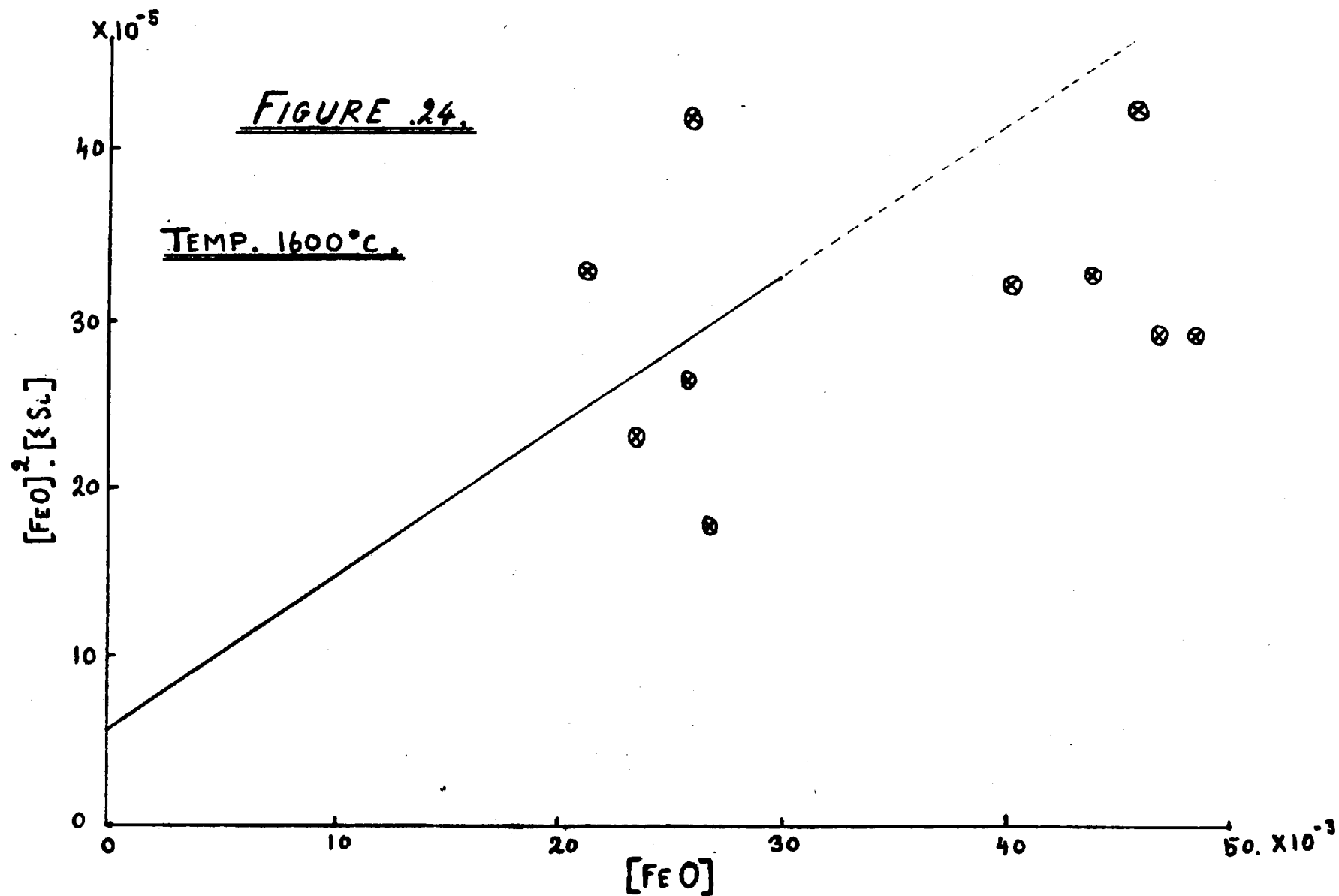
Run	(Σ Si)	H_2O/H_2	(FeO)	$(FeO)^2/(\Sigma Si)$
1	0.728%	0.0146	21.2×10^{-3}	32.6×10^{-5}
2	0.409	0.0163	23.6	22.8
3	0.172	0.0302	43.7	32.8
4	0.133	0.0323	46.8	29.2
5	0.124	0.0334	48.5	29.2
6	0.207	0.0282	40.1	~~29.2~~ 32.4
7	0.250	0.0183	26.7	17.7
8	0.40	0.0177	25.7	26.4
9	0.63	0.0178	25.8	41.7
10	0.201	0.0316	45.8	42.0

Taken alone these results have little significance because of the considerable probable error in measuring the water vapour - hydrogen ratio in the gas mixture. This error probably arises both from the errors of measurement and from the uncertainty in detecting the attainment of equilibrium. A plot of these points, which were obtained at a temperature as near as possible to $1600^\circ\text{C}.$, is shown in Fig.24.

The scatter of the points is very wide, but the majority of them lie below the line which represents the points obtained by the ketharometer technique. This may mean that at the higher oxygen pressures the gradient of the

FIGURE 24.

TEMP. 1600°C.



plot changes.

The data are insufficient for any definite conclusions to be drawn, but even so the points agree among themselves to a greater degree than points obtained by other workers. Evidently the ferrous oxide activity increases as the product $(\text{FeO})^2 \cdot (\Sigma \text{Si})$ increases.

SECTION V.

THE PHOTOMICROGRAPHIC EXAMINATION OF MELTS.

The Photomicrographic Examination of some Melts.

The assumption has hitherto been made that the silicon content of the melt does not alter while the ingot is allowed to cool. Such an assumption can be justified only when it is shown that segregation of silica, that may be formed, does not take place during cooling. If during cooling some silicon is oxidised to silica which rises to the surface, the total silicon measured by analysis will not represent the total silicon content of the melt at equilibrium.

Analysis of an ingot produced under conditions conducive to the formation of silica in the melt showed that little segregation took place. The ingot was sawn laterally through its centre and each part analysed.

Analysis:

	Lower portion.	Upper portion.
Wt. of sample	5.2545 g.	7.7330 g.
Wt. of SiO_2 ppt.	0.1254 g.	0.1921 g.
% SiO_2	1.11%	1.16%

Three melts were prepared, one under highly reducing conditions, one under highly oxidising conditions, and one under conditions normal to the technique adopted in the measurements. These three ingots were cut vertically

through their centres, polished, and examined for the occurrence, size and dispersion of inclusions.

Besides a uniformly scratched surface, three distinctive types of dark patches could be seen readily in the surface; these were probably (i) blow-holes produced by the evolution of gas; (ii) large inclusions, or the holes left by large inclusions being torn from the surface during polishing; or (iii) small inclusions. Their identification rested on the size and shape of the particular patch examined. These various types of inclusions were confined to certain clearly defined areas, and photomicrographs were made of representative areas of each type. Diagrams of the three melts are shown and each melt is considered in turn.

Fig.25, with plates 5 and 6, shows the cross section of an ingot, with photomicrographs of the portion indicated at a magnification of eighty diameters. The ingot was obtained by heating a charge of carbonyl iron containing 4.5 wt.-% of powdered silicon. This was heated in a silica crucible to a temperature of 1620°C . in an atmosphere of dry hydrogen. When this temperature was reached, hydrogen containing a very high water-vapour content was admitted into the tube and oxidation of the silicon in the liquid iron allowed to take place for a period of

FIGURE 25.

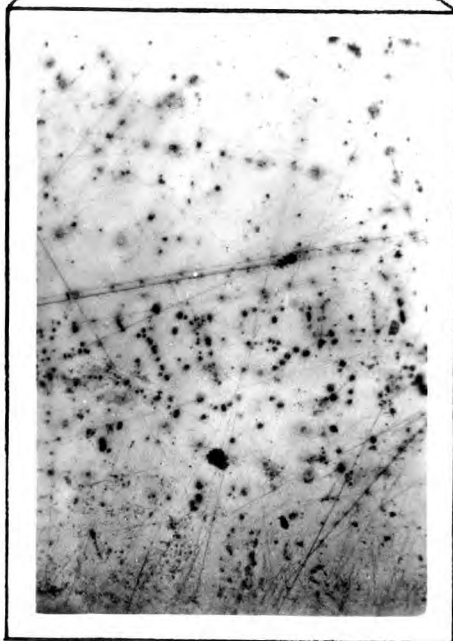
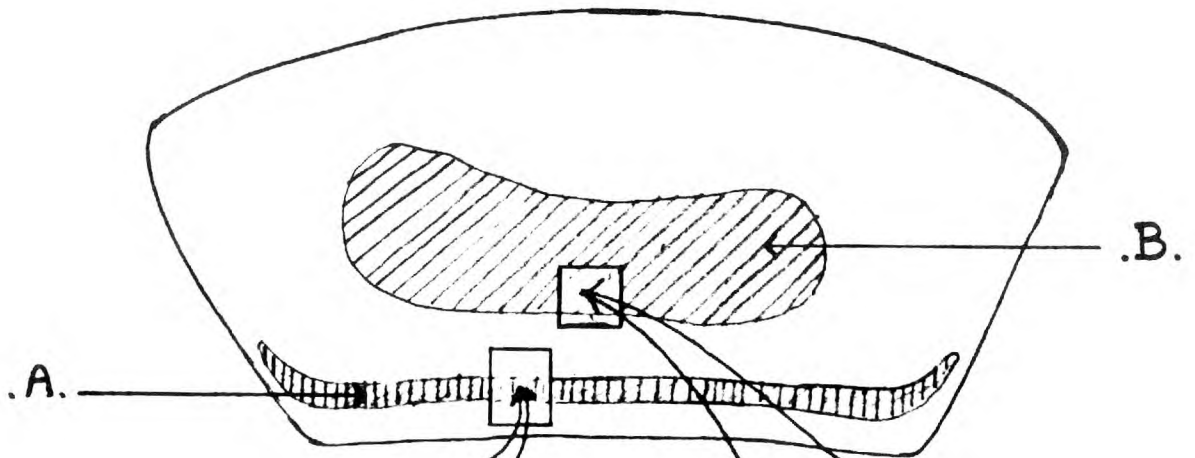


PLATE . 5 .

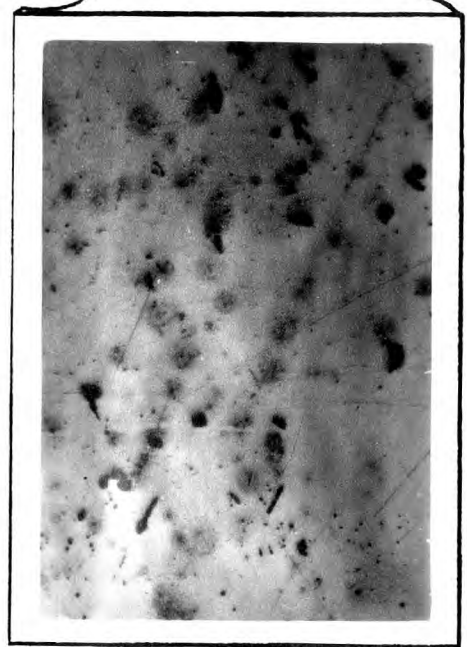


PLATE . 6 .

about half an hour. After this period the furnace was swept out with a swift stream of argon and cooled.

Examination of the polished surface of the ingot showed primarily that no blow holes were present. Except for a band (A), containing a high concentration, the dispersion of small inclusions was even throughout the surface.

Approximately in the centre was located a large and well defined area (B), ^{containing large inclusions} as well as some small inclusions lying in the space between. The large inclusions were confined completely to this central area.

Fig.26, with plates 7 and 8, shows the melt made under vigorously reducing conditions. The silicon content of this melt was 1.5%, and the magnification of the photomicrographs is again eighty diameters.

An area (A), near the top surface of the ingot, was found to contain a general scattering of blow holes with small inclusions uniformly distributed between. The greater radius of curvature of the upper surface is indicative of gas evolution. Small inclusions were scattered evenly throughout the surface, showing no segregation to take place. As with the previous melt a well defined area (B) was found approximately in the centre of the melt; this area again containing a general scattering of much larger

FIGURE 26.

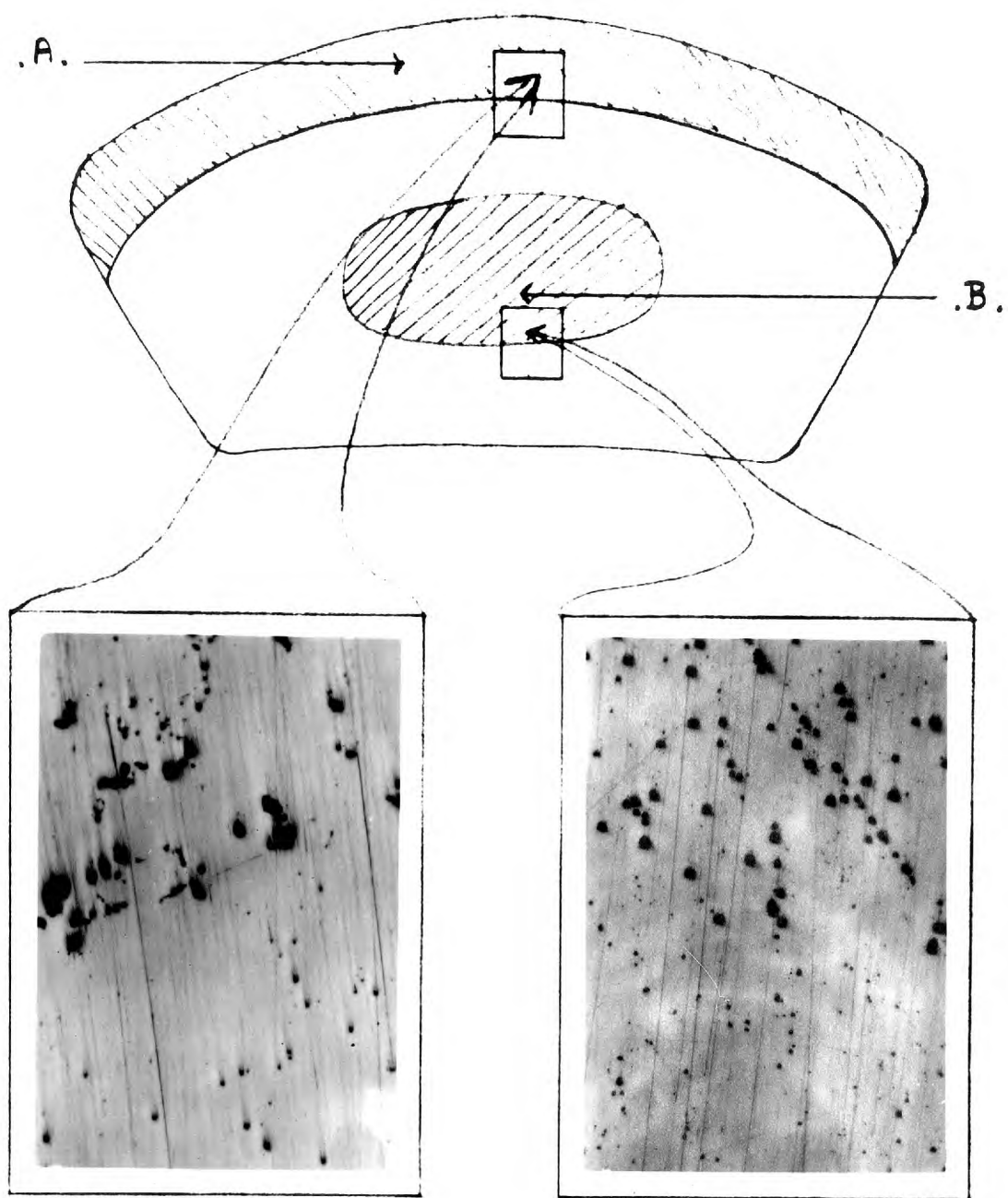


PLATE . 7 .

PLATE . 8 .

inclusions. These larger inclusions are shown clearly on plate 8.

Fig. 27, with plates 9 and 10, shows the results of the examination of a melt carried out under normal conditions. The melt, containing about 1% of silicon, was heated to 1600°C., and then the surrounding atmosphere brought to equilibrium with it before the melt was cooled in a stream of pure argon.

A small area (A) near the top surface contained blow holes, but their concentration was much less than the concentration of blow holes found in the melt made under reducing conditions. A general scattering of small inclusions was found over the whole surface, but again no segregation could be seen. In the centre was found an area (B) containing a localised concentration of the larger inclusions.

From these observations it may be stated that only on oxidation of a melt containing high silicon concentrations did any segregation of the small inclusions take place. This segregation was so small and localised that its effect may be regarded as insignificant. The larger inclusions were found to be localised at the centre of each melt. This must be in consequence of uneven cooling of the melt, the centre being the last portion of the melt to solidify.

FIGURE 27.

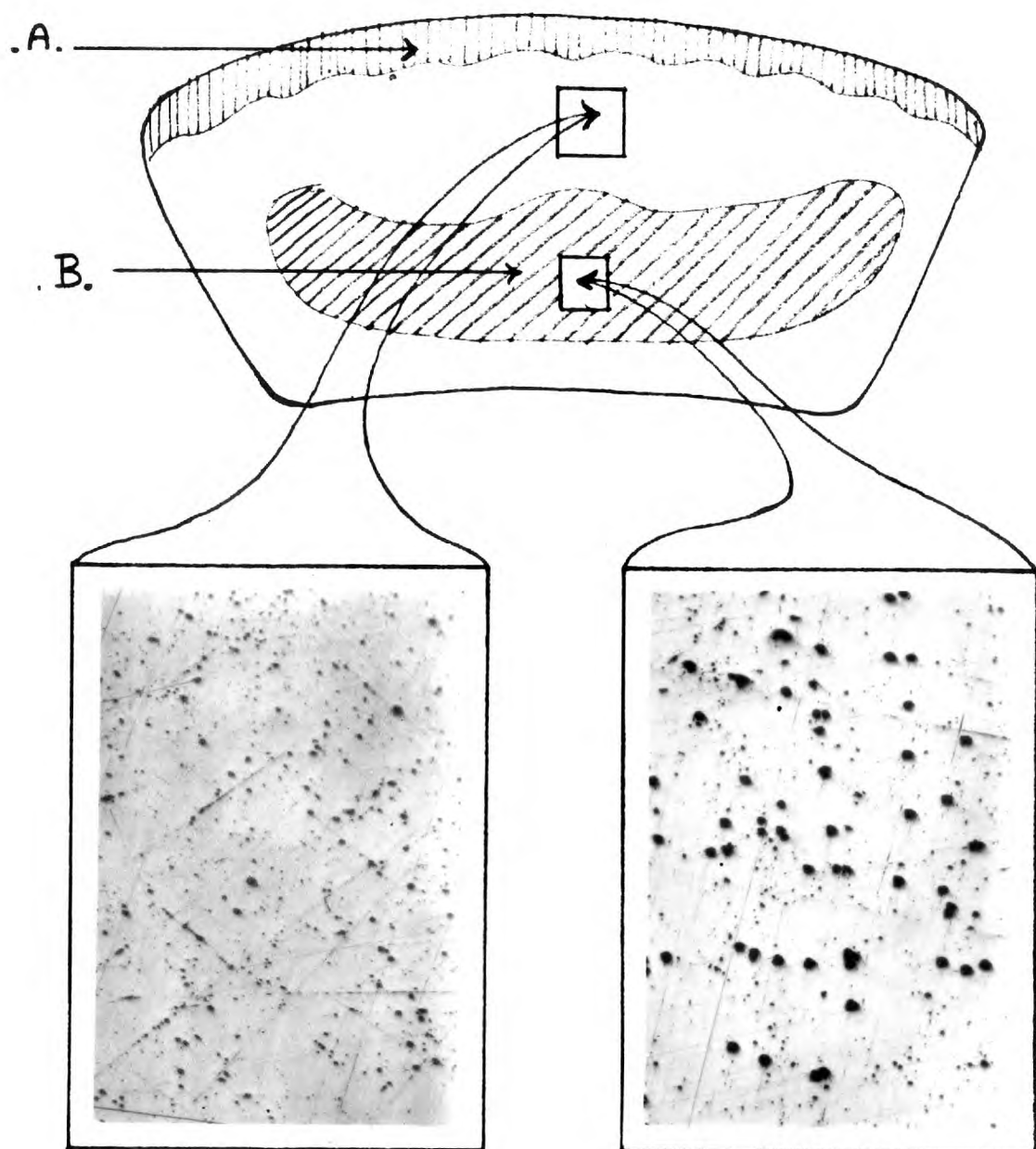


PLATE 9.

PLATE 10.

No evidence was found to suggest that the silicon analyses were vitiated by the elimination of silica from the melt during the process of cooling.

SECTION VI

DISCUSSION

Errors and the Accuracy of the Thermodynamic Data.

All thermodynamic data derived have been calculated from the interpretation of the plots of the products $(\text{FeO})^2 \cdot (\Sigma \text{Si})$ against the ferrous oxide activity. The equilibrium constant of the two reactions involved in the equilibrium are measured by the gradient and intercept of these plots, and the accuracy of measurement depends on the scatter of the points forming each plot.

Experimental errors may arise from measurements of (i) temperature, (ii) ferrous oxide activity, and (iii) total silicon content of the melt.

The errors cannot be assessed easily to give some fixed measure of the accuracy of the data, so the standard deviation and variance of each of the plots was calculated. They are tabulated below.

TABLE 14.

Temperature	Standard deviation	Variance
1550°C.	2.98×10^{-5}	8.88×10^{-10}
1575°C.	2.46 "	6.05 "
1600°C.	2.24 "	5.02 "
1625°C.	2.23 "	4.97 "
1650°C.	2.10 "	4.41 "
1675°C.	1.82 "	3.31 "
1700°C.	2.20 "	4.84 "

The accuracy of the temperature measurement is much greater than that normally met with in similar investigations. The calibration against the melting points of nickel and iron makes it possible to eliminate all errors due to emissivity corrections, which have to be applied when calibration is indirect. Although 3°C . differences in temperature were readily measurable, the final measurement of temperature is not claimed with this accuracy. The calibration relies on the latent heat of fusion being detected sharply in the cooling curve. The highest point on the calibration chart is at the melting point of iron, 1535°C . Temperature measurement above this point relies on extrapolation and assumes that the emissivity of the surface from which the temperature is measured remains constant. This assumption is not completely justified and involves an error of about $\pm 8^{\circ}\text{C}$. Measurements relying on differences of temperature are subjected to much greater accuracy, about $\pm 3^{\circ}\text{C}$.

When the plot of the logarithm of the equilibrium constant against the reciprocal of the absolute temperature is constructed, the gradient of the curve will depend on accurate measurement of differences in temperature. The intercept of the plot relies on the absolute calibration

of temperature, and is therefore not known so accurately as the gradient. Before the accuracy of the heat of reaction and the standard entropy change is discussed, the accuracy with which the equilibrium is measured must be considered.

The maximum error of the silicon analysis is $\pm 0.2\%$. Errors derived from the inaccurate measurement of the ferrous oxide activity by the katharometers are estimated to be $\pm 0.4\%$. When the two errors are considered together they are insufficient to account for the relatively large standard deviation.

Although the equilibrium system was approached as nearly as the accuracy of the measurements would allow, some deviation must inevitably occur. This deviation from true equilibrium probably accounts for the greater part of the error shown by the scatter of the points on the plots of $(\text{FeO})^2(\Sigma \text{Si})$ against the ferrous oxide activity.

For reaction 2, involving the oxidation of silicon monoxide the heat of reaction term may be taken to be accurate to ± 0.4 kg.-cal. This term in the expression for the standard free-energy change for the reaction may only be regarded as an estimate, for it implies that the heat of reaction is independent of temperature, an

assumption not wholly justified. The entropy term of the equation is subject to a larger error, ± 0.10 g.-cal. per $^{\circ}\text{C}$.

Reaction 1, involving the oxidation of silicon to silicon monoxide, is subject to larger errors than reaction 2. The heat of reaction is probably accurate to ± 0.6 kg.-cal. and the entropy term to ± 0.9 g.-cal. per $^{\circ}\text{C}$.

Table 15 shows the results obtained by other workers. Except for the results calculated and those of Zapffe and Sims, the product $(\text{FeO})^2(\text{Si})$ was determined at one temperature only - a temperature in the region of 1600°C . Some results have been omitted altogether as the reliability of temperature measurement was too vague for the values to merit serious consideration. Most of these results were obtained at greatly varying oxygen pressures and the silicon concentration term represented the total silicon determined by analysis. Only in the results of this work and the results of Zapffe and Sims is the silicon term corrected for the presence of silicon monoxide.

Comparison of results with those of other workers.TABLE 15.

AUTHOR	TEMP.	$(\text{FeO})^2(\text{Si})$	REMARKS
H. Schenck	1600°C.	2.8×10^{-5}	Experiment
Körber & Oelsen	"	71	"
Herty & Fitterer	"	14.9	"
Herty & Christopher	"	20.7	Plant data
" " "	"	16.5	Keon result
Portevin & Perrin	"	60	Experiment
Darken	"	61	"
Herasymenko	"	110	"
Schenck & Brüggemann	"	35.5	
McCance	"	5.6	Calculated
J. Chipman	"	4.8	"
Zapffe & Sims	"	9.5	Experiment
Results from this work 1600°C. 5.21			Experiment.

From table 15, Zapffe and Sims' result for the product $(\text{FeO})^2(\text{Si})$ at 1600°C. is 9.5×10^{-5} when corrected for silicon monoxide. This value was increased to 14.5×10^{-5} when the analysis indicated in Section 1 was applied to their data. The value obtained in this research at a temperature of 1600°C. was 5.21×10^{-5} . These figures are about the same order of magnitude and compare favourably when the results of previous investigators are considered too. The values of K_1 and K_2 obtained by Zapffe and Sims

are compared with the results of this investigation in the table below.

TABLE 16.

TEMPERATURE	ZAPFFE and SIMS		THIS INVESTIGATION	
	K_1	K_2	K_1	K_2
1550°C.	30.9	7.69×10^2	5.29×10^2	77.8
1600°C.	26.3	4.00×10^2	2.75×10^2	69.8
1650°C.	22.3	2.08×10^2	2.78×10^2	57.8

In general it may be stated that the product $(FeO)^2(Si)$ increases with increase in oxygen pressure where the data were obtained by experiment. Körber and Oelsen's results were obtained from melts in contact with slag and open to an atmosphere of air. It is not surprising that such a high value is obtained when it is understood that the oxygen pressure of the melt must be relatively high.

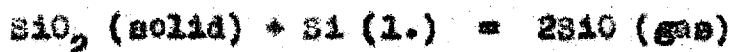
Much closer agreement is found between the results obtained in this work and the calculations of McGance and the separate work of Chipman. It is interesting to note that the value of the product of the square of the ferrous oxide activity with the corrected silicon concentration obtained in this work is the mean of the results of

McCance and Chipman.

The presence of measurable proportions of silicon monoxide in silicon-rich slags has been suggested by several Russian workers, notably P. V. Gel'd and M. I. Kochnev (Zhurnal Prikladnoi Khimii., 1948, 21, 1249) and P. V. Gel'd and O. A. Esin (Doklady Akademii Nauk SSSR, 1950, 70, 473). Although the presence of silicon monoxide in the slag phase has been confirmed no thermodynamic data are given.

The Free Energy of Dissolution of SiO in liquid Fe.

In the temperature range 1823 - 1973°K. the standard free energy recharge for the reaction



has been found by A. J. E. Welch and N. C. Tombs (Paper to be published). It is given by the equation:

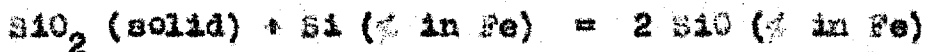
$$\Delta G^\circ = 117.1 - 0.0509 T \text{ (in kg.-cals.)}.$$

Richardson and Jeffes (J. Iron Steel Inst., Dec. 1949, 417) calculated the standard free energy change for the reaction



$$\Delta G^\circ_{1473 - 1973^\circ\text{K}} = -28,500 - 0.00064 T \text{ (kg.-cals.)}$$

For the reaction



$$\Delta G^\circ = 20,500 - 0.0137 T. (\text{kg.-cals.}).$$

Consequently for reaction



$$\Delta G^\circ = -62.6 + 0.0189 T. (\text{kg.-cals.}).$$

Possible Extensions of this Work.

The results of this investigation, although conclusive over the range investigated, leave some problems still to be solved. The most important from the academic viewpoint is the extension of the range of ^{ferrous oxide} oxygen activity in the liquid phase to the point of saturation at 1% by wt. The activity coefficients of the various reactants probably remained constant over the range investigated otherwise the plot $(\text{FeO})^2 (\Sigma \text{Si})$ would not be linear. If this plot could be extended to the saturation point, any change of gradient would probably be due to a change in one or more of the activity coefficients. Any extension of the range relies on the accurate measurement of the water vapour content of the surrounding atmosphere. A useful tool in this direction would be a katharometer analyser adapted so that it could be maintained in a

thermostat bath at a temperature of 65°C . and used to measure very much higher water vapour-pressures. This high temperature is necessary to prevent the deposition of dew on the walls of the analyser from the gas stream.

No reliable measurements have been made to show the part silicon monoxide takes in reactions occurring in the slag phase.