VANADIUM-OXYGEN INTERACTIONS AND

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PHOSPHORUS TRANSFER KINETICS

VANADIUM-OXYGEN INTERACTIONS IN LIQUID IRON AND THE KINETICS OF PHOSPHORUS TRANSFER IN SLAG/METAL SYSTEMS

by

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TITLE: Vanadium-Oxygen Interactions in Liquid Iron and the Kinetics of Phosphorus Transfer in Slag/Metal Systems

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SCOPE AND CONTENTS:

Iron-vanadium alloys were levitation melted and equilibrated at controlled temperatures with water vapour/hydrogen atmospheres of controlled composition, quenched and analysed for oxygen. The effect of vanadium on the behaviour of oxygen has been expressed in terms of first order free energy, enthalpy and entropy interaction parameters.

The reduction of phosphorus from synthetic blast furnace slags by carbon saturated iron was studied under laboratory conditions. The rate of phosphorus transfer was determined and the results have been interpreted in terms of chemical reaction control at the slag/ metal interface.

The dephosphorisation of induction melted mild steel by synthetic basic slags was investigated. The rate of dephosphorisation was determined and the results have been interpreted in terms of mass transfer control in the slag phase.

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NOTATION

	The following symbols recur frequently in Part 1:
a _i	Raoultian activity of solute i.) Molar scale
a'i	Henrian activity of solute i.)
e ^(j) i	First order free energy interaction parameter, wt. pct. scale.
f	Henrian activity coefficient - wt. pct. scale.
f ⁽ⁱ⁾ i	Activity coefficient for solute in 1 - i binary.
f ^(j) i	Interaction coefficient - effect of solute j on activity coefficient of i.
F ^o	Molar free energy.
\mathbf{F}_{i}^{o}	Molar free energy of pure component i.
F _i	Partial molar free energy.
$\bar{\mathbf{F}}_{\mathbf{i}}^{\mathbf{id}}$	Ideal partial molar free energy.
$\mathbf{F}_{\mathbf{i}}^{\mathbf{E}}$	Excess partial molar free energy - Raoultian standard state.
$\mathbf{F'}_{i}^{E}$	Excess partial molar free energy - Henrian mole fraction scale.
$\boldsymbol{\mathfrak{F}}_{\mathrm{i}}^{\mathrm{E}}$	Excess partial molar free energy - wt. pct. scale.
h _i	Henrian activity - wt. pct. scale.
h ^(j) _i	First order enthalpy interaction parameter - wt. pct. scale.
но	Molar enthalpy.
$\overline{\mathrm{H}}_{\mathbf{i}}$	Partial molar enthalpy.
\overline{H}_{i}^{id}	Ideal partial molar enthalpy.
H_{i}^{E}	Excess partial molar enthalpy - Raoultian standard state.
¥ ^E _i	Excess partial molar enthalpy - wt. pct. scale.
1 ^(j) i	Second order enthalpy parameter - wt. pct. scale.

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M	Mole weight of component i.
p ^(j) i	Second order entropy parameter - wt. pct. scale.
r(j) i	Second order free energy parameter - wt. pct. scale.
R	Gas constant.
s(j) i	First order entropy interaction parameter - wt. pct. scale.
s	Molar entropy.
s_i^E	Excess partial molar entropy - Raoultian standard state.
g_{i}^{E}	Excess partial molar entropy - wt. pct. scale.
Т	Absolute temperature, ^o K.
x,	Mole fraction of component i.
Υ_i	Raoultian activity coefficient.
γ_i^o	Henry's law coefficient.
Y'i	Henrian activity coefficient - mole fraction scale.
$\gamma'_{i}^{(i)}$	Henrian activity coefficient of solute i in 1 - i binary.
Y ^(j) i	Interaction coefficient, effect of solute j on activity coefficient of i.
$\epsilon_{i}^{(j)}$	First order free energy interaction parameter - mole fraction scale.
η ^(j)	First order enthalpy interaction parameter - mole fraction scale.
λ ^(j) _i	Second order enthalpy interaction parameter - mole fraction scale.
$\pi_{i}^{(j)}$	Second order entropy interaction parameter - mole fraction scale.
$\rho_{i}^{(j)}$	Second order free energy interaction parameter - mole fraction
	scale.
$\sigma_{i}^{(j)}$	First order entropy interaction parameter - mole fraction scale.
2	The "characteristic temperature".

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INTRODUCTION

The three projects which were undertaken for this Thesis involve reactions associated with different stages in the manufacture of steel, namely ironmaking, steelmaking and deoxidation. The Thesis is divided into two parts representing equilibrium gas/metal and kinetic slag/metal studies. Part 1 is an equilibrium study entitled "Vanadium-Oxygen Interactions in Liquid Iron". Chapters, Appendices, Tables and Figures have been prefixed with the letter V for vanadium.

Kinetic studies are described in Part 2 under the heading of "The Kinetics of Phosphorus Transfer in Slag/Metal Systems", and is subdivided into two sections. In Section 2 R, entitled "The Kinetics of Phosphorus Transfer in Ironmaking Slag/Metal Systems", the results of experiments involving the reduction of phosphate bearing slags by carbon saturated iron is described. The prefix R relates to this section. Section 2 S is entitled "The Kinetics of Dephosphorisation of Liquid Steel by Synthetic Steelmaking Slags" and relates to experiments which were conducted under laboratory conditions in an induction furnace. The prefix S is used to denote this section.

References in the text are given as the name of the author and date of publication and may be referred from any section to the combined bibliography at the end of the Thesis where they are listed in alphabetical order. Where there are several references to one author, they are listed chronologically. In order to avoid confusion, Appendices, Tables and Figures are located at the end of the Thesis and are referred to by the appropriate prefix letter V, R or S.

1

PART 1

VANADIUM-OXYGEN INTERACTIONS IN LIQUID IRON

CHAPTER V-1

INTRODUCTION

In steelmaking processes, impurity elements in the unrefined metal are removed by oxidation. Consequently, the oxygen content of steel after refining is usually excessive for most purposes and is generally reduced prior to teeming by the addition of one or more deoxidising agents. These are elements which have a greater affinity for oxygen than iron, an example of which is vanadium. It is found that vanadium behaves as a moderate deoxidiser when added to certain grades of rimming steels. Deoxidising agents not only impose a limit on the amount of oxygen retained by the liquid steel but also reduce the activity of the amount remaining.

Few results have been published with reference to the ironvanadium-oxygen system and those values which have been reported vary considerably. The present investigation was undertaken with the intention of determining the effect of vanadium on the activity coefficient of oxygen in iron over a wide temperature range by levitating molten iron and alloy droplets in controlled water vapour/hydrogen atmospheres. The levitation melting technique is particularly suitable for such an investigation since the reaction may be studied over a wide range of temperatures without fear of crucible contamination thus enabling temperature dependent data to be determined with a high degree of accuracy.

2

In this section, the thermodynamic treatment of liquid metal solutions is reviewed. A literature survey has been made with reference to investigations on the solubility of oxygen in liquid iron and iron-vanadium alloys.

The experimental apparatus and techniques are described and the results of experiments conducted at temperatures in the range 1450° to 1800°C for iron and 1550° to 1750°C for alloys containing from 0.1 to 1.0 wt. pct. vanadium are reported. The spread of the experimental data is discussed in terms of experimental errors. The data for the solution of oxygen in iron has been employed as a basis for determining the relative effect of vanadium on the activity of oxygen in iron-vanadium alloys. The data have been expressed in terms of the free energy, enthalpy and entropy interaction parameters.

CHAPTER V-2

THE THERMODYNAMIC TREATMENT

OF LIQUID METAL SOLUTIONS

V-2.1 Excess Free Energy and Activity Coefficients

When a solute dissolves in a solvent, a free energy change occurs. By definition, (Darken and Gurry, 1953), the partial molar free energy of the ith component may be expressed in terms of its activity in solution by the equation:

$$d\overline{F}_{i} = RTd\ln a_{i}$$
 (V. 2. 1)

If the standard state is taken as the pure component for which the Raoultian activity is unity, then integration of equation (V. 2. 1) gives:

$$\overline{F}_{i} - F_{i}^{O} = RT \ln a_{i} \qquad (V. 2. 2)$$

where F_i^o is the molar free energy of the pure component i. For ideal solutions, a_i may be replaced by molar fraction, X_i , and equation (V. 2. 2) becomes:

$$\overline{F}_{i}^{id} - F_{i}^{o} = RT \ln X_{i} \qquad (V. 2. 3)$$

Few solutions exhibit such behaviour and the activity coefficient, $\gamma_i = \frac{a_i}{X_i}$, is a measure of the deviation from ideality. The excess partial molar free energy associated with non-ideality is defined as:

$$F_{i}^{E} = \overline{F}_{i} - \overline{F}_{i}^{id} \qquad (V. 2. 4)$$

and may be conventiently expressed in terms of the activity coefficient by substitution of equations (V. 2. 2) and (V. 2. 3) in (V. 2. 4)

i.e.
$$F_{i}^{E} = RT \ln Y_{i}$$
 (V.2.5)

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This choice of standard state would be appropriate for the solvent component in dilute solutions or the solute component in concentrated solutions. However, a solute component in an infinitely dilute solution obeys Henry's law for which

$$\frac{a_i}{X_i} = \Upsilon_i^o$$

where Υ_i^o is Henry's law coefficient. The value of Υ_i^o corresponds to the Raoultian activity for the pure component in the hypothetical standard state based on the behaviour at infinite dilution. For dilute solutions, a standard state based on Henry's law is appropriate and deviations from Henrian behaviour are measured in terms of the Henrian activity coefficient, Υ_i' , where

$$Y'_{i} = \frac{a'_{i}}{X_{i}} ; \text{ and } \begin{array}{c} a'_{i} \neq X_{i} \\ Y'_{i} \neq 1 \end{array} \right\} \text{ as } X_{i} \rightarrow 0$$

On this basis the excess partial molar free energy may be expressed in the same form as equation (V2.5).

i.e.
$$F_{i}^{E} = RT \ln \gamma_{i}^{\prime}$$
 (V.2.6)

A third standard state, which is based on wt. pct. rather than molar concentration is generally used in steelmaking studies. The infinitely dilute solution is chosen for the reference state and the activity coefficient is defined as:

$$\mathbf{f}_{i} = \frac{\mathbf{h}_{i}}{\left[\text{wt. } \% \text{ } \overline{i} \right]}; \text{ where } \left\{ \begin{array}{c} \mathbf{h}_{i} \rightarrow \text{wt. } \% \text{ } i \\ \mathbf{f}_{i} \rightarrow 1 \end{array} \right\} \text{ as wt. } \% \text{ } i \rightarrow 0$$

 h_i is taken as unity in the hypothetical standard state of 1 wt. pct. The

excess partial molar free energy \Im_{i}^{E} is then of the form:

$$\mathcal{F}_{i}^{E} = 2.303 \text{ RT} \log f_{i}.$$
 (V. 2. 7)

It should be noted that the excess partial molar free energy terms F_i^E and \mathfrak{F}_i^E have the same value at high dilution regardless of the concentration scale chosen since the activity units alter accordingly. This does not apply in the general case since the linear relationship between wt. pct. i and X_i is only an approximation for dilute solutions. Conversion is readily made to the Raoultian standard state term F_i^E provided that the Henrian coefficient Υ_i^o is known. V-2.2 Free Energy Interaction Parameters

In practice the type of solutions encountered are no longer in a state of infinite dilution and generally consist of a solvent 1 containing several solute components 2, 3, 4, etc. Deviations from ideal behaviour are reflected in the activity coefficient of the solute under investigation and it is important to determine the effects of the remaining solutes. From a consideration of experimental data Chipman et al (1950) have shown that the activity coefficient of a solute in a multi-component system could be expressed as follows:

$$Y'_2 = Y'^{(2)}_2 Y^{(3)}_2 Y^{(4)}_2$$
 (V. 2. 8)

where (i) the reference state for the activity coefficient χ'_2 is based on Henry's law, (ii) $\chi'_2^{(2)}$ is the activity coefficient in the binary solution 1-2 containing the same molar fraction of 2 as the multicomponent system, and (iii) $\chi'_2^{(3)}$ and $\chi'_2^{(4)}$ are interaction coefficients representing the effect of components 3 and 4 on the behaviour of 2. Wagner (1952) used a Taylor series expansion to express the Raoultian activity coefficient of component 2, and hence the excess partial molar free energy, in terms of the concentrations of the various solutes present:

i.e.
$$\ln \Upsilon_2(X_2, X_3, ...) = \ln \Upsilon_2^0 + \left[X_2 \cdot \frac{\partial \ln \Upsilon_2}{\partial X_2} + X_3 \cdot \frac{\partial \ln \Upsilon_2}{\partial X_3} + ... \right] + \left[\frac{1}{2} \cdot X_2^2 \cdot \frac{\partial \ln \Upsilon_2}{\partial X_2^2} + X_2 \cdot X_3 \cdot \frac{\partial^2 \ln \Upsilon_2}{\partial X_2 \cdot X_3} + ... \right] +$$

$$(V. 2. 9)$$

The reference state here is taken as the pure component and the derivatives are expressed as the limiting values at zero concentration of all solutes.

If 2nd and higher order terms are neglected, equation (V. 2. 9) may be expressed in the form:

$$\ln Y_2 (X_2, X_3, ...) = \ln Y_2^{\circ} + X_2 \epsilon_2^{(2)} + X_3 \epsilon_2^{(3)} + (V. 2.10)$$

where the free energy interaction parameters are defined as:

$$\boldsymbol{\epsilon}_{2}^{(2)} \doteq \left(\frac{\partial \ln \boldsymbol{\chi}_{2}}{\partial \boldsymbol{X}_{2}}\right)_{\boldsymbol{X}_{1} \rightarrow \boldsymbol{Y}}; \quad \boldsymbol{\epsilon}_{2}^{(3)} = \left(\frac{\partial \ln \boldsymbol{\chi}_{2}}{\partial \boldsymbol{X}_{3}}\right)_{\boldsymbol{X}_{1} \rightarrow \boldsymbol{Y}}, \quad \text{etc}$$

If the infinitely dilute solution is chosen as the reference state, equation (V. 2.10) expresses the Henrian activity coefficient as:

$$\ln \mathbf{Y}_{2}'(\mathbf{X}_{2}, \mathbf{X}_{3}, \dots) = \mathbf{X}_{2} \boldsymbol{\epsilon}_{2}^{(2)} + \mathbf{X}_{3} \boldsymbol{\epsilon}_{2}^{(3)} + \dots \qquad (V. 2. 11)$$

If the reference state is taken as the infinitely dilute solution on a weight percent scale, the following relationships are obtained:

$$\log f_{2} (wt. \% 2, wt. \% 3, ...) = e_{2}^{(2)} [wt. \% 2] + e_{2}^{(3)} [wt. \% 3] + ... (V. 2. 12)$$

where the interaction parameters are defined as

$$e_{2}^{(2)} = \left(\frac{\partial \log f_{2}}{\partial \left[\frac{\%}{2}\right]}\right)_{\text{wt. }\%1 \rightarrow 100} e_{2}^{(3)} = \left(\frac{\partial \log f_{2}}{\partial \left[\frac{\%}{3}\right]}\right)_{\text{wt. }\%1 \rightarrow 100}, \text{ etc.} \quad (V. 2. 13)$$

V-2.3 Relationships Between Free Energy Interaction Parameters

The interaction parameters $\boldsymbol{\epsilon}_{i}^{(j)}$ and $e_{i}^{(j)}$ are a measure of the effect of solute j on the behaviour of solute i, and there are parameters $\boldsymbol{\epsilon}_{j}^{(i)}$ and $e_{j}^{(i)}$ which correspond to the reciprocal effect. Wagner (1952) showed for an infinitely dilute solution that

$$\begin{pmatrix} \frac{\partial \ln \chi_{i}}{\partial x_{j}} \end{pmatrix}_{X_{1} \to 1} = \begin{pmatrix} \frac{\partial \ln \chi_{j}}{\partial x_{i}} \end{pmatrix}_{X_{1} \to 1}$$
$$\boldsymbol{\varepsilon}_{i}^{(j)} = \boldsymbol{\varepsilon}_{j}^{(i)} \qquad (V. 2. 14)$$

or

The parameters $\boldsymbol{\varepsilon}_{i}^{(j)}$ and $\boldsymbol{\varepsilon}_{i}^{(j)}$ are related through the conversion from mole fraction to weight percent concentrations and natural to common logarithms. Thus:

$$\boldsymbol{\varepsilon}_{i}^{(j)} = 230. \frac{M_{j}}{M_{1}} \cdot e_{i}^{(j)} (X_{1} \rightarrow 1)$$
 (V.2.15)

and for the binary 1 - i solution, the self-interaction parameter,

$$\epsilon_{i}^{(i)} = 230. \frac{M_{i}}{M_{1}} \cdot e_{i}^{(i)}$$

However, Lupis and Elliott (Jan., 1965) pointed out that even in the limit where i and $j \rightarrow O$, an additional term should be included, i.e.:

$$\boldsymbol{\epsilon}_{i}^{(j)} = 230. \frac{M_{j}}{M_{1}}. e_{i}^{(j)} + \frac{M_{1} - M_{j}}{M_{1}}$$
 (V.2.16)

$$\epsilon_{i}^{(i)} = 230. \frac{M_{i}}{M_{1}}. e_{i}^{(i)} + \frac{M_{1} - M_{i}}{M_{1}}$$
 (V. 2. 17)

Consideration of equations (V. 2.14) and (V. 2.15) gives the relationship:

$$e_{j}^{(i)} = e_{i}^{(j)} \cdot \frac{M_{j}}{M_{i}} \qquad (X_{1} \ge 1)$$
 (V.2.18)

and the corrected form from equations (V. 2.14) and (V. 2.16):

$$e_{j}^{(i)} = e_{i}^{(j)} \cdot \frac{M_{j}}{M_{i}} + \frac{1}{230} \cdot \frac{M_{i} - M_{j}}{M_{i}}$$
 (V. 2. 19)

The correction terms in equations (V.2.16), (V.2.17), and (V.2.19) will be particularly significant if the difference in molecular weights is considerable.

V-2.4 Enthalpy and Entropy Interaction Parameters

The generalised form of equation (V. 2.10) expresses the excess partial molar free energy of the ith component as

$$\mathbf{F}_{i}^{E} = \operatorname{RT} \ln \boldsymbol{\gamma}_{i} = \operatorname{RT} \ln \boldsymbol{\gamma}_{i}^{o} + \operatorname{RT} \sum_{j=2}^{m} \boldsymbol{\epsilon}_{i}^{(j)} \mathbf{X}_{j}$$
 (V.2.20)

where:

$$\varepsilon_{i}^{(j)} = \left(\frac{\partial \ln \Upsilon_{i}}{\partial X_{j}}\right) X_{1} \rightarrow 1$$
 (V.2.21)

Wagner's (1952) treatment of multicomponent solutions has been extended by Lupis and Elliott (April, 1965) to include excess enthalpy and entropy effects. Enthalpy and entropy interaction parameters are defined by expressions analogous to equation (V. 2. 21):

$$\eta_{i}^{(j)} = \left(\frac{\partial H_{i}^{E}}{\partial X_{j}}\right) X_{1} \rightarrow 1$$
$$\sigma_{i}^{(j)} = \left(\frac{\partial S_{i}^{E}}{\partial X_{j}}\right) X_{1} \rightarrow 1.$$

and

where the excess properties are related through the equation:

$$F_{i}^{E} = H_{i}^{E} - TS_{i}^{E}$$

$$H_{i}^{E} = \overline{H}_{i} \quad \text{since } \overline{H}_{i}^{id} = O$$

$$(V. 2. 22)$$

and

Taylor series expansions for H_i^E and S_i^E , with second and higher order terms omitted, yield analogues of equation (V.2.20):

$$H_{i}^{E} = H_{i}^{E^{o}} + \sum_{j=2}^{m} \eta_{i}^{(j)} \cdot X_{j}$$
 (V.2.23)

and

$$S_{i}^{E} = S_{i}^{E^{O}} + \sum_{j=2}^{m} \sigma_{i}^{(j)} \cdot X_{j}$$
 (V.2.24)

where the superscript, o, denotes the state of infinite dilution. By substitution of equations (V.2.20), (V.2.23) and (V.2.24) in (V.2.22), it can be shown that:

RT
$$\boldsymbol{\epsilon}_{i}^{(j)} = \eta_{i}^{(j)} - \boldsymbol{T} \boldsymbol{\sigma}_{i}^{(j)}$$

 $\boldsymbol{\epsilon}_{i}^{(j)} = \frac{\eta_{i}}{RT} - \frac{\boldsymbol{\sigma}_{i}^{(j)}}{R}$ (V.2.25)

or

Over limited temperature ranges, the enthalpy and entropy functions are practically independent of temperature and $\varepsilon_i^{(j)}$ will then vary linearly with $\frac{1}{T}$. In view of equation (V.2.14), it is clear that

$$\eta_{i}^{(j)} = \eta_{j}^{(i)}$$

$$\sigma_{i}^{(j)} = \sigma_{j}^{(i)}$$

and

It has already been mentioned that for practical applications, it is often convenient to express concentrations in terms of weight percent, with the infinitely dilute solution as reference state. Under these conditions, Lupis and Elliott (April, 1965) have expressed the excess partial molar free energy in terms of enthalpy and entropy factors:

i.e.
$$\Im_{i}^{E} = 2.303 \text{ RT} \log f_{i} = \Im_{i}^{E} - T \Im_{i}^{E}$$
 (V.2.26)

The enthalpy and entropy interaction parameters are then defined as:

$$\mathbf{h}_{i}^{(j)} = \left(\frac{\partial \not \stackrel{E}{\downarrow}}{\partial \left[\sqrt[m]{j} \right]}\right) \quad \text{wt. } \sqrt[m]{1 \to 100} \qquad (V. 2. 27)$$

and

$$s_{i}^{(j)} = \left(\frac{\partial \mathscr{S}_{i}^{L}}{\partial [\% j]}\right) \quad \text{wt. } \%1 \rightarrow 100 \qquad (V. 2. 28)$$
Consequently,
$$e_{i}^{(j)} = \frac{h_{i}^{(j)}}{2.3 \text{ RT}} - \frac{s_{i}^{(j)}}{2.3 \text{ R}} \qquad (V. 2. 29)$$

dependent and independent terms when equations (V. 2. 25) and (V. 2. 29)

are substituted in equation (V. 2. 16):

$$\eta_{i}^{(j)} = 100 \frac{M_{j}}{M_{1}} h_{i}^{(j)}$$
 (V.2.30)

and

$$\sigma'_{i}^{(j)} = 100 \frac{M_{j}}{M_{1}} s_{i}^{(j)} - R \frac{M_{1} - M_{j}}{M_{1}}$$
 (V. 2. 31)

V-2.5 The Characteristic Temperature, 2

A considerable amount of data are available for solute interactions within the iron-nitrogen system. Using this information, Chipman and Corrigan (1965) found an empirical correlation between enthalpy and free energy parameters at 1600°C:

$$h_{N}^{(j)} = 15000 \cdot e_{N}^{(j)}$$
 (1600°C)

From published data for the effect of alloying elements on the solubility

of hydrogen in liquid iron, Chipman (1966) has derived a similar relationship:

$$h_{H}^{(j)} = 25000 e_{H}^{(j)}$$
 (1600°C)

It was noted by Lupis and Elliott (Jan., 1966, Feb., 1967) that generally, an increase in temperature of the system results in a closer approach to ideality. They suggest that it is reasonable to assume as a first approximation, that the excess partial molar free energy is a linear function of temperature:

$$\mathbf{F}_{i}^{E} = \boldsymbol{\alpha} (\boldsymbol{\tau} - \mathbf{T})$$

where $\boldsymbol{\kappa}$ is the "characteristic temperature" at which the solution becomes ideal if the results at the operating temperature are linearly extrapolated. Thus:

$$F_{i}^{E} = H_{i}^{E} - T S_{i}^{E}$$
At $T = \boldsymbol{\gamma}$, $F_{i}^{E} = 0$ and $H_{i}^{E} = \boldsymbol{\gamma} S_{i}^{E}$

i.e. $F_{i}^{E} = H_{i}^{E} - T \cdot H_{i}^{E} = H_{i}^{E} (\boldsymbol{\gamma} - T)$ (V.2.32)

However, this relation is likely to be valid only within a limited temperature range since at the temperature, $\boldsymbol{\gamma}$, for which the system becomes ideal, H_i^E and S_i^E should also become zero because both are functions of temperature and should decrease with increasing temperature.

Differentiation of equation (V. 2. 32) with respect to composition leads to:

$$\epsilon_{i}^{(j)} = \frac{\eta_{i}^{(j)}}{R} \cdot (\frac{1}{T} - \frac{1}{\alpha})$$
 (V.2.33)

and $\eta_{i}^{(j)} = \gamma \sigma_{i}^{(j)}$ (V.2.34) At constant temperature it will be seen that equation (V.2.33) reduces to the form:

$$\varepsilon_{i}^{(j)} = C \eta_{i}^{(j)}$$
 (V.2.35)

where C is a constant. Equation (V. 2. 35) would account for the correlation between free energy and enthalpy parameters observed by Chipman and Corrigan for the effect of alloying elements on the solubility of nitrogen and hydrogen in liquid iron. Relationships of this type can be very useful in that they provide a means of estimating solubilities at different temperatures from a knowledge of the free energy interaction parameter at 1600°C. Until the present time there has been insufficient information available for the determination of a similar relationship for the effect of alloying elements on the behaviour of oxygen in liquid iron.

V-2.6 Second Order Interaction Parameters

With the accumulation of more precise experimental data, deviations from linearity have become measurably significant, especially at higher solute concentrations, and Wagner's (1952) first order approximation of the series expansion of ln Υ_i in equations (V. 2. 9) and (V. 2. 20) is no longer adequate. Lupis and Elliott (April, 1966) have proposed additional parameters to account for these deviations and have formulated generalised nth order interaction parameters by the Taylor series expansion of ln Υ_i to include nth order terms. By this convention ln Υ_i^o is of zero order and $\varepsilon_i^{(j)}$ is a first order interaction parameter. Expanding the series to include second order terms, equation (V.2.9) may be expressed as:

$$\ln \gamma_{i} = \ln \gamma_{i}^{\circ} + \sum_{j=2}^{m} \varepsilon_{i}^{(j)} x_{j} + \sum_{j=2}^{m} \rho_{i}^{(j)} x_{j}^{2}$$
$$+ \sum_{j=2}^{m} \sum_{k=2}^{m} \rho_{i}^{(j,k)} x_{j} x_{k}$$
$$j \neq k$$

where

$$\rho_{i}^{(j)} = \frac{1}{2} \cdot \left(\frac{\partial_{i}^{2} \ln \gamma_{i}}{\partial x_{j}^{2}} \right)$$

and $\rho_{i}^{(j,k)} = \frac{\partial^{2} \ln Y_{i}}{\partial X_{i} \partial X_{k}}$

 $\rho_{i}^{(j)}$ is termed the squared second order free energy interaction parameter and measures the second order effects of solute j on the behaviour of solute i whilst the cross product parameter $\rho_{i}^{(j, k)}$ measures the combined effect of two solutes j, k on solute i.

Likewise, second order enthalpy and entropy parameters have been defined together with corresponding parameters expressed in weight percent concentrations and for a reference state of infinite dilution. The various parameters are listed in Table V-1 for purposes of comparison.

The relationship between second order free energy, enthalpy and entropy parameters is similar to equation (V. 2.25) for first order:

$$\rho_{i}^{(j,k)} = \frac{\lambda_{i}^{(j,k)}}{RT} - \frac{\pi_{i}^{(j,k)}}{R}$$

Other relationships between second order parameters have been established by Lupis and Elliott (April, 1966) but are not included here since they are beyond the scope of the present study.

V-2.7 Prediction of Interaction Parameters

Interaction parameters have been defined by means of Taylor series expansions of the excess free energy, enthalpy and entropy functions. However, several attempts have been made to predict and interpret these parameters in terms of solution models.

Alcock and Richardson (1958) approached the problem from a chemical standpoint in their treatment for ternary systems. Their random solution model assumed that, for a dilute solution of solutes i, j in solvent 1:

- (i) The distribution of atoms in solution is random.
- (ii) The coordination number, Z, for all three types of atoms 1, i, j is the same.
- (iii) The pairwise interaction energies are independent of concentration.
- (iv) At high dilution no i-i or j-j pairs are formed, i.e. solute atoms have no like atoms in the nearest neighbour shells.
- (v) Regular solution behaviour.

By considerations of energy changes during rupture and formation of pair interactions in the ternary and separate binary systems, the excess partial free energy for the ternary may be expressed as a function of the binaries. The ternary interaction parameter is then given in terms of the binary activity coefficients for infinitely dilute solutions:

$$\epsilon_{i}^{(j)} = \ln \Upsilon_{i}^{\circ} - \ln \Upsilon_{i}^{\circ} - \ln \Upsilon_{i}^{\circ} - \ln \Upsilon_{i}^{\circ} - \ln \Upsilon_{j}^{\circ} - \ln \Upsilon_{j}^{\circ} - \ln \Upsilon_{i}^{\circ} - \ln \Upsilon_{j}^{\circ} - \Gamma_{j}^{\circ} -$$

This relationship was applied to sulphur and oxygen ternary data but was only satisfactory in predicting the sign and not the magnitude of the interaction parameter, thus implying that these solutions behaved in a non-random manner.

This led to the development of a quasi-chemical theory of ternary solutions by Alcock and Richardson (1960). This was basically the same as the previous model with a random distribution assumed for the bulk solution. However, the distribution was assumed to be nonrandom around each solute atom. The non-randomness in the coordination shell of a solute atom, i, is accounted for through the equation:

$$\frac{n_{i-j}}{n_{i-1}} = \frac{X_j}{X_1} \cdot \exp(W/ZkT)$$

where Z is the coordination number, X is the mole fraction and n is the number of pairwise interactions specified by the subscript between solute atom, i, and atoms in its nearest neighbour shell. $\frac{W}{Z}$ is the energy change when a j atom is replaced by a solvent 1 atom in the coordination shell. When $w \neq 0$, it is clear that there is a non-random distribution. Again by considerations of the excess partial enthalpy in terms of changes in pairwise interaction energies the following relationship was derived:

$$\boldsymbol{\varepsilon}_{i}^{(j)} = \frac{Z (K-1)}{X_{1} + KX_{j}}$$
where

$$\mathbf{K} = \left[\frac{\left(\boldsymbol{\gamma}_{i}^{\circ} \cdot \boldsymbol{\gamma}_{j}^{\circ} \right)_{X_{1} \rightarrow 1}}{\boldsymbol{\gamma}_{i}^{\circ} \boldsymbol{\gamma}_{j}^{\circ} \boldsymbol{\gamma}_{1}^{\circ}} \right]^{\frac{1}{Z}}$$

The predictions of the theory were found to be an improvement on the earlier random solution model. However, the discrepancies between the observed and predicted values indicated that pairwise interaction energies varied with composition.

Lupis and Elliott (Sept., 1966) attempted to use the quasichemical theory to predict first and second order free energy interaction parameters. Their model was developed for a quaternary system in order to predict the cross product parameter $\rho_i^{(j,k)}$ which involves three solute components. The assumptions were the same as those of the Alcock and Richardson (1960) model. The treatment was based on the contribution of the configurational partition function to the excess thermodynamic properties, whilst vibrational effects were omitted.

The theory gave satisfactory agreement between observed and predicted values for relationships between zero and first order parameters and qualitative agreement for first and second order parameters. However, the theory did not take into account the concentration dependence of pairwise interaction energies and neglected the vibrational effects so that only the configurational excess entropy was considered. This can only be negative whereas experimental evidence indicates that the excess entropy may, on occasions, be positive.

A more recent model has been developed by Lupis and Elliott

(Feb., 1967) which predicts relationships between zero and first order free energy, enthalpy and entropy parameters in fair qualitative agreement with experimental data. The "central atoms" theory is the basis for the model and the excess thermodynamic properties of a solution are expressed in terms of the partition function for the probabilities associated with different configurations in the coordination shell and its influence on the central atom. Account is taken of both configurational and non-configurational excess entropies. A "quasi-regular" solution is considered for which the configurational excess entropy is zero and the excess entropy is accounted for by the non-configurational contribution. From this treatment, a theoretical expression is derived for the value of the characteristic temperature $\boldsymbol{\tau}$ which was evolved as a consequence of empirical correlations of the free energy and enthalpy parameters.

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CHAPTER V-3

LITERATURE REVIEW

V-3.1 Solutions of Oxygen in Liquid Iron

The role of oxygen as an agent in the refining of steel is of major importance since the quality of the finished product is dependent on the controlled removal of solute impurities by oxidation and the final removal of oxygen by a deoxidising agent. Consequently, many investigations have been undertaken in order to determine the thermodynamic behaviour of oxygen in liquid iron and liquid iron alloys.

Reference to the iron-oxygen phase diagram (Darken and Gurry, 1953) shows that at high temperatures a measurable amount of oxygen dissolves in liquid iron. The oxygen content may be increased until liquid wustite forms. When an iron-oxygen solution is slowly cooled, a monotectic change occurs at $1528^{\circ}C$ and 0.16 wt. pct. oxygen where-by solid iron and liquid wustite (22.5 wt. pct. <u>O</u>) separate out. If, however, the cooling rate is increased, it is possible to retain the high temperature composition and suppress wustite formation. At $1600^{\circ}C$, the solubility limit occurs at an oxygen partial pressure of 10^{-8} atmosphere which is too small to measure experimentally. The investigation of dilute iron-oxygen solutions would necessitate the use of even lower oxygen pressures. The oxygen potential in the gas phase is generally controlled by the use of CO/CO_2 or H_2/H_2O mixtures, on the basis of

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the reactions:

$$CO + \frac{1}{2}O_2 = CO_2$$

 $H_2 + \frac{1}{2}O_2 = H_2O$

and

Chipman (1933) showed that oxygen dissolves in liquid iron in

the monatomic form:

$$\frac{1}{2}$$
 $O_2 = O$

so that in H_2O / H_2 mixtures, oxygen dissolves in liquid iron according to the reaction:

$$H_2 + \underline{O} = H_2O \qquad (V.3.1)$$

The effect of composition on the equilibrium constant

$$K = \left(\frac{{}^{P}H_{2}O}{{}^{P}H_{2}}\right) \cdot \frac{1}{{}^{h}O}$$
(V. 3. 2)

is measured experimentally in terms of the apparent equilibrium constant,

$$K' = \left(\frac{{}^{P}H_{2}O}{{}^{P}H_{2}}\right) \cdot \underbrace{\frac{1}{wt. \% O}}_{wt. \% O}$$
(V. 3. 3)

and these are related through the activity coefficient

$$f_{O} = \underbrace{\frac{h_{O}}{\left[wt. \% O\right]}} (V. 3. 4)$$

where the reference state is taken as the infinitely dilute solution. Dividing equation (V. 3. 3) by (V. 3. 2) therefore gives the relationship:

$$\frac{K'}{K} = f_{O} \qquad (V.3.5)$$

If the value of the activity coefficient is dependent on the oxygen concentration, i.e. there is a deviation from Henry's law, it follows from equation (V.2.12) that:

$$\log f_{O} = \log f_{O}^{(O)} = e_{O}^{(O)} \cdot \left[wt. \% \underline{O} \right] \qquad (V.3.6)$$

where the self-interaction parameter is defined as:

$$e_{O}^{(O)} = \frac{\partial \log f_{O}}{\partial [wt. \% O]}$$

Eliminating f_{O} from equations (V. 3. 5) and (V. 3. 6) yields:

$$\log K' = \log K + e_{O}^{(O)} \cdot [wt. \% O]$$
(V.3.7)

The variation of the experimentally measured apparent equilibrium constant with the oxygen content of the metal may, therefore, be used to calculate the equilibrium constant, K, and the value of the free energy interaction parameter, $e \begin{pmatrix} O \\ O \end{pmatrix}$.

In one of the earliest investigations (Chipman, 1933), induction heated electrolytic iron melts contained in alundum or alumina crucibles were exposed to controlled water vapour/hydrogen mixtures for periods of up to two hours. The experiments covered a temperature range of 1500-1750°C. A disappearing filament pyrometer was used for temperature measurement. After the power supply had been cut off, the charge was allowed to solidify and samples were subsequently analysed for oxygen by vacuum fusion. The results showed that the activity coefficient, f_O , was dependent on the oxygen content of the melt which implied that iron-oxygen solutions did not obey Henry's law. The temperature dependence of log K was found to be:

$$\log K = \frac{6200}{T} - 3.28$$

This method was refined by Fontana and Chipman (1936) who preheated

the incoming water vapour/hydrogen mixture to 1600°C by means of a refractory tube furnished with a platinum resistance heater. Some melts were quenched in liquid tin in order to retain the high temperature equilibrium composition. It was found that K' was independent of the oxygen content of the melt so that the activity of oxygen could be taken as equal to the oxygen concentration expressed in terms of weight percent. Using a similar technique, Chipman and Samarin (1937) studied the temperature dependence of the equilibrium constant, K, and their results were represented by the following equation:

$$\log K = \frac{10200}{T} - 5.5 (1600 - 1770^{\circ}C)$$

On the basis of their preliminary studies into the effects of thermal diffusion on the equilibrium oxygen content of liquid iron (1948), Dastur and Chipman (1949) made further modifications to Chipman's (1933) technique. A preheated mixture of argon/hydrogen/water vapour was directed by means of a preheater tube onto the surface of an induction heated melt contained in an alumina crucible. The authors claimed that when the gas mixture was preheated to about 1500° C, a ratio of Ar: H_2 of 4:1 completely eliminated any thermal diffusion effects. A disappearing filament pyrometer was used for temperature measurement and the iron was solidified by holding in a stream of argon in the cold part of the furnace.

On the basis of the work of Fontana and Chipman (1936), it was assumed that iron-oxygen solutions obeyed Henry's law. At lower temperatures good agreement was observed with Fontana's value of log K. However, the data were not in accord with the work of Chipman and Samarin (1937) for the temperature dependence of the equilibrium constant:

$$\log K = \frac{7050}{T} - 3.17 \quad (1500 - 1760^{\circ}C).$$

A negative deviation from Henry's law was reported by Averin et al (1955) who used a melting and equilibration technique similar to that of Dastur and Chipman. Sampling was effected by aspiration into silica tubes. However, the scatter in their results would not permit the precise calculation of the activity coefficient. The temperature dependence of the equilibrium constant was found to be:

$$\log K = \frac{9440}{T} - 4.536$$

Further investigations were carried out by Gokcen (1956) using a different technique in order to eliminate thermal diffusion. A resistance furnace was employed to reduce thermal gradients within the system and the gas mixture, heated to 100° C in order to prevent condensation, was bubbled through the melt. A mixture of Ar/ H₂ / H₂O with an Ar H₂ ratio of 4.5:1 was used to prevent hydrogen-porosity in the solidified metal which was quenched on a water-cooled plate in the lower region of the furnace. In additional experiments the melt was quenched in liquid tin with no noticeable difference in results. Experiments were carried out at 50C^o intervals from 1550^o to 1700^oC, and temperatures were measured with an optical pyrometer. The oxygen content of the iron was determined by vacuum fusion analysis. His results for the effect of temperature on log K were reproducible within $\frac{1}{2}$ 0.02 logarithmic units. Errors of this magnitude could be entirely accounted for by uncertainties in temperature and analysis. The temperature dependence of the equilibrium constant was found to be:

$$\log K = \frac{6670}{T} - 3.05$$

Floridis and Chipman (1958) studied the effect of oxygen content on the apparent equilibrium constant, K', at 1500° and 1600° C. A technique, similar to that of Gokcen and Chipman (1952) was used in which the melt was quenched in helium. A preheated Ar/ H₂ / H₂O mixture with a 6:1 ratio of Ar: H₂ was directed onto the surface of the induction heated melt contained in an alumina or magnesia crucible. Additional experiments were performed in an apparatus similar to that of Gokcen (1956) in which the gas mixture was bubbled through the melt and samples were obtained by the suction technique. The results obtained from the two types of experiment were in good agreement and showed no effects of thermal diffusion.

In this work it was again found that iron-oxygen solutions exhibited negative deviations from Henrian behaviour. This was in qualitative agreement with the observations of Chipman (1933) and Averin et al (1955). The activity coefficient of oxygen between 1550° and 1600°C was given by:

 $\log f_{O} = -0.20 \quad [wt. \% O] \quad (0-0.2 wt. \% O)$

The effect of temperature on the equilibrium constant was in reasonable

agreement with the work of Dastur and Chipman (1949) and was, in fact, represented by Floridis and Chipman as a line drawn through their data parallel to that of Dastur and Chipman:

$$\log K = \frac{7050}{T} - 3.20$$
 (1500-1600°C)

Sakao and Sano (1960) using a similar induction heating technique also found a negative deviation from Henrian behaviour:

$$\log f_{O} = (\frac{-1750}{T} + 0.76)$$
 [wt. % O]

This equation gives a value of -0.17 for the interaction parameter, $e_{O}^{(O)}$, at 1600°C. The temperature dependence of the equilibrium constant was found to be:

$$\log K = \frac{7040}{T} - 3.224$$
 (1550-1650°C).

Negative deviation from Henry's law for iron-oxygen solutions has been reported by Matoba and Gunji (1963). A similar technique to that of Floridis and Chipman (1958) was used but the water vapour/ hydrogen ratios in many of their experiments were much higher. Many of their experiments were virtually conducted under a liquid slag layer and for this reason their results are not considered substantial support for non-Henrian behaviour of dilute iron-oxygen solutions.

More recently, Matoba and Kuwana (1965) found that the activity coefficient was strongly dependent on oxygen content, the value of $e_{O}^{(O)}$ being given by:

$$e_{O}^{(O)} = \frac{-10130}{T} + 4.94$$
, for oxygen concentrations

up to 0.18 wt. % O. At 1600°C this equation gives a value for $e_{O}^{(O)}$ of

-0.47. The temperature dependence of the equilibrium constant was given as:

$$\log K = \frac{7480}{T} - 3.421$$

In this work an induction heating technique was used and preheated $Ar/H_2/H_2O$ mixtures were bubbled through the melt.

Tankins et al (1964), using equipment similar to that of Gokcen (1956), bubbled Ar/ H_2 / H_2O mixtures through resistance heated melts. Under these conditions equilibrium was attained within one hour at 1550°C. Melts were quenched in a stream of argon whilst standing on a water-cooled brass plate so that freezing occurred from the top within four seconds. The effect of oxygen on the apparent equilibrium constant at 1550°C was determined to be:

 $\log K' = 0.617 - 0.055 \ wt. \% O$

The calculation of the temperature dependence of the equilibrium constant included the data of Gokcen (1956) with which there was good agreement and the equation obtained was:

$$\log K = \frac{6817}{T} - 3.13$$
 (1550-1700°C)

The difference in the values of log K' for oxygen concentrations between 0 and 0.18% could be accounted for by ± 2.5 C^o error in temperature measurement. It was therefore concluded that the apparent equilibrium constant was independent of the oxygen content and that ironoxygen solutions obeyed Henry's law.

Tankins et al point out that their conclusions are supported by the work of Wreidt and Chipman (1955) who found that the activity coefficient of oxygen was independent of oxygen content in a 75% iron -25% nickel solution for which the free energy of solution of oxygen is only slightly more positive than that for pure iron.

Negative deviations from Henrian behaviour were reported by Schenck and Steinmetz (Nov. 1967). Their experiments were carried out in a Tammann carbon resistance furnace. Charges of 200 gm. of high purity iron were melted in alumina crucibles and $Ar/H_2/H_2O$ mixtures with a 5:1 ratio of $Ar:H_2$ were directed onto the surface of the melt. Samples were obtained by an aspiration technique using quartz tubing, quenched in a water-cooled copper mould and analysed by the vacuum fusion method.

They obtained values of $e_{O}^{(O)} = -0.13$ at 1600°C and $e_{O}^{(O)} = -0.32$ at 1625°C. The more negative value for the free energy interaction parameter at the slightly higher temperature is unexpected. Further experiments were undertaken in the temperature range 1550° to 1700°C and with a water vapour/hydrogen ratio of 0.3. The temperature dependence of the apparent equilibrium constant was found to be:

$$\log K' = \frac{6722}{T} - 3.049$$
 (1550°-1700°C)

In view of the negative values of $e_{O}^{(O)}$, Schenck and Steinmetz note that the value of the equilibrium constant is over-estimated and give the value:

$$\log K = \frac{6730}{T} - 3.05$$
 (1550°-1700°C)

which is in close agreement with the finding of Tankins et al (1964).

Data from several recent investigations for the effect of oxygen on the apparent equilibrium constant are shown in Figure 1.

A recent study was made by Shiraishi (1966) using a levitation melting technique. Liquid iron droplets were equilibrated in H_2O / H_2 mixtures at controlled temperatures before quenching in a copper mould. The author claimed that thermal diffusion effects were negligible and that equilibrium was attained within five minutes. A two-colour optical pyrometer was used for temperature measurement and oxygen analyses were made using an inert gas fusion method.

In this work it was assumed that Henry's law was obeyed for iron-oxygen solutions. The experiments were carried out over a temperature range 1470 to 1750°C and the temperature dependence of the equilibrium constant was found to be:

$$\log K = \frac{7159}{T} - 3.23$$
 (1470-1750°C)

Although this equation is apparently in good agreement with the work of Dastur and Chipman (1949), it was based on a limited number of experiments and the data exhibited a considerable degree of scatter (about 0.15 logarithmic units at 1500°C).

Although equilibrium in the iron-oxygen system has been the subject of many investigations, it would appear that the two main points of disagreement concern the Henrian behaviour of oxygen in liquid iron and the temperature dependence of the equilibrium constant. It is difficult to establish with certainty the reasons for the disagreement between the various workers. The discrepancies may be due to errors associated

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with temperature measurement, thermal diffusion effects, cruciblemelt interaction, quenching effects or chemical analysis.

Optical temperature measurements may be subject to several sources of error, for example, excessive extrapolation to high temperatures, fume formation and emissivity effects. D'Entremont (1963) showed that unexpected errors may arise due to variations in emissivity with the oxygen content of the melt. The extent of these variations are unknown but may be important since Kozakevitch and Urbain (1961) have shown that oxygen has a drastic effect on the surface tension of iron.

Thermal diffusion effects are likely to occur in the presence of excessive temperature gradients. Under such conditions the heavier of two gases in a mixture will tend to diffuse to the cold region so that the gas composition is no longer uniform. However, the addition of a gas of high molecular weight will reduce this effect. Much of the earlier work was subject to uncertainty of this nature, particularly where an induction furnace was used without the precautions of preheating the incoming gas mixture or introducing argon into the gas stream.

Most of the previous work on the solubility of oxygen in liquid iron has been conducted using alumina crucibles. Under these conditions, the following reaction will occur to some extent:

$$A1_2O_3$$
 (s) = 2 A1 + 3 O

When aluminum dissolves in liquid iron, the activity coefficient of dissolved oxygen is greatly decreased. In this context, values for $e_{O}^{(A1)}$ at 1600°C of -12, -1 and -4.6 have been obtained by Gokcen and

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Chipman (1953), d'Entremont et al (1963) and McLean and Bell (1965) respectively. Since the oxygen activity in the melt is fixed by the oxygen potential of the gas phase, this means that the oxygen concentration will be increased and hence the value calculated for the equilibrium constant will be less than the true value.

The quenching procedure can have an effect on the final oxygen content of the metal. On slow solidification, oxygen may be lost from the metal either by reaction with hydrogen in the gas phase or through separation of iron oxide.

Many of the vacuum fusion analysers used in the earlier investigations were not equipped with baffles and consequently there was a possibility of sample loss due to spattering on initial melting. In addition, the quenched samples were generally cut into sections for analysis and thus, if segregation occurred within the ingot, erroneous results could be obtained.

In the present investigation, an attempt has been made to eliminate errors of the type discussed above by the use of:

- (i) A two-colour radiation pyrometer
- (ii) High gas flow rates
- (iii) Levitation melting
- (iv) Rapid quenching
- (v) Analysis of complete samples by inert gas fusion.
- V-3.2 The Effect of Vanadium on the Activity of Oxygen in Liquid Iron Equilibrium between oxygen dissolved in liquid iron-vanadium

alloys and water vapour/hydrogen mixtures may be represented by equations (V. 3. 1) to (V. 3. 5). The activity coefficient of oxygen, f_O, may be expressed by virtue of equation (V. 2. 8) in terms of the activity coefficient of oxygen in the binary Fe-O system and the interaction coefficient for the effect of vanadium on oxygen:

$$f_{O} = f_{O}^{(O)} \cdot f_{O}^{(V)}$$
 (V.3.8)

By comparison with equation (V. 2.12), f_0 may be expressed in terms of the free energy interaction parameters:

$$\log f_{O} = e_{O}^{(O)} \cdot \left[wt. \ \% \ \underline{O} \right] + e_{O}^{(V)} \cdot \left[wt. \ \% \ \underline{V} \right]$$
(V. 3. 9)

where

$$\log f_{O}^{(V)} = e_{O}^{(V)} \cdot \left[wt. \% \underline{V} \right]$$
(V.3.10)

Eliminating f_{O} between equations (V. 3. 5) and (V. 3. 9) gives the following expression:

log K' = log K + $e_{O}^{(O)}$ wt. $\% O + e_{O}^{(V)}$ wt. % V (V.3.11) If the value of $e_{O}^{(O)}$ has been determined, the experimentally measured value of K' and the equilibrium vanadium and oxygen contents of the metal may be used to determine the value of the free energy interaction parameter $e_{O}^{(V)}$.

The earliest studies on vanadium-oxygen equilibrium in liquid iron were carried out by Chipman and Dastur (1951). The apparatus used by these workers was similar to that which they had used previously for their investigations of the iron-oxygen binary system (Dastur and Chipman, 1949). In order to minimise thermal diffusion effects, a preheated mixture of Ar/ H_2/H_2O with an Ar: H_2 ratio of 4:1 was directed onto the melt surface. Melts were equilibrated at a temperature of $1600^{\circ}C$ for about 45 minutes, the power supply switched off and the melts quenched by lowering into the cooler region of the furnace.

Experimental conditions were varied by gradually increasing the water vapour/hydrogen ratio in successive experiments whilst maintaining a constant vanadium content. This was continued until the melt had reached oxygen saturation at which point an oxide layer was formed. Experiments were conducted for a range of vanadium contents up to 1.3 wt. pct. V.

Using the value of log K which they had previously determined for the liquid iron-oxygen system and again assuming iron-oxygen solutions obey Henry's law, Chipman and Dastur found that for a particular oxygen potential in the gas phase, vanadium additions increased the solubility of oxygen in liquid iron. Their data gave a value for $e_{O}^{(V)}$ of -0.27 at 1600°C.

A similar investigation has been carried out by Pargeter (1967) who used a resistance furnace and a controlled gas mixture of He / H₂ / H₂O. An 8 mm. I. D. alumina gas inlet tube terminated in a loosely fitting 0.5 mm. I. D. capillary the end of which was positioned just below the surface of the melt. By this arrangement, the gas mixture was concurrently directed onto the surface of, and bubbled through, the melt. Experiments were made at 1600° C for periods extending up to nine hours.

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The liquid alloys were quenched by lowering into a chamber where they were sprayed with helium. This gas was chosen because of its high thermal capacity. By this procedure the temperature was lowered to about 500°C within five seconds. Oxygen analysis was performed by the vacuum fusion technique.

Pargeter obtained a value for the interaction parameter, $e_{O}^{(V)}$, of -0.29 at 1600°C which is in good agreement with Chipman and Dastur's (1951) original work. It is worth noting, however, that Pargeter's data in comparison with those of Chipman and Dastur exhibit considerable scatter, particularly at low vanadium contents and for experiments of less than six hours duration.

A more recent investigation was made by Schenck and Steinmetz (Dec. 1967) using the same apparatus and techniques which were employed for their work on the iron-oxygen system (Nov. 1967). Experiments were conducted at 1600°C for alloy compositions within the range 0.2 to 0.7 wt. pct. vanadium and the water vapour/hydrogen ratio was maintained at 0.04. The values of log K and $e_{O}^{(O)}$ at 1600°C obtained by Schenck and Steinmetz (Nov. 1967) were included in the calculation and the value of the parameter $e_{O}^{(V)}$ was found to be -0.11. This value is not in agreement with the work of Chipman and Dastur (1951) or that of Pargeter (1967). This may be due to the uncertainty in determining the value of $e_{O}^{(V)}$ from the gradient of the line representing a plot of their experimental data which exhibits a considerable scatter, particularly at higher vanadium concentrations. Data for the effect of vanadium on the activity coefficient of oxygen have been obtained by Fischer and Janke (1966) using an electrochemical technique. The cell consisted of a lime stabilised zirconia tube with a closed end through which a controlled atmosphere was circulated. This was immersed in an iron-vanadium melt and platinum contacts, one in the base of the cell and one immersed in the melt, completed the circuit. The activity coefficient was determined by e.m.f. measurements and at 1600° C the value obtained for the interaction parameter, $e_{O}^{(V)}$, was -0.13, which is considerably different from the value obtained by Chipman and Dastur (1951) but in good agreement with that obtained by Schenck and Steinmetz (Dec. 1967).

The effect of temperature on the free energy interaction parameter $e_{O}^{(V)}$ was investigated by Narita (1958) who employed a technique similar to that of Chipman and Dastur (1951). An Ar₂H₂ ratio of 4:1 was employed and argon/water vapour/hydrogen mixtures, preheated to 1200°C, were directed onto the surface of an induction heated charge of 50 to 80 gm. of iron. It was assumed that the selfinteraction parameter, $e_{O}^{(O)}$, had a zero value, and the values obtained for the vanadium-oxygen interactions were:

e ^(V)	T°C
-0.365	1600
-0.287	1650
-0.196	1700

Narita (1958) did not calculate the temperature dependence of $e_{O}^{(V)}$; however, on the basis of the data available, this would be given by:

$$e_{O}^{(V)} = \frac{-6230}{T} + 2.96$$
 (1600°-1700°C) (V.3.12)
The value of $e_{O}^{(V)}$ at 1600°C is considerably larger in magni-

tude than that obtained by Chipman and Dastur (1951). Sawamura and Sano (1966) reported that Sano and Sakao (1964) recalculated the values for $e_{O}^{(V)}$ from the data of Narita. They included in their calculations the value of the self-interaction parameter:

$$e_{O}^{(O)} = \frac{-1750}{T} + 0.76$$

which they had previously determined (Sakao and Sano, 1960). They obtained the following temperature dependent expression:

$$e_{O}^{(V)} = \frac{-2500}{T} + 1.01$$
 (1550°-1700°C) (V.3.13)

which provides values for the interaction parameter:

	T ^o C
-0.36	1550
-0.32	1600
-0.29	1650
-0.26	1700

Sawamura and Sano (1964) claim that these values show fairly good agreement with the work of Chipman and Dastur (1951). However, if the value for $e_{O}^{(V)}$, obtained by the latter workers, were corrected by inclusion of the value of $e_{O}^{(O)}$, obtained by Sakao and Sano (1960), the disagreement would be somewhat greater.

The differences in values for the vanadium-oxygen parameter

may be due in part to contamination of the melt by crucible material or to the presence within the solidified samples of entrapped vanadium oxides. In the present investigation, these sources of uncertainty have been avoided by the use of levitation melting and by controlling the oxygen potential of the atmosphere at a level sufficiently low to prevent the formation of oxides. Experiments have been conducted over the temperature range 1550° to 1750°C and values determined for the first order free energy, enthalpy and entropy interaction parameters.

CHAPTER V-4

EXPERIMENTAL CONSIDERATIONS

V-4.1 Introduction

The purpose of this gas-metal equilibrium study is to determine the effects of composition and temperature on the activity of oxygen in iron-vanadium melts. It is therefore necessary to control the oxygen potential of the system in this case by the use of hydrogen/water vapour atmospheres in contact with the liquid iron alloy. Levitation melting is particularly suitable for such investigations since the reaction may be studied over a wide range of temperatures thus enabling temperature dependent data to be established with a greater degree of accuracy. A further advantage is the complete elimination of crucible contamination.

V-4.2 Apparatus

A general view of the apparatus used for the determination of oxygen activity in liquid iron and iron-vanadium alloys is shown in Figure V-2. The high frequency generator is seen in the background and is connected to the levitation coil surrounding the taped reaction tube in the centre of the picture. On the extreme left, partially hidden by the gas cylinders, are the water vapour pre-saturator and saturator units while on the extreme right is the "wet-test" meter which is used for measuring hydrogen flow rates. The two-colour optical pyrometer and temperature indicator are seen in the centre foreground.

V-4.2.1 The Reaction Chamber

A photograph of the reaction chamber is shown in Figure V-3. The electrical heating tape in which the apparatus is wrapped has been removed for clarity.

The reaction chamber is also shown diagrammatically in Figure V-4. The design was chosen to reduce the time of purging to a minimum and to enable an experiment to be effected under completely controlled atmospheric conditions thus eliminating the possibility of contamination from the air.

The molten droplet is levitated inside a 15 mm. O.D. Vycor tube which is located within the levitation coil. The lower end of the tube is connected by a ground glass union to a 50 mm. O.D. Pyrex chamber furnished with a gas inlet. The chamber is sealed by an aluminum disc which is fitted with an O-ring and supports a Vycor charging rod, an optical flat aligned with a 45° prism, and a copper mould on the end of a steel rod. These are located so that any one may be aligned concentrically with the axis of the reaction tube by rotation of the disc. The mould and charger are supported in the base by Swagelok connections with Teflon sealing rings. This gives a gastight seal and enables the charger or mould to be pushed up into the reaction zone.

The reaction tube and base are wrapped in heating tape to

avoid condensation of water vapour. The design of the gas exit prevented any water which may have condensed in the unheated exhaust tube from re-entering the reaction zone.

V-4.2.2 The Gas Supply

The two separate gas systems which were employed are shown in Figure V-5. In the production of water vapour/hydrogen atmospheres, purified hydrogen was bubbled through a presaturator, C, which contained distilled water maintained at a temperature some 20C° higher than that of the saturator.

The saturator unit consisted of eight 500 ml. flasks, the first seven of which were partially filled with distilled water in order to produce a gradual decrease in the pressure head of water, thus enhancing equilibration at atmospheric pressure. The final flask served as a mixer and was packed with glass raschig rings. The saturator unit was submerged in a constant temperature water bath, D, which was thermostatically controlled to $\frac{1}{2}$ 0.05C°. From the saturator unit the gas mixture passed to the reaction chamber through a tube wound with heating tape.

The efficiency of the saturator system was checked by inserting a series of magnesium perchlorate drying tubes between the gas outlet of the reaction tube and the wet test meter. The actual moisture content of the gas mixture can be calculated from a knowledge of the weight of moisture absorbed from a measured volume of hydrogen, the internal pressure and the ambient temperature, which are indicated by the wet test meter. For flow rates of approximately 0.3 to 6.0 l.p.m; and bath temperatures between 28° and 49°C, the measured water vapour pressures were within $\frac{1}{2}$ 3% of the theoretical values, (Table V-2).

A secondary gas supply was required for purging the reaction chamber and for deoxidation of the molten droplet during the initial stages of an experiment. The appropriate gas was introduced through a three-way stock-cock, H, and dried with magnesium perchlorate, B.

The two three-way stock-cocks, F and G, were arranged so as to allow either the dry gas or a hydrogen/water vapour mixture to enter the reaction chamber. In the former case, the water vapour/ hydrogen mixture was diverted through the by-pass in order to maintain steady state conditions in the saturator. On changing to the mixture, the by-pass was closed at 'F' and the dry gas isolated at 'G'.

V-4.3 Experimental Techniques

V-4.3.1 Temperature Control

The characteristics and design of levitation coils along with the advantages and disadvantages of the technique and its applications have been discussed in reviews by Peifer (1965) and Rostron (1967). It is sufficient to note that for a given power supply, the temperature of the sample depends on the coil design, the size and electrical properties of the sample, and the gas flow rate and composition.

A 450-kc/s., 10 kw. Tocco generator was coupled to a 7.5:1

step-down transformer in order to reduce the power input to the coil. The coil used was constructed from one eighth of an inch O. D. copper tubing and was similar in design to that developed by Jenkin's et al (1963), Figure V-6. The lower section of the coil was wound on a conical former with a 30° semi-angle. This section consisted of five turns the last two of which were co-planar with an I. D. of 15 mm. The upper stabilising ring consisted of a double reverse turn wound helically on a 15 mm. diameter spindle. This coil design gave the high lateral stability required for levitation within the confined area of a 13 mm. I. D. reaction tube.

Harris et al (1959) demonstrated that gas flow rate and composition determine the efficiency of heat removal from the levitated sample. The cooling efficiency decreases with increasing atomic weight, i.e. with decreasing thermal conductivity of the gas. Thus the sample may reach temperatures greater than 2000°C in atmospheres such as argon or nitrogen at flow rates of 4 l.p.m. This is advantageous for a rapid melting of samples at the beginning of an experiment. On the other hand, since hydrogen is the most efficient coolant, temperatures in the region of 1500°C are readily attained with the hydrogen/water vapour mixtures used for atmospheric control in the present study.

In general both sample size and gas flow rate were maintained reasonably constant at one gm. and one l.p.m., respectively, and temperature adjustment made solely through the power input control. A decrease in the power input produces an increase in the temperature of the droplet which is now located at a lower position within the coil where the heating effect is greater. Under these conditions the temperature could be controlled to within $\frac{+}{-}$ 5C° of the desired value in the range 1450-1750°C.

V-4.3.2 Temperature Measurement

A Milletron two-colour optical pyrometer and direct reading indicator were used to measure sample temperatures. This instrument measures the intensity ratio of two wavelengths, green and red, of the light emitted by the specimen. Generally, emissivity is independent of wavelength, in which case the intensity ratio is independent of emissivity and dependent only on temperature. This leads to advantages over other forms of optical pyrometry since temperature measurement is relatively independent of the surface properties and size of the radiation source and the absorption properties of the intervening media.

The pyrometer was initially calibrated against a standardised Pt/Pt - 13% Rh thermocouple over the temperature range 1400° to 1700°C. A graphite crucible containing approximately 200 gm. of carbon saturated iron was used for temperatures below the melting point of iron whereas an alumina crucible containing Armco iron was used for higher temperatures. The thermocouple, which was protected by an alumina sheath, was immersed in the melt and the pyrometer was focused on the surface through an optical system identical to that used in the levitation experiments. The couple was positioned centrally within the crucible since it was found that the temperature reading could be affected by as much as $30C^{\circ}$ when the couple was moved towards the wall. A further precaution was taken of grounding the thermocouple to eliminate induced currents in the galvanometer.

The power input was increased stepwise and the corresponding pyrometer and thermocouple readings compared. The same technique was used during cooling only for the Armco iron melt since the carbon saturated iron on cooling precipitates graphite which interferes with the optical pyrometer reading.

It was found that the accuracy of the pyrometer was within $\pm 5C^{\circ}$ of the true temperature from 1400° to 1700°C and it was assumed that this would apply up to 1800°C. The applicability of the calibration data to levitation experiments was confirmed by observing the melting and freezing temperatures of levitated iron droplets. For this purpose the pyrometer was focused on the lower surface of the droplet from a distance of about two feet by means of the prism arrangement in the base of the reaction tube. The speed of response of the instrument was high and the melting point was observed as an arrest in the indicated temperature. During freezing the sample was invariably supercooled and, on solidification, the indicator needle was rapidly deflected to the melting point.

This procedure was also used to check the stability of the

pyrometer at frequent intervals during each series of experiments. Under normal operating conditions the observed temperatures were always within $\frac{1}{2}$ 10C° of the true melting point of iron. The high frequency current induces vigorous stirring within the droplet and Jenkins et al (1963) have demonstrated that the temperature at the surface and centre of a simulated levitation droplet are essentially the same. It is considered that the actual temperatures reported in the present study are accurate to within $\frac{1}{2}$ 10C°.

V-4.3.3 Preparation of Samples

Specimens weighing approximately 1 gm. were prepared from Armco and Ferrovac 'E' iron and iron-vanadium alloys the analyses of which are given in Tables V-3 and V-4. Armco and Ferrovac 'E' iron samples were cut from 0.25'' diameter rod and cleaned with acetone to remove grease prior to levitation.

A series of master alloys ranging in composition from 0.1 to 1 wt. pct. vanadium were prepared in the form of alloy rods. A 250 gm. melt of Armco iron was induction heated in an alumina crucible and, after deoxidising with hydrogen, maintained under an inert atmosphere of argon. Calculated amounts of vanadium were added to the melt at frequent intervals. Ten minutes after each addition, suction samples were drawn from the melt with five mm. I. D. silica tubes. The alloy rods, weighing approximately 20 gm. were cleaned by filing and then cut into one gm. specimens suitable for levitation. Analysis of samples taken from the ends of each rod showed no significant difference in vanadium content (Table V-4). This indicated that the vanadium was uniformly distributed throughout each rod.

Several iron-vanadium alloy specimens were levitated in dry and moist hydrogen for ten minutes at temperatures between 1550° and 1730°C and quenched. Analysis of the specimens indicated no significant change in vanadium content (Table V-5). In all subsequent equilibrium experiments the vanadium content of the droplet was taken as that of the master alloy.

V-4.3.4 Vanadium Analysis

Samples were analysed spectrographically for vanadium. The readings were corrected against calibration curves obtained for chemical standards analysed at the same time as the samples. The estimated error in determination was $\frac{1}{2}$ 0.005 wt. pct. vanadium.

The spectrograph was designed to take samples not less than 0.5" diameter and 0.5" thick, located with flat faces in a horizontal plane. The lower face was sparked with a tungsten electrode in an argon atmosphere. The circuit was completed by an electrical contact with the upper surface. The dimensions of the alloy specimens were much less than those required for spectrographic analysis and for this reason the samples were first compressed, using tension/compression machine to form discs approximately 0.5" diameter and one mm. thick. A 0.5" length of 0.25" diameter copper rod was soldered to the centre of one face and the sample was mounted in a 1.0" diameter bakelite disc, which was subsequently machined to expose the copper contact. The sample face was then polished in final preparation for analysis.

V-4.3.5 Oxygen Analysis

A Leco No. 734-100 analyser was used for oxygen determinations: A one gm. sample contained in a graphite crucible is induction melted in a stream of helium. The oxygen dissolved in the metal is evolved as carbon monoxide and flushed through a catalytic furnace where it is oxidised to carbon dioxide and subsequently collected in a molecular sieve. After two minutes the molecular sieve is heated and the carbon dioxide is carried in the stream of helium through a thermal conductivity cell. This device measures the change in resistance of the cell due to the difference in thermal conductivities of helium and carbon dioxide. The integrated output is indicated on a digital counter.

The actual oxygen content of a metal sample was determined from a calibration curve which was constructed with the aid of standard samples of known oxygen content. The oxygen values reported in the present work are considered to be accurate to within $\frac{1}{2}$ 10 p. p. m.

V-4.3.6 Experimental Procedure

The saturator unit was allowed to equilibrate overnight at the selected water bath temperature and the flow rate was adjusted to approximately one l. p. m. as indicated by the wet test meter. Water vapour/hydrogen ratios of (3 to 9) $\times 10^{-2}$ were obtained by passing puri-

fied hydrogen through the saturator unit at controlled water bath temperatures in the range 25° to 43°C. A ratio of 25 x 10^{-2} was obtained by passing a 19.6 pct. H₂/Argon mixture through the saturator system at 31.7°C.

At the beginning of an experiment the aluminum base was removed and the sample pushed up into the reaction tube where it was held by a magnet until the base had been replaced. The sample was then supported by the Vycor charging rod well above the coil. After flushing the chamber for five minutes in nitrogen, argon or helium, the power input was increased to a maximum and the specimen levitated. As soon as possible after melting, generally about 30 seconds, the atmosphere was changed to hydrogen for deoxidation purposes and then to the hydrogen/water vapour mixture.

The aluminum base was rotated to align the prism with the reaction tube and the pyrometer focused on the molten droplet. Experiments were conducted at temperatures in the range 1450° to 1800°C. Preliminary studies showed that equilibrium was attained within one minute (Table V-6). In order to ensure the attainment of equilibrium during an actual experiment the droplet was maintained at constant temperature for five minutes. A gas flow rate of one 1. p. m. was chosen for operating convenience after preliminary studies (Table V-7) had shown no effect of flow rate on oxygen content in the range 0.5 - 4.01. p. m.

At the end of an experiment the base was again rotated, the

copper mould (1" long x 7/16" diameter) pushed into the reaction chamber, the power supply cut off, and the specimen quenched. The chamber was flushed with an inert gas for several minutes and the sample removed for oxygen analysis. Since the complete sample is used for analysis, errors due to oxygen segregation effects are eliminated.

CHAPTER V-5

PRESENTATION OF RESULTS

V-5.1 Introduction

The behaviour of oxygen in liquid iron was investigated for the temperature range 1450° to 1750° C using water vapour/hydrogen atmospheres and for 1700° and 1800° C using argon/water vapour/hydrogen atmospheres. Water vapour/hydrogen ratios ranging from (3 to 25) x 10^{-2} were employed. Further data were obtained for the activity of oxygen in iron-vanadium alloys. These studies covered the temperature range from 1550° to 1750° C, concentrations from 0.1 to 1.0 wt. pct. vanadium and water vapour/hydrogen ratios from (3 to 9) x 10^{-2} .

In this chapter, the experimental data are presented in tabular and graphical form and the temperature and composition dependent relationships for the solution of oxygen in iron and iron-vanadium alloys are statistically determined.

V-5.2 Experimental Data

The experimentally determined values of K for iron-oxygen alloys are given in Tables V-8 to V-11 and cover, at $50C^{\circ}$ intervals the temperature range 1450° - $1800^{\circ}C$. The number notation for the experiments serves to identify the series by the number preceeding the slash, /. The experiment number within a series preceeds the hyphen and the type of iron used, either Armco, A, or Ferrovac 'E', F, follows the hyphen.

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Experimental details of the saturator bath temperature, the gas flow rate and melting technique are also listed. Values of P_{H_2O} were taken from water vapour pressure-temperature tables for particular saturator temperatures. In computing the water vapour/hydrogen ratio, a correction was made for the slight head of pressure within the system as indicated by the wet test meter. K was then calculated directly from the quotient of this ratio and the oxygen analysis value which is also tabulated.

In Figures V-7 and V-8, log K'is plotted as a function of oxygen content for temperatures between 1550° and 1750° C. The data from Tables V-8 to V-11 are also plotted as log K versus $\frac{1}{T}$ in Figure V-9 where, for the sake of clarity, the mean values of all 'n' points at each temperature are shown with error bars of one standard deviation and these values are listed in Table V-12. Figure V-9 shows a statistical line with 95% confidence limits determined by the method of least squares on all the data. The statistical details are given in Table V-13. A further correlation is made between log \sqrt{wt} . $\frac{\%}{0}$ and $\frac{1}{T}$ in Figure V-10.

Values of the apparent equilibrium constant, K', for ironvanadium-oxygen alloys are given in Tables V-14 to V-18 for temperatures 1550° to 1750° C. The number notation for the experiments is similar to that used in Tables V-8 to V-11 except that the number following the hyphen identifies the iron-vanadium master alloy. These data are plotted as log K' versus wt. pct. <u>V</u> in Figures V-11 and V-12 and pure iron data from Tables V-8 to V-11 have been included for location of the intercepts at zero wt. pct. <u>V</u>. Log K' shows a linear dependence on composition and the equations for these curves, which were statistically determined by the method of least squares on all data, are given in Table V-19.

V-5.3 Experimental Errors

Concerning the data obtained for the iron-oxygen alloys, the scatter in values of log K' (Figures V-7 and V-8) is associated with the experimental errors in oxygen analyses, temperature control and measurement, and control of the water vapour/hydrogen atmosphere. However, Figures V-7 and V-8 represent data at isolated melt temperatures, and, since log K is temperature dependent, it is of more direct value to compare experimental errors with the statistical scatter of all the data in Figure V-9. Although the mean values of points at any temperature lie very close to the statistical line, the 95% confidence limits represent a spread of 0.1 logarithnic units.

The most lucid and convenient method of evaluating the experimental errors is to express them only in terms of their effect on log K at the desired operating temperatures. Thus, the estimated error in temperature measurement of $\frac{+}{-}$ 10C^o results in an error in log K which may be calculated from the statistically determined equation given in Table V-13. For example, the error at 1600^oC was found by difference between the values of log K at 1590^o, 1600^o and 1610^oC to be $\frac{+}{-}$ 0.025

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logarithmic units. This error contribution decreases with increasing temperature as illustrated in Table V-20.

A gas flow rate of 1 l. p. m. of hydrogen was used for most of the experiments for which the water vapour/hydrogen ratio was controlled to within $\frac{1}{2}$ l pct. of the theoretical value, (Table V-2). This corresponds to an error of $\frac{1}{2}$ 0.004 logarithmic units in log K and is independent of melt temperature. Where higher flow rates were used, the accuracy of atmospheric control was estimated to be within $\frac{1}{2}$ 3 pct. which results in an error in log K of only 0.013 logarithmic units.

Finally, errors in oxygen analysis estimated to be within $\stackrel{+}{}$ 0.001 wt. pct. are included in the value of log K through the log $\left[wt. \% \underline{O} \right]$ term. This becomes more significant at low oxygen contents in the order of 0.010 wt. pct. oxygen.

These three sources of error are involved in the experimental determination of log K through their combined effects on the oxygen content of the sample. The temperature dependence of the equilibrium constant in the present study is given by the expression:

$$\log K = \frac{8670}{T} - 3.88 \tag{V.5.1}$$

Since the value of K for the iron-oxygen data has been measured as:

$$K = \left(\frac{P_{H_2O}}{P_{H_2}}\right) \frac{1}{\left[wt. \% O\right]}$$
(V.5.2)
it follows by elimination of K between equations (V. 5. 1) and (V. 5. 2) that:

$$\log[wt. \% \underline{O}] = -\frac{8670}{T} + \log\left(\frac{p_{H_2O}}{p_{H_2}}\right) + 3.88 \quad (V. 5.3)$$

Variations in temperature and water vapour/hydrogen ratio will lead to additive errors in the value of log wt. % O and consequently in log K. The accuracy of oxygen analyses leads to a further additive error in the log wt. % O and log K terms. Error limits corresponding to the uncertainty in temperature and atmospheric control could be indicated on the temperature dependent plot of log K in Figure V-9. However, the experimental work was undertaken at several water vapour/ hydrogen ratios and, at specific temperatures, superimposed values of log K are obtained which cover a range of oxygen contents. The individual error limits due to the uncertainty in oxygen analysis cannot be clearly illustrated since the experimental points are too numerous.

However, the data may be classified on the basis of water vapour/hydrogen ratios and the errors related to log $\begin{bmatrix} \text{wt. }\% & \underline{O} \end{bmatrix}$ rather than log K. Equation (V. 5. 3) shows that a plot of log $\begin{bmatrix} \text{wt. }\% & \underline{O} \end{bmatrix}$ versus $\frac{1}{T}$ should give a series of parallel lines corresponding to specific water $\frac{1}{T}$ vapour/hydrogen ratios. These have the negative value of the gradient given by equation (V. 5. 1) which is graphically represented in Figure V-9.

Data from Tables V-8 to V-11 are plotted as log wt. % Oversus <u>1</u> in Figure V-10 where the points separate along five lines corresponding to distinct water vapour/hydrogen ratios. The line through the points represented by squares and indicated by the letter C in Figure V-10 has been omitted for the sake of clarity. The water vapour/hydrogen ratios are listed in Table V-21 together with the extent of variation resulting from fluctuations in atmospheric pressure. The corresponding variations in the log P_{H_2O} term amount to less than 0.01 logarithmic units for all ratios and are neglected in the calculation of the parallel lines in Figure V-10. These are derived by substitution in equation (V. 5. 3) of the appropriate water vapour/hydrogen ratio.

The error bands from each line in Figure V-10 represent the combined effects of $\frac{1}{2}$ 10C^o and variations in the water vapour/hydrogen. The error in the water vapour/hydrogen ratio is taken as $\frac{1}{2}$ 1 pct. for lines A and B where flow rates of 1 l. p. m. were used and $\frac{1}{2}$ 3 pct. for lines D and E, where several experiments were conducted at flow rates in the range 4 to 7 l. p. m.

Data from Tables V-8 to V-11 and V-14 to V-18 are plotted as log K' versus wt. pct. \underline{V} in Figures V-11 and V-12 with statistical information given in Table V-19.

The experimental errors associated with the pure iron studies also apply to the iron-vanadium work, with a further consideration of the effect of errors in vanadium analysis estimated at 0.005 wt. pct. \underline{V} . The maximum effect would be expected at the lowest melt temperature where the value of the interaction parameter is largest. The maximum effect of $\frac{1}{2}$ 0.005 wt. pct. \underline{V} on log K' is then 0.0014 logarithmic units which is negligible compared with other experimental errors and may be ignored for all temperatures.

Thus, the error bands represent the effect of $\frac{1}{2} 10C^{\circ}$ and $\frac{1}{2} 1$ pct variation in water vapour/hydrogen ratio. The scatter of points is seen to be greater at the lower temperatures where oxygen contents are lower. Error bars, which correspond to an uncertainty in analysis of 0.001 wt. pct. <u>O</u>, are shown on points which fall outside the error bands. Thus, the vast majority of points are accounted for by the three sources of experimental error mentioned previously.

CHAPTER V-6

DISCUSSION

V-6.1 Introduction

The effects of variations in experimental conditions on the behaviour of oxygen in liquid iron are discussed. The experimental data for iron-oxygen alloys are then considered in terms of the effect of oxygen on the activity coefficient of oxygen and the effect of temperature on the equilibrium constant K. The results are compared with those of previous workers and the discrepancies are accounted for by thermal diffusion in the water vapour/hydrogen atmospheres. However, this does not invalidate the results of these experiments since the main purpose in studying iron-oxygen alloys is to establish a set of data which will serve as a basis for comparing the effects of different amounts of vanadium on the activity of oxygen in liquid iron.

The effect of vanadium on the activity of oxygen in liquid iron alloys and the temperature dependence of this effect are evaluated. The data are represented in terms of free energy, enthalpy and entropy interaction parameters for molar and wt. pct. concentrations. The values are compared with data calculated from the results of previous workers for vanadium, chromium and aluminum-oxygen interactions in liquid iron and a correlation is tentatively made between the free energy and enthalpy interaction parameters at 1600°C. The excess partial

molar enthalpy and entropy of solution of oxygen in iron-vanadium alloys is calculated for the present work.

V-6.2 Experimental Considerations

V-6.2.1 Gas Melting Procedure

Levitated samples were melted in argon, helium or nitrogen as specified in the "Melt Technique" column of Tables V-8 to V-11 and V-14 to V-18. Particular reference to Tables V-9 and V-10 shows that the initial melting procedure has no significant effect on the final oxygen content of samples equilibrated at the same water vapour/hydrogen ratio. V-6.2.2 <u>Attainment of Equilibrium</u>

Armco iron samples were used for pure iron investigations. The untreated material contains 0.07 - 0.08 wt. pct. <u>O</u> and, after melting in an inert gas, the atmosphere was generally changed directly to a water vapour/hydrogen mixture of controlled composition. Table V-22 shows the extent of deoxidation during the initial stages of a typical experiment up to the point where equilibration at controlled temperature begins. By comparing the data with the equilibrium oxygen contents in Tables V-8 to V-11, it will be seen that equilibrium is approached from the excess oxygen side. In some experiments the samples were prereduced in hydrogen before equilibration so that equilibrium was approached from oxygen deficient conditions. The oxygen concentrations shown in Tables V-9 and V-10 represent the values obtained when equilibrium was approached from opposite directions and it is evident that there is no significant difference in the final oxygen levels. The effect of time at temperature on the oxygen content of the melt is shown for equilibration times of one to 15 minutes at 1685°C in Table V-6. From these data it was concluded that five minutes at temperature was ample time for equilibration.

V-6.2.3 Gas Flow Rate

Experiments conducted at flow rates of 0.5 to 4 l.p.m. (Table V-7) indicated that the final oxygen content of the sample, after five minutes at temperature, was independent of gas flow rate within this range. The majority of experiments were carried out at a flow rate of 1 l.p.m. of hydrogen.

V-6.2.4 Purity of Initial Iron Samples

Armco iron was used for most of the pure iron studies. Apart from its relatively high oxygen content, Armco iron contains other impurities listed in Table V-3. Several experiments were undertaken using high purity "Ferrovac E" and are referred to in Tables V-9 and V-10 under "Experimental Modifications". The equilibrium oxygen contents for identical conditions may be compared both for water vapour/ hydrogen and a mixture with argon. No significant difference was observed using the two types of iron. This indicates that the minor impurities in Armco iron had little effect on the equilibrium values. V-6. 2. 5 Casting Techniques

In the present work the sample on casting fell a distance of approximately 0.5 to 1" into a copper mould where it solidified within

one second. In order to check the suitability of this quenching technique for the present study, levitated Armco iron samples were dropped three inches into the mould which was located at the base level in the same reaction tube in order to simulate the conditions which existed in Shiraishi's (1966) experiments. Shiraishi's reaction tube incorporated separate side-arms for gas input and output, copper mould and optical system, conditions therefore more susceptible to atmospheric leaks and entrapped air pockets than the present technique. Both of these effects could give rise to higher oxygen contents in the experimental melts. These design conditions were simulated and several experiments were undertaken. They are referred to in Tables V-9 and V-10 under "Experimental Modifications" and the results are in good agreement with those obtained by the standard technique. Employing levitation melting in conjunction with the piston quench technique (Gomersall, 1967) which yields high quench rates estimated at 10⁶C⁰/sec., Larche (1968) has obtained reproducible values of log K at $1600^{\circ}C$ (0.73 ⁺ 0.05) which are in good agreement with the present work. The results which have been obtained by these various techniques serve to confirm the reliability of the quenching procedure used for the present study.

V-6.3 Iron-Oxygen Alloys

V-6.3.1 The Effect of Oxygen on the Activity Coefficient f

The values of K which are given in Tables V-8 to V-11 are calculated on the assumption of Henrian behaviour for dilute solutions of, in general, less than 0.035 wt. pct. \underline{O} in the molten iron. If there is a deviation from Henry's law, then it would be expected that the behaviour would be represented by equation (V. 3. 6) and (V. 3. 7).

A linear plot of log K' versus wt. pct. O would have values for gradient and intercept of $e_{O}^{(O)}$, and log K, respectively. If the activity coefficient, $f_{O}^{(O)}$, is unity, then the slope, $e_{O}^{(O)}$, is zero and log K is independent of oxygen content.

In Figures V-7 and V-8, log K is plotted as a function of oxygen content for temperatures between 1550° and 1750°C. At each temperature the points fall into two groups which correspond to the two saturator bath temperatures employed. Operation of the bath at approximately 30° and 42°C gave a factor of two difference in water vapour/ hydrogen ratios. The scatter in oxygen contents is partly due to slight variations in the water vapour/hydrogen ratio caused by changes in saturator temperature and atmospheric pressure. However, the scatter can be accounted for in terms of experimental errors, discussed previously in Section V-5.3, and this is reflected in the values of log K. An uncertainty of 10 ppm or $\frac{+}{-}$ 0.001 wt. pct. in the oxygen determination is particularly important at lower oxygen contents since log K'involves a log wt. % O term. The limits shown in Figures V-7 and V-8 represent the effect of this + 0.001 wt. pct. O on log K. At higher temperatures errors in oxygen determination become insignificant and errors in temperature control and measurement become important.

Although the data extend over only a small range of oxygen concentrations, it is evident that the effect of oxygen content on log K is insignificant compared with the spread of the data about the mean value of log K. Thus, for the oxygen levels involved in the present work, the activity coefficient, $f_{O}^{(O)}$, can be taken as unity without introducing appreciable error.

This is supported by the work of Matoba and Kuwana (1965) who determined the temperature dependence of the interaction parameter:

$$e_{O}^{(O)} = \frac{\partial \log f_{O}}{\partial [wt. \% O]} = -\frac{10130}{T} + 4.94$$

In this particular study the value of $e_{O}^{(O)}$ corresponds to the strongest deviation from Henry's law yet reported for the iron-oxygen system. The above equation predicts the values of log $f_{O}^{(O)}$ tabulated below:

Temp ^o C	wt. % 0	e ^(O)	$\log f_{O}^{(O)}$
1550	0.014	-0.62	-0.009
1700	0.090	-0.19	-0.017
1750	0.033	-0.07	-0.002

The values of temperature and oxygen concentrations selected above represent the experimental conditions which would be expected to have the greatest effect on log $f_{O}^{(O)}$. Hence the largest correction to log K through the log $f_{O}^{(O)}$ term at 1550° and 1750°C is less than the contribution from the estimated error in the oxygen analysis whilst at 1700°C an additional variation in temperature of \pm 5C° would more than compensate for this correction. V-6.3.2 The Effect of Temperature on Oxygen Solution in Liquid Iron

Experimental data for the effect of temperature on oxygen solubility in liquid iron were obtained for temperatures between 1450° and 1800°C. Using the conventional crucible technique, it has not been possible in the past to obtain data within the super-cooled region.

The free energy change for components in their standard states is given by the relationships:

$$\triangle F^{O} = -RT \ln K = -4.575 T \log K$$
 (V.6.1)

and
$$\triangle F^{\circ} = \triangle H^{\circ} - T \triangle S^{\circ}$$
 (V.6.2)

Eliminating $\triangle F^{O}$ from equations (V.6.1) and (V.6.2)

$$\log K = \frac{-\Delta H^{\circ}}{4.575 \text{ T}} + \frac{\Delta S^{\circ}}{4.575} \qquad (V.6.3)$$

If it is assumed that $\triangle H^{\circ}$ and $\triangle S^{\circ}$ are constant over the range of temperatures investigated, then a plot of log K versus $\frac{1}{T}$ should be linear with a gradient of $\frac{\triangle H^{\circ}}{4.575}$ and an intercept of $\frac{\triangle S^{\circ}}{4.575}$.

The data from Tables V-8 to V-11 are plotted as log K versus $\frac{1}{T}$ in figure V-9. The statistical considerations associated with this plot have been discussed previously in Section V-5.2. The equation of the line is:

$$\log K = \frac{8674 \left(\frac{1}{2} 263\right)}{T} - 3.876 \left(\frac{1}{2} 0.102\right) \qquad (V.6.4)$$

and the statistical details are given in Table V-13.

The standard free energy change for the reaction is given by:

$$\triangle F^{\circ} = -39680 + 17.73 \text{ T} \text{ cal/mole.}$$

V-6.3.3 Comparison with Previous Work

The temperature dependence of log K for the reaction

$$H_2 + O = H_2O$$

which is given in Figure V-9 is compared with the results of other workers in Figure V-13 and Table V-23. It will be seen that the present work covers a more extensive temperature range, apart from that of Shiraishi, than any of the previous studies. Values of log K are consistently higher at corresponding temperatures than previous work would indicate although at the upper temperature limit the extrapolated curves of some previous workers fall within the scatter band of the present study.

The previous data were obtained using conventional crucible techniques with the exception of the levitation studies of Shiraishi (1966), the results of which lie closest to the present work. However, a reexamination of Shiraishi's data indicated that there was considerable scatter associated with the experimental points. Rationalising these data in Figure V-14 by the same method of grouping according to water vapour/hydrogen ratios as in Figure V-10 indicates that approximately 30 pct. of his experimental points are misleading. (See Appendix V-1) Although the remaining points are in fairly close agreement with the present work, the actual values of log K cannot be considered too significant in view of the lack of data.

Although the experimental errors account for the scatter of the date, they do not account for the relatively high values obtained for log K. At 1600°C the difference in log K amounts to about 0.2 logarithmic

units. To account for this difference in terms of the errors discussed previously, the temperature readings would require to be in error by approximately 70C^o, or the water vapour/hydrogen ratio over-estimated by 60 pct., or the oxygen determinations low by 60 pct. In view of the preliminary investigations and previous discussion of errors, the possibility of errors of this magnitude from these sources may be justifiably discounted.

One factor, which has been the source of error in a number of gas-metal studies in the past, is worthy of consideration in the present context. When a gas mixture is contained in a heated chamber where there is a temperature gradient, the heavier gas tends to diffuse to the cold zone. This phenomenon, termed "thermal diffusion", may have a serious effect on the composition of controlled gas mixtures.

The degree of separation, which is a measure of thermal diffusion, increases with increasing difference in molecular weights and with increasing temperature difference between the hot and cold zones. (Chapman, 1916). Alcock (1958) demonstrated that thermal diffusion also decreases with increasing flow rate and Richardson and Alcock (1951) concluded that if changing the flow rate by a factor of four does not affect the results, then thermal diffusion may be neglected. Gillespie (1939) has shown that thermal diffusion in a mixture of two gases is inversely proportional to the square root of the mean molecular weight. Dastur and Chipman (1948) added argon to the mixture in order to increase the mean molecular weight and thus reduce thermal

diffusion effects.

In the case of a molten droplet which is levitated within a cold reaction tube in a flowing water vapour/hydrogen gas mixture, sharp temperature gradients are set up within the gas phase which could give rise to thermal diffusion and consequently an evaluation of this effect is essential.

If thermal diffusion effects were present, the gaseous mixture at the droplet interface would tend to be hydrogen rich in which case the water vapour/hydrogen ratio would be smaller than that measured. This would result in equilibrium oxygen contents lower than those expected and could account for higher values of log K. On the other hand, the difference in log K values is more marked at lower temperatures whereas the effects of thermal diffusion are expected to be most severe at higher temperatures. However, the comparison at higher temperatures (1800°C) is with data extrapolated from low temperatures and there may be some error introduced in extrapolation. It should be noted that in the present work, an eight-fold change in gas flow rate did not change the results significantly (Table V-7).

The effects of thermal diffusion may be reduced by addition of a heavy gas to the mixture. In the present work several experiments were carried out under an atmosphere of argon/water vapour/hydrogen using an optimum argon/hydrogen ratio of 4:1 and the results are listed in Table V-10. Unfortunately, temperatures below 1700^oC could not be obtained since the heat transfer efficiency of the gas mixture is reduced considerably by addition of argon, which has a lower thermal conductivity than hydrogen. (The value for argon is 3.89×10^{-5} and hydrogen 3.27×10^{-4} cal./C^o/cm./sec. at 0^oC.)

Table V-10 shows that the mean value for log K of 0.464 for experiments carried out at 1700°C in argon mixtures at flow rates in the range 4 to 7 l. p. m. is less than the mean value of 0.530 for the remainder. If the data are plotted as shown in Figure V-15, then the true value for the equilibrium constant should correspond to the intercept value obtained when the mean molecular weight of the gas mixture is infinitely great (Dastur and Chipman, 1948). At 1700°C, this procedure yields a value for log K of 0.430. The value for log K obtained under these conditions, which were chosen to minimise thermal diffusion, lies within the confidence limits of much of the earlier data when these are extrapolated to higher temperatures. (See footnote.) This, it may be noted is at the upper temperature limit where the effects of thermal diffusion should be most marked.

Toop and Richardson (1967) have recently published data for the solubility of oxygen in liquid nickel. Molten levitated droplets were equilibrated with CO/CO_2 gas mixtures of controlled composition, quenched and analysed. These gas mixtures would not be as susceptible to thermal

(Matoba and Kuwana, 1965; Floridis and Chipman, 1958; and Dastur and Chipman, 1949.)

diffusion effects as those used in the present study and, in fact, good agreement was observed between the results from levitation experiments and those from conventional crucible work. Larche (1968) has conducted some similar experiments with molten iron droplets and CO/CO_2 gas mixtures and again the data are in good agreement with those obtained from crucible studies.

The effects of thermal diffusion are amply illustrated in Table V-24 which gives data for levitation and crucible experiments in CO/CO_2 , H_2/H_2O and H_2/H_2S gas mixtures. In the case of solubility measurements of sulphur in liquid iron droplets where H_2/H_2S gas mixtures were used to control the sulphur potential of the system, (Sunderland, 1967) the effects of thermal diffusion were particularly pronounced. On the basis of these observations and the results obtained during the present study with $H_2/H_2O/Ar$ mixtures, it is considered that the oxygen content of droplets exposed to H_2/H_2O mixtures alone will be influenced by thermal diffusion effects. For this reason, the data obtained for the solubility of oxygen in liquid iron should be regarded, not as absolute values, but rather as a basis for determining the change in oxygen concentrations of melts containing different amounts of vanadium.

From the above comments, it will be evident that where the determination of thermodynamic functions requires an accurate knowledge of the water vapour/hydrogen ratio, the use of a levitation melting technique could produce misleading results. In the present work, the primary aim was the establishment of a base line which would then serve as a reference state for determining the relative effects of vanadium additions on the oxygen content of liquid iron. The use of H_2/H_2O rather than CO/CO_2 gas mixtures was particularly suitable since temperature control is much easier and the interaction effects can be studied at lower temperatures where the atomic associations are more pronounced.

V-6.4 <u>Iron-Vanadium Oxygen Alloys</u> V-6.4.1 The Interaction Parameter, e^(V)_O

Figures V-11 and V-12 show that, at constant temperature, vanadium additions decrease the value of log K' in which case it is clear from equation (V. 3. 3) that, under a fixed oxygen potential, the equilibrium oxygen content of the metal is increased. Consequently, the activity coefficient of oxygen, f_O , must decrease with increasing vanadium content. From equation (V. 3. 11) it will be seen that the slopes of the lines in Figures V-11 and V-12 correspond to the values of the interaction parameter, $e_O^{(V)}$, at particular temperatures. Details of the statistically determined equations are given in Table V-19.

The value of $e_{O}^{(V)}$ at 1600°C obtained in the present work is compared with those of previous workers in the following table:

e ^(V) O	Reference
-0.24	Present work
-0.27	Chipman and Dastur (1951)
-0.365	Narita (1958)
-0.32	Sano and Sakao (1964)
-0.13	Fischer and Janke (1966)
-0.290	Pargeter (1967)
-0.11	Schenck and Steinmetz (1967)

The previous investigators used conventional crucible techniques for their experiments, except for Fischer and Janke (1966) who employed an electrochemical technique and Sano and Sakao (1964) who calculated a corrected value from the data of Narita (1958). The value of $e_{O}^{(V)}$ for the present work is in good agreement with that obtained by Chipman and Dastur (1951) and Pargeter (1967).

The effect of vanadium on the activity coefficient, $f_O^{(V)}$, is shown in Figure V-16 where the curves representing equation (V. 3. 10) are drawn with slopes corresponding to the values of $e_O^{(V)}$ given in Table V-19. This indicates that dilute solutions of oxygen in ironvanadium alloys do not exhibit Henrian behaviour since a change in log f_O is associated with an excess free energy of solution. The interaction parameter is negative and this implies that oxygen has a greater affinity for vanadium than for iron and that there is a tendency for short range ordering in the solution.

V-6.4.2 The Interaction Parameter $\epsilon_{0}^{(V)}$

Values of the interaction parameter, $e_{O}^{(V)}$, are generally obtained experimentally on the wt. percent scale with the reference state being the infinitely dilute solution. The corresponding value of the interaction parameter, $\epsilon_{O}^{(V)}$, which is based on the mole fraction scale, may be calculated from:

$$\epsilon_{O}^{(V)} = \frac{230}{M_{Fe}} \frac{M_{V}}{M_{Fe}} = e_{O}^{(V)} + \frac{M_{Fe} - M_{V}}{M_{Fe}}$$
 (V.6.5)

Calculated values of $\epsilon_{O}^{(V)}$ are given in Table V-25.

The value of $\epsilon_{O}^{(V)}$ at 1600°C is compared with those of previous workers, which were also calculated from corresponding values of $\epsilon_{O}^{(V)}$, in the following table:

€ ^(V)	Reference	
- 51	Present work	
- 57	Chipman and Dastur (1951)	
-77	Narita (1958)	
-67	Sano and Sakao (1964)	
-27	Fischer and Janke (1966)	
-61	Pargeter (1967)	
-23	Schenck and Steinmetz (1967)	

The correction term in equation (V. 6. 5) has not been included in the 'calculation since its value of 0.09 representing a 0.2 pct. difference in $\mathbf{e}_{O}^{(V)}$ is negligible compared with the statistical error on the experimental values.

For purposes of comparison, the effect of vanadium, chromium, silicon and aluminum on the solubility of oxygen in liquid iron at 1600°C

are given below:

x	e ^(X) O	ε ^(X)	Reference
V	- 0.24	- 51	Present work
Cr	- 0.064	- 13.7	Turkdogan (1954)
Si	- 0.16	- 18.5	Chipman and Pillay (1961)
A1	- 1.07	- 119.0	d'Entremont et al (1963)
A1	- 12.0	- 1340	Gokcen and Chipman (1953)
A1	- 5.4	- 620	McLean and Bell (1965)

These interaction effects are of particular interest with regard to deoxidation and reoxidation in steelmaking.

V-6.4.3 The Effect of Oxygen on the Activity Coefficient of Vanadium

From Wagner's reciprocity relationship:

$$\boldsymbol{\varepsilon}_{O}^{(\mathrm{V})} = \boldsymbol{\varepsilon}_{V}^{(O)} \qquad (\mathrm{V.6.6})$$

and

$$\varepsilon_{V}^{(O)} = 230. \frac{M_{V}}{M_{Fe}} \cdot e_{V}^{(O)} + \frac{M_{Fe} - M_{O}}{M_{Fe}}$$
 (V.6.7)

It follows from equations (V. 6. 6) and (V. 6. 7) that values may be obtained for the interaction parameter $e_V^{(O)}$, using the values of $\varepsilon_O^{(V)}$ given in Table V-25, and these are listed in the same table. At 1600°C values of $\varepsilon_V^{(O)} = -51.2$ and $e_V^{(O)} = -0.788$ were obtained. In this case, the correction factor in equation (V. 6. 7) with a value of 0. 7 has been included in the calculation. The values of $e_V^{(O)}$ at 1600°C are compared below:

e (O) V		Reference	
- 0.78		Present work	
- 0.88		Chipman and Dastur (1951)	
- 1.18		Narita (1958)	
- 1.03		Sano and Sakao (1964)	
- 0.42		Fischer and Janke (1966)	
- 0.94	•	Pargeter (1967)	
- 0.36		Schenck and Steinmetz (1967)

V-6.4.4 The Effect of Temperature on the Interaction Parameter e'_{O}

The effects of vanadium on the activity coefficient of oxygen for temperatures between 1550° and 1750°C are shown in Figure V-16. As the temperature increases, the gradient of the curve becomes less negative and, consequently, the interaction parameter becomes less negative. This implies that the solution is becoming more Henrian in behaviour at higher temperatures.

The temperature dependence of the free energy interaction parameter, $e_{O}^{(V)}$, is given by:

$$e_{O}^{(V)} = \frac{h_{O}^{(V)}}{4.575 \text{ T}} - \frac{s_{O}^{(V)}}{4.575}$$
 (V.6.8)

where $h_{O}^{(V)}$ and $s_{O}^{(V)}$ are the enthalpy and entropy interaction parameters, respectively. These are defined as:

$$h_{O}^{(V)} = \left(\underbrace{\partial \#}_{Wt. \% \underline{V}}^{E} \right); s_{O}^{(V)} = \left(\underbrace{\partial & \underbrace{\partial & e}_{O}}_{Wt. \% \underline{V}} \right)_{\text{%Fe} \rightarrow 100} (V. 6. 9)$$

where $\nexists \stackrel{E}{O}$ and $\aleph \stackrel{E}{O}$ are excess partial molar enthalpy and entropy for solution of oxygen in the alloy. For dilute solutions, these parameters

are considered to be independent of temperature within the range under consideration.

Data from Table V-19 are plotted as $e_{O}^{(V)}$ versus $\frac{1}{T}$ in Figure V-17 and show a linear dependence. The equation of this line was calculated by the method of least squares and the statistical details are given in Table V-26. The line is represented by the relationship:

$$e_{O}^{(V)} = -\frac{1740}{T} + 0.689$$
 (V. 6.10)

It follows from equations (V. 3. 10) and (V. 6. 10) that the temperature and concentration dependence of the activity coefficient of oxygen, f_O , may be expressed on one equation:

$$\log f_{O} = \left(-\frac{1740}{T} + 0.689\right) \cdot \left[\text{wt. \% } \underline{V}\right] \quad (V. 6.11)$$

For the benefit of the reader, values of the activity coefficient of oxygen have been calculated for the temperature range 1550° to 1750°C and the composition range zero to 1.0 wt. pct. vanadium. These values are listed in Table V-27.

The gradient and intercept of equation (V. 6. 10) correspond to the terms $\frac{h_{O}^{(V)}}{4.575}$ and $\frac{s_{O}^{(V)}}{4.575}$, respectively, in equation (V. 6. 8).

Thus the following values for the enthalpy and entropy parameters have been obtained:

$$h_{O}^{(V)} = -7.96 \text{ K cal. /gm. atom } O/\text{wt. } \% V$$
 (V. 6.12)

$$s_{O}^{(V)} = -3.15 \text{ cal/gm. atom } O/^{\circ} \text{K/wt. } \% V$$
 (V. 6.13)

The non-zero value of the entropy interaction parameter indicated that

the iron-vanadium-oxygen solutions do not exhibit regular solution behaviour.

Since the enthalpy and entropy interaction parameters are constant for the range of concentrations investigated, it follows from equation (V. 6. 9) that the excess partial molar enthalpy and entropy of solution are given by:

and

for which the calculated values are:

$$\frac{E}{O} = -7960 \left[(wt. \% \underline{V}] (cal/gm. atom) (V. 6. 16) \right]$$

and
$$\$ = -3.15 \ [wt. \% V] (cal/gm. atom/°K) (V. 6.17)$$

 $\mathcal{S}_{O}^{E} = s_{O}^{(V)} \cdot \left[\text{wt. } \% \underline{V} \right]$

Equations (V. 6. 16) and (V. 6. 17) are illustrated in Figure V-18. As the vanadium content of the solution increases, the excess entropy becomes more negative which implies that there is greater ordering in the alloy. This again suggests that the greater affinity of oxygen for vanadium rather than iron increases short range ordering in the alloy.

The temperature dependence of the free energy interaction parameter $e_{O}^{(V)}$ calculated from the data of Narita (1958) assuming $e_{O}^{(O)} = 0$, is given by equation (V. 3. 12). Sano and Sakao (1964) reported a value which was corrected for a non-zero value of $e_{O}^{(O)}$ and is given by equation (V. 3. 13). The values calculated for the enthalpy and entropy interaction parameters are compared below:

(V.6.15)

h ^(V) O	s (V) O	
cal./gm. atom O/wt. % V	cal./gm. atom O/ ^O K/wt. % V	Reference
- 7960	- 3.15	Present work
-28500	-13.55	Narita (1958)
-11440	- 4.62	Sano & Sakao (1964)

It will be seen that the values obtained in the present work are in reasonable agreement with those of Sano and Sakao (1964).

The effect of another deoxidant, chromium, on the activity of oxygen in liquid iron was investigated by Kojima and Sano (1965). They reported that the temperature dependence of the interaction parameter $e_{O}^{(Cr)}$ was expressed by the relationship:

 $e \frac{(Cr)}{O} = \frac{-369}{T} + 0.137$

An estimate of the temperature dependence of aluminum-oxygen interactions has also been made from the results of several investigators and the free energy interaction parameters may be represented by the following expressions:

Range ^o C	Reference
1760-1866	Gokcen and Chipman (1953)
1740-1910	d'Entremont et al (1963)
1723-1823	McLean and Bell (1965)
	Range ^o C 1760-1866 1740-1910 1723-1823

The enthalpy and entropy interaction parameters for the effect of chromium and aluminum on oxygen dissolved in liquid iron are compared below with the values obtained for vanadium-oxygen interactions in the present work:

х.	h ^(X) O cal./gm. atom <u>O</u> / wt. % X	s (X) O cal./gm. atom O/ °K/wt. % X	Reference
v	- 7960	- 3.15	Present work
Cr	- 1690	- 0. 627	Kojima and Sano (1965)
A1	- 18900	- 5.18	d'Entremont et al (1963)
A1	- 250,000	- 185	Gokcen and Chipman (1953)
A1	-269,000	- 119	McLean and Bell (1965)

V-6.4.5 The Enthalpy and Entropy Parameters, $\eta_{O}^{(V)}$ and $\sigma_{O}^{(V)}$

The parameters $\eta_{O}^{(V)}$ and $\sigma_{O}^{(V)}$ are based on the mole fraction scale. They may be calculated from the corresponding parameters $h_{O}^{(V)}$ and $s_{O}^{(V)}$; equations (V. 2. 30) and (V. 2. 31) give the relationships:

$$\eta_{O}^{(V)} = 100. \frac{M_{V}}{M_{Fe}} \cdot h_{O}^{(V)}$$
 (V. 6. 18)

$$O''_{O} = 100. \frac{M_{V}}{M_{Fe}} \cdot s_{O}^{(V)} - R. \frac{M_{Fe} - M_{V}}{M_{Fe}}$$
 (V. 6. 19)

Substituting equation (V. 6. 12) in (V. 6. 18) and (V. 6. 13) in (V. 6. 19) gives values of:

$$\eta \stackrel{(V)}{O} = -726 \text{ K cal/gm. atom } \underline{O}/\text{mole fraction } \underline{V}$$
 (V. 6. 20)
 $O' \stackrel{(V)}{O} = -287 \text{ cal/gm. atom } \underline{O}/^{\circ} \text{K/mole fraction } \underline{V}$ (V. 6. 21)

These values are compared with previous work on vanadium, chromium and aluminum interactions with oxygen in the following table:

x	η (X) K cal./gm. atom O/ mole fraction X	O ^(X) O cal./gm. atom O/ °K/mole fraction X	Reference
v '	-726	-287	Present work
v	-2600	-1240	Narita (1958)
v	-1045	-506	Sano and Sakao (1964)
Cr	-158	-584	Kojima and Sano (1965)
A1	-915	-250	d'Entremont et al (1963)
Al	-21800	-8950	Gokcen and Chipman (1953)
A1	-13500	-5950	McLean and Bell (1965)

V-6.4.6 The Characteristic Temperature

The excess free energy of a solution exhibiting Raoultian behaviour is zero. Since the interaction parameter $\mathcal{E}_{O}^{(V)}$ is a measure of the excess free energy, its value would also be zero. Equation (V. 2. 33) gives a zero value of $\mathcal{E}_{O}^{(V)}$ at a temperature, \mathcal{T} , where:

$$\mathcal{C} = \frac{\eta_{0}^{(V)}}{\sigma_{0}^{(V)}}$$
(V. 6. 22)

Substituting values from equations (V. 6.20) and (V. 6.21) in (V. 6.22)

ζ ∼ 2500°K (2527°K),

and is the linearly extrapolated temperature at which the solution becomes ideal.

The characteristic temperature obtained in the present work is compared with those calculated from the data of previous workers for vanadium, chromium and aluminum interactions with oxygen.

	6	옷이야는 것같아. 그는 바람들은 백만 것같아 ?
System	(°K)	Reference
V-0	2500	Present work
V-0	2500	Narita (1958)
V-0	2100	Sano and Sakao (1964)
Cr-0	2700	Kojima and Sano (1965)
A1-0	3800	d'Entremont et al (1963)
A1-0	2400	Gokcen and Chipman (1953)
A1 -0	2300	McLean and Bell (1965)

These values are in agreement with the value of γ for metallic solutions which was suggested by Lupis and Elliott (Jan., 1966) to be approximately 3000° \pm 1000°K.

A useful empirical correlation between enthalpy and entropy interaction parameters was found by Chipman and Corrigan (1965) for the iron-nitrogen-j system and by Chipman (1966) for the iron-hydrogen-j system. This provided a convenient method for estimating the solubilities at different temperatures from the solubility at 1600°C. A similar correlation has not yet been made for the iron-oxygen-j system for which few temperature dependent data are available. The values at 1600°C of the free energy and enthalpy interaction parameters presented below have been plotted as shown in Figures V-19 and V-20:

		, (X)		m (X)	이 집에 관계하는 것 같아요. 것이 같아.
		^h O		10	
	(X)	K cal. / gm.	(X)	Kcal./gm.	
	e O	atom O/	EO	atom O/mole	
Х	(1600°C)	wt. % X	(1600°C)	fraction X	Reference
v	-0.24	- 7.96	-51	- 726	Present work
v	-0.365	-28.50	-77	- 2600	Narita (1958)
v	-0.32	-11.44	-67	- 1045	Sano & Sakao (1964)
Cr	-0.060	- 1.69	-12.9	- 158	Kojima & Sano (1965)
A1	-1.08	-18.9	-119.0	- 915	d'Entremont et al (1963)
A1	-12.0	-450	-1340	-21800	Gikcen & Chipman (1953)
A1	-5.4	-269	-620	-13500	McLean & Bell (1965)

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The extremely high values obtained by McLean and Bell (1965) and Gokcen and Chipman (1953) have been excluded in order to clearly present the smaller values on a large scale. However, the direction in which their data are located with respect to the origin is indicated. A line has been tentatively drawn in each graph which best represents the available data and ultimately passes through the value for Gokcen and Chipmans' work. The values obtained in the present investigation and by Sano and Sakao (1964) for vanadium-oxygen interactions and also Kojima and Sanos' data for chromium-oxygen interactions lie close to this line. It will be seen that both lines pass through the origin in agreement with the findings of Chipman and Corrigan (1965) and Chipman (1966) for solute-nitrogen and solute-hydrogen interactions, respectively. However, it would be unwise to place excessive emphasis on the use of these curves as a means of estimating the value of enthalpy parameters for other solute-oxygen interactions in liquid iron at the present time.

CHAPTER V-7

CONCLUDING REMARKS

V-7.1 Summary

The behaviour of oxygen dissolved in iron and iron-vanadium alloys has been investigated by the technique of levitating molten iron or iron alloy droplets in controlled water vapour/hydrogen atmospheres.

The effect of temperature on the concentration of oxygen in liquid iron has been evaluated for the temperature range 1450° to 1800°C, the primary aim being the establishment of a base line which would then serve as a reference state for determining the relative effects of vanadium additions on the activity coefficient of oxygen in liquid iron-vanadium alloys.

The absolute values for the iron-oxygen data were found to differ considerably from the results of previous workers who employed conventional crucible techniques. This discrepancy has been accounted for by thermal diffusion effects in the water vapour/hydrogen atmospheres under levitation conditions. It must therefore be emphasised that caution is required where levitation melting is employed to obtain data for equilibrium concentrations and heats of reaction which require an accurate knowledge of the gas composition. This particularly applies when the components in the gas mixture have very different molecular weights, e.g. H_2/H_2O and H_2/H_2S . The present work shows

that even at high gas flow rates, thermal diffusion effects are still present since an eight-fold change in flow rate did not indicate any significant variation in the results.

The data obtained for the solution of oxygen in liquid iron in the present work should, therefore, be regarded not as absolute values but rather as a basis for determining the change in oxygen concentration of melts containing different amounts of vanadium.

The effect of vanadium on the activity of oxygen in liquid iron-vanadium alloys has been calculated in terms of the free energy interaction parameters $e_{O}^{(V)}$ and $\mathcal{E}_{O}^{(V)}$ for concentrations in the range 0.1 to 1.0 wt. pct. vanadium and at temperatures 1550° to 1750°C at 50C° intervals. The value for $e_{O}^{(V)}$ of -0.24 at 1600°C is in satisfactory agreement with that of Chipman and Dastur (1951).

The temperature dependence of the free energy interaction parameters for the temperature range 1550° to 1750°C has been expressed in terms of the enthalpy and entropy interaction parameters, the values of which are given below:

$$h_{O}^{(V)} = -7.96 \text{ K cal. /gm. atom } \underline{O}/\text{wt. } \% \underline{V}$$

$$s_{O}^{(V)} = -3.15 \text{ cal. /gm. atom } \underline{O}/^{\circ}\text{K/wt. } \% \underline{V}$$

$$\eta_{O}^{(V)} = -726 \text{ K cal. /gm. atom } \underline{O}/\text{mole fraction } \underline{V}$$

$$\sigma_{O}^{(V)} = -287 \text{ cal. /gm. atom } \underline{O}/^{\circ}\text{K/mole fraction } \underline{V}$$

There values are compared with those calculated from the data of previous workers and show satisfactory agreement with the values of Sano and Sakao (1964).

A correlation is tentatively made between the free energy and enthalpy interaction parameters at 1600° C using available temperature dependent data for solute-oxygen interactions in liquid iron. Although this correlation could provide a means of estimating concentrations of oxygen at different temperatures in solutions for which data are unavailable, it would be unwise at this stage to place too much emphasis on such values in view of the lack of data at temperatures other than 1600° C.

For measurement of relative effects, the levitation technique is excellent since there is neither crucible reaction nor contamination and, consequently, the temperature range may be extended without risk of error from this source. Furthermore, equilibrium is rapidly approached and errors in chemical analysis due to segregation in the metal do not arise since the entire sample is used for analysis.

V-7.2 Suggestions for Further Work

In the present investigation, the oxygen potential of the water vapour/hydrogen atmosphere was controlled at a sufficiently low level that the formation of oxides was prevented. When saturation of the melt and subsequent formation of oxides occurred, temperature control was impossible and there was a rapid decrease in levitation power resulting in the loss of the levitated sample. Thus the application

of the levitation technique to an investigation of the deoxidation reactions in saturated iron-vanadium-oxygen systems would not appear to be feasible. It is therefore suggested that the present work should be extended to include an investigation of the deoxidation reactions and their temperature dependence by means of a conventional crucible technique.

Although gas/metal studies employing the levitation technique may be susceptible to errors arising from thermal diffusion effects when certain gas mixtures are used, the method is ideally suited for the evaluation of relative effects. It is suggested that the effect of chromium on the activity of oxygen in iron-chromium alloys, the temperature dependence and the behaviour up to relatively high chromium levels could be determined successfully by this procedure. This work could also be extended to include oxygen activity studies in multi-component systems.

PART 2

THE KINETICS OF PHOSPHORUS

TRANSFER IN SLAG/METAL SYSTEMS

SECTION 2 R

THE KINETICS OF PHOSPHORUS TRANSFER

IN IRONMAKING SLAG/METAL SYSTEMS

CHAPTER R-1

INTRODUCTION

In ironmaking, the blast furnace burden essentially consists of iron ore, coke and limestone. The ore is reduced to metallic iron by carbon monoxide and coke while the gangue, coke ash and sulphur are fluxed by the limestone to form low melting point acid slag. Unfortunately, some iron oxides contain appreciable amounts of P_2O_5 which is readily reduced under the conditions existing within the blast furnace. Consequently, virtually all the phosphorus in the burden is transferred to the iron and its removal can only be achieved by oxidation during steelmaking.

Since phosphorus is an impurity in hot metal which cannot be eliminated in the production of iron, the purpose of the present investigation of the kinetics of phosphorus transfer in ironmaking slag/ metal systems is of a purely academic nature. Synthetic blast furnace slags containing P_2O_5 were reacted with carbon saturated iron under laboratory conditions. A review of the pertinent literature has been made and experimental details of the apparatus and techniques are described. The results are considered in terms of mass transfer in the metal phase and chemical reaction at the slag/metal interface and indicate that chemical reaction controls the rate of phosphorus transfer.

CHAPTER R-2

LITERATURE REVIEW

There appears to be no published work involving the kinetics of phosphorus transfer in ironmaking slag/metal systems. This is in complete contrast with the reactions of sulphur and silicon in ironmaking for which a considerable amount of kinetic data are available. The reasons for this lack of data are possibly the purely academic aspect of the problem and probably the extreme difficulty in developing satisfactory experimental techniques for phosphorus transfer studies.

CHAPTER R-3

EXPERIMENTAL CONSIDERATIONS

R-3.1 Introduction

It was originally intended that both iron and steelmaking experiments would be carried out in a carbon resistance furnace. However, it was found that oxide crucibles could not withstand the highly corrosive iron oxide bearing steelmaking slags and an induction melting technique was used for these investigations (Section S.). Consequently, the apparatus and techniques which are described below apply only to ironmaking systems.

R-3.2 Apparatus

R-3.2.1 The Carbon Resistance Furnace

The furnace was operated from a three-phase power supply. The resistance element consisted of six carbon rods, 0.5" diameter x 9" in length, arranged in a cage construction as shown in Figure R-1. Two rods were located in each of the three segments of the carbon base and the power input was supplied through three water-cooled copper conductors which were screwed into the base. The circuit was completed in a three-phase "star" arrangement by the graphite top ring. This design was advantageous insofar as return conducting leads were not required and defective elements were easily replaced.
The furnace design is shown in Figure R-2. The héating element (A) was contained in a vacuum-tight steel casing (B), 17" diameter x 0.5" wall thickness x 20" in length. The furnace lining (C), consisted of refractory insulating brick which was faced with magnesite cement. Under operating conditions, the heating element was situated within a graphite cylinder (D), 6" O.D. x 0.5" wall thickness x 10.5" in length, which was electrically insulated from the carbon base blocks (E) by a ring, 0.5" thick, cut from refractory insulating brick. This arrangement reduced temperature fluctuations due to gas circulation and, at the same time, acted as a radiation shield.

The furnace body was surmounted by an "air-lock" in order that charging and sampling could be effected without admitting air into the furnace. The "air-lock" consisted of a valve chamber (F) and a charging chamber (G). The valve chamber was of rectangular steel construction inside which a sliding toggle valve could be screw-tightened into position in order to isolate the main furnace body from the charging chamber. The latter consisted of a steel cylinder, 3" O. D. x 3/8" wall thickness x 14" in length.

The furnace was designed for easy dismantling. The base and top plates, (H) and (J), were bolted to flanges welded onto the furnace casing and "O" rings were employed to provide gas-tight seals. The top plate of the valve chamber (K) which was welded to the charging chamber (G) was also bolted and made gas-tight by means of a rubber gasket. The upper face of the toggle valve (L) was furnished with an

"O" ring seal for the same reason.

A series of 0.25" diameter copper tubes, connected by "Tygon" tubing, were soldered to the equipment as close as possible to the rubber seals in order to prevent over-heating. Two separate supplies of cooling water were provided for the top and bottom furnace plates. The exit ends were attached to water pressure micro-switches which were connected in series with the temperature controller so that, in case of water supply failure, the power was automatically switched off.

The furnace was equipped with two horizontal tubes (M) which had been drilled through the steel casing and refractory lining. These were aligned between the resistance elements at the height of the constant temperature zone and at an angle of approximately 120° to each other. The tubes were fitted with closed-ended recrystallised alumina sheaths of 5/16" and 7/8" O.D. for thermocouple protection and optical pyrometer sighting, respectively. The sheaths extended into the centre of the furnace and were situated in contact with the crucible. Gas tight connections were made with the furnace casing by means of a Swagelok fitting with a Teflon ferrule for the thermocouple sheath and an "O" ring seal for the sighting tube.

R-3.2.2 The Power Supply

The furnace elements and associated electrical equipment were designed for an operating capacity of 10 KVA. The power supply was

connected through a mercury-relay switch to a 13.3 KVA Váriac variable transformer and matching 20:1 step-down transformer, all of which were designed for three-phase operation. For a 10 KVA load, a minimum voltage input on the transformer primary of 230 v., phase to phase, drew a current of roughly 30 amps. with an output on the secondary of 600 amps. at 11.6 v. phase to phase. The low voltage, high amperage current gave a greater heating efficiency for the furnace elements.

The three output power leads from the transformer were made from heavy flexible copper braid in order to carry the heavy current without significant heat losses and for the convenience of furnace assembly. The ends were permanently soldered to copper connecting lugs, 3" in length x 2" in width x 1/4" in thickness, which were bolted at one end to the transformer output terminals.

The water-cooled, threaded copper leads projecting down from the furnace bottom plate were supported on flanges (Figure R-1) which were provided with gas-tight "O" ring seals. A Micarta ring and knurled nut electrically insulated and firmly positioned each lead in the bottom plate (Figure R-3). The connecting lug for the flexible braid was then placed in position and held by a second hand-tightened knurled nut. R-3. 2. 3 The Gas Supply

The furnace was equipped with a series of tubes (T), shown in Figure R-2, which were inter-connected by five Edwards 0.5" "Speedivac"

valves (V). Separate connections were made with a gas supply, gas exhaust and vacuum pump. The arrangement permitted the evacuation or gas flushing of the furnace and isolated charging chamber.

The carbon heating elements were maintained in an inert atmosphere of nitrogen to prevent oxidation. The nitrogen was first passed through an auxiliary resistance furnace containing heated copper turnings at 600°C in order to remove any oxygen. It was then circulated through the carbon resistance furnace after which it was bubbled through a flask containing dibutyl pthalate and finally exhausted into the atmosphere. This eliminated back-diffusion of air into the furnace, minimised back-diffusion of vapour since dibutyl pthalate has a low vapour pressure at room temperature, and provided an instant check on the circulation of gas through the furnace.

A general view of the furnace and auxiliary equipment is shown in Figure R-4.

R-3.3 Experimental Techniques

R-3.3.1 Temperature Control and Measurement

Initially, temperature measurement was effected by the use of a Type R Pt/Pt - 13 pct. Rh thermocouple, the hot junction of which was protected by the alumina thermocouple sheath located in the hot zone of the furnace. The thermocouple was connected by means of Type SX copper-alloy 11 compensating leads to a Honeywell "Pyro-O-Vane" millivoltmeter indicator and proportional controller, which was adjusted to operate on a three-second cycle. The output signal from the controller actuates the three-phase mercury relay switch thus controlling the input to the furnace. The accuracy of temperature control was found to be within \pm 5C° at 1600°C. The controller was equipped with a safety device which drives the indicator above the controlled set point in case of a break in the thermocouple circuit and automatically switches off the power supply. Sustained use of the thermocouple at steelmaking temperatures lead to its rapid deterioration resulting in frequent breakdowns of the power supply.

It was therefore found expedient to use an optical pyrometer for temperature control. A Honeywell "Radiamatic" pyrometer was used in conjunction with a matched "Pyro-O-Vane" proportional controller and temperature indicator and the control output signal operated the mercury relay switch. The "Radiamatic" contains a lens which is sighted on the heat source in order to focus the radiant energy on a thermopile and the resulting e.m.f. output is measured by the millivoltmeter indicator. The pyrometer was sighted on the closed end of the 7/8" O.D. alumina tube situated in the hot zone of the furnace. The arrangement at the thermocouple and optical pyrometer ports is seen in Figure R-5.

Temperature control was found to be as accurate as was attained using the thermocouple technique. However, the pyrometer indicator could not be directly calibrated over a range of temperature since the sighting geometry used in these experiments did not meet with the optimum specifications, which required a tube of larger diameter than the 5/8" I. D. tube actually used. Control at a specific temperature was effected by gradual adjustment of the control setting until the required temperature was measured by the thermocouple located in the other port.

Temperature measurement was always carried out with a thermocouple which had been previously checked against a standardised couple. Normally the thermocouple was withdrawn from the furnace hot zone in order to increase its working life and temperature checks were made only when necessary.

R-3. 3. 2 Temperature Profile of the Furnace

The temperature profile was obtained in the following manner. The optical pyrometer was used for temperature control and a "dummy" crucible, consisting of a graphite block was positioned so as to simulate experimental conditions. An 18" alumina thermocouple sheath, which was supported by a gas-tight Swagelok fitting in the furnace bottom plate, extended up the centre of the furnace to the heating element top ring. The thermocouple was moved along the sheath at 0.5" intervals and the corresponding temperature was measured after sufficient time had been allowed for temperature equilibration.

The results, which are plotted in Figure R-6, show a 3.5" hot zone at 1600°C which is uniform within \pm 10C°. At 1400°C the 3" hot

zone is uniform within $\frac{1}{2}$ 5C°. The reacting phases lie within this region.

The steep temperature gradient below the zone is due to heat losses from the water-cooled carbon base blocks whilst the temperature gradient above is caused by radiation losses.

R-3.3.3 Materials Preparation

(i) Metal

Preliminary experiments showed that a charge of solid iron, saturated with carbon at the operating temperature, would discharge graphite on heating beyond the eutectic temperature. This was undesirable since graphite would interfere with the reaction between slag and metal phases. To eliminate this effect iron-carbon alloys of approximately eutectic composition were prepared.

An induction furnace was used to melt Armco iron in a graphite crucible loosely packed with graphite powder. After melting the iron, the temperature was gradually decreased and a discharge of graphite from solution was observed. This was continuously removed from the surface of the melt by skimming with a mild steel rod until the temperature was slightly above the eutectic temperature. The furnace was then turned up to full power for half a minute in order to super heat the melt and minimise carbon solution. The melt was immediately cast into a split steel mold to produce rods of white cast iron 5/16" diameter x 7". After cleaning by surface grinding, the brittle material was easily broken by tapping with a hammer into 1" lengths which were of a suitable form for use in the present experiments.

(ii) Slags

Synthetic blast furnace slags having low liquidus temperatures $(1200^{\circ} \text{ to } 1300^{\circ}\text{C})$ were chosen in order that experiments could be undertaken at a relatively low temperature of 1400°C . The compositions were based on the studies of Osborne et al (1954) in CaO-SiO₂-Al₂O₃-MgO melts and were modified by the addition of 5 wt. pct. P₂O₅. These phosphate bearing slags were prepared from reagent grade CaO, SiO₂, Al₂O₃, MgO and 3CaO. P₂O₅ powder components. The SiO₂ powder was prepared from meta-silicic acid which had been heated in a Pyrex dish for 20 hours at 500°C. The remaining components were dried as a precautionary measure since it was found that the moisture content of these reagents could be as much as 6 pct.

The components were weighed out to give 200 gm. lots which were mixed for one hour in a bottle by slow rotation on a lathe. The powder mix was then compressed into 10 gm. pellets by means of a standard metallographic mounting press and dies. The pellets were then placed on a mound of the same powder mix and flame fused with an oxygen/gas torch to give a cylindrical pellet, roughly 1.25" diameter x 0.75", weighing 60 gm. This method of preparation avoided crucible contamination and produced a compact fused pellet suitable for experimental use.

R-3.3.4 Crucible Materials and Design

Preliminary investigations were carried out for the purpose of finding suitable crucible materials with which to contain the reactive phosphate bearing slags and carbon saturated iron. Graphite, silica, zircon and zirconia were tested and, for reasons given in detail in Appendix R-1, difficulties were always encountered which were associated with the containment of phosphorus within the reaction vessel. Further tests which are also discussed in Appendix R-1 showed that MgO crucibles were unsuitable for steelmaking studies in the carbon resistance furnace.

However, zircon and zirconia were found to be the most suitable refractory materials and were successfully used for phosphorus transfer studies. The use of zircon was restricted because of surface tension effects which caused the slag to climb over the refractory wall. The disadvantage in using zirconia was its absorption of slag although there was apparently little slag/crucible reaction as can be seen in Figure R-7.

In designing the crucible, it was taken into consideration that carbon saturation should be maintained in the iron phase and the slag should be protected from reaction with the crucible. For these reasons, a graphite crucible, 2" O. D. \times 4.5", was used (Figure R-8) and was lined with a refractory sleeve of either zircon or zirconia. Both types of sleeves were approximately 3.5" in length, 1.5" I. D. \times 1.75" O. D., but the I.D. was measured for each experiment in order to ćalculate the cross-sectional area. Since stirred metal systems were to be used, the graphite crucible was long enough to be firmly supported by graphite pegs projecting from the top ring of the heating element.

R-3.3.5 Stirring in Slag/Metal Systems

Stirring the melt from above and below were both considered. The disadvantages of stirring the melt from above were threefold: sampling would be restricted because of the confined space; the metal phase alone could not be stirred; the slag would be contaminated by the stirrer. Bottom stirring was advantageous since these problems could be eliminated, and in fact it was found to be a highly successful technique.

A graphite impeller, situated in the metal phase, was driven at 100 r.p.m. by a graphite drive shaft which was located in the 0.5" thick base of the crucible (Figure R-8). The high surface tension of the carbon saturated iron prevented leakage through the connection. In the cooler, lower region of the furnace the shaft was screwed into an electrically insulating Transite rod, 1" in length, which acted as a radiation shield and was connected through a flexible spring coupling to a steel drive shaft (Figure R-1). This projected through a Swagelok fitting in the bottom plate of the furnace, and it was sealed with a Teflon ferrule which also acted as a bearing. The end of the steel shaft was supported on bearings and transmission from the variable speed electric motor was effected by means of the rubber belt and pulley wheels shown in Figure R-3.

R-3.3.6 Materials Charging

The metal charge and crucible were placed inside the furnace prior to heating and the slag phase was charged whilst the furnace was at temperature. The slag charging assembly (Figure R-9) consisted of a shaft to the end of which was attached a graphite tube for holding the slag. The tube, 1.7" O.D. x 3" in length, was slightly smaller in diameter than the crucible into which it was lowered in order to facilitate its location. Iron wire was threaded through perforations in the lower rim in order to support the slag pellet. This design enabled the preheating of the slag to a sufficiently high temperature during charging before it finally dropped into the melt. This occurred when the iron wire was soft enough to break or when sufficient carbon had dissolved in it to form a liquid.

The shaft consisted of a 0.25" diameter, 20" long steel rod which was screwed into a 0.5" diameter, 6" long graphite rod. The end of this shaft was screwed into a graphite disc which fitted snugly in the top of the charging tube and was pinned with graphite screws. The steel shaft was supported and designed to slide through a gas-tight Swagelok fitting in a Plexiglass disc which sealed the charging chamber. Graphite was used for the lower portion of the shaft to withstand the high temperatures in the furnace reaction zone.

R-3.3.7 Sampling Techniques

(i) Radio-Tracer Technique

It was originally intended that a radio-tracer technique would be employed to continuously monitor the transfer of the P-32 isotope from slag to metal. However, experimental difficulties associated with the complete containment of phosphorus within the crucible prevented the use of this technique. The principles involved are discussed in Appendix R-2.

(ii) Conventional Sampling Techniques

Slag samples were obtained with difficulty. The technique of dipping a cold steel rod into the slag phase was unsatisfactory since it resulted in either too much or too little slag removal from such a small charge. Another method which involved the use of a graphite spoon could not be used with phosphate bearing slags since the graphite reacted with the slag.

Consequently, interest was directed towards obtaining metal samples which could be analysed for phosphorus. The phosphorus content of the slag could then be calculated by mass balance considerations. The most satisfactory method for metal sampling was found to be an aspiration technique. This apparatus consisted of a 2 mm. I.D. silica tube attached to an aspirator bulb. A Plexiglass disc enclosing the top of the charging chamber was equipped with a Swagelok fitting through which the sampling tube could be pushed into the furnace and at the same time maintain a gas-tight seal. After flushing the charging chamber with nitrogen, the air-lock was opened and the sampling tube was lowered into the melt. The aspirator bulb was squeezed at the same time as the tip of the tube was pushed through the slag phase into the metal, thereby avoiding pick-up of slag. A suction sample was taken immediately and the tube was withdrawn and allowed to cool in the air-lock before removal for chemical analysis. In order to retain a check on mass balance in the slag/metal system, the slagged length of silica tubing was weighed along with the metal sample. A prior knowledge of the unit length weight of the tubing enabled the calculation of the amount of slag removed.

R-3.3.8 Analysis of Samples-

The iron carbon alloy samples were pulverised using a steel pestle and mortar in preparation for chemical analysis.

The phosphorus contents of metal and slag samples were determined by the photometric technique of Adelt and Gruendler (1948) which involved the development of the molybdenum blue complex. (Appendix S-1)

A Leco unit was used for carbon determinations. The induction melted sample was burnt in oxygen and the resulting volume of carbon dioxide was measured to give the equivalent carbon content. R-3. 3. 9 <u>Experimental Procedure</u>

The procedure which was finally adopted applies to the successful experiments where zircon and zirconia sleeves were used. The sleeved crucible was pegged inside the heating elements and the drive shafts were placed in position so that the impeller could be screwed on to the shaft thread which protruded through the base of the crucible. The free rotation of the drive shaft was then checked and a weighed charge of 200 gm. of metal was packed inside the sleeve. The graphite cylinder was placed around the elements and the whole assembly was replaced within the furnace body. After connecting the power leads from the furnace to the transformer, the electric motor and drive belt were set in place, and the water-cooling tubes were connected. The alumina tubes were pushed into the ports so as to touch the crucible and all seals were tightened ready for operation of the furnace.

After evacuating and flushing the furnace with nitrogen the power was switched on with the Variac at zero setting. The furnace was heated to operating temperatures by step-wise increases in the Variac output over a period of approximately six hours in order to avoid shattering the refractory sleeve and tubes. In the proximity of the required temperature the set point of the pyrometer indicator was adjusted to provide temperature control and further adjustments were made until the thermocouple indicated the required operating temperature. At this time the impeller was set in motion in experiments where stirring was employed. The furnace was allowed to sit at this temperature for one hour in order to attain carbon saturation.

The charger, containing a prefused slag sample weighing 60 gm., was placed inside the charging chamber which was then evacuated and

flushed with nitrogen. The charger was slowly lowered into the top of the crucible in order to preheat the slag which was observed to reach orange-yellow heat before it finally dropped into the crucible. At this time the indicator registered a drop in temperature and after a lapse of some 15 to 30 seconds temperature control recommenced. This was taken as the zero time for the reaction.

Metal samples were taken after two minutes and at increasing intervals until the end of the first hour when samples were taken at 30-minute intervals. Experiments were carried out for periods of up to six hours after which the furnace was dismantled. The crucible was then cut open and the contents were weighed for a mass balance determination.

CHAPTER R-4

EXPERIMENTAL RESULTS

The conditions under which phosphorus reduction experiments were conducted are given in Table R-1. Carbon saturated iron, graphite supporting crucibles and Slag A were common to all experiments. The composition of Slag A, operating temperatures, type of protective sleeve, stirring conditions and the internal cross-sectional area of each sleeve are listed for all experiments.

Details of sampling times, the corresponding phosphorus analyses and the weight of metal and slag removed during sampling are given in Tables R-2 to R-6. Data for experiments R-38 and R-39, taken from Tables R-2 and R-3, are plotted in Figure R-10 to illustrate the variation of the phosphorus content of the metal with time. These curves represent the typical behaviour in all experiments. The rate of change of phosphorus concentration in the metal is measured by the slope of the curves and, after the initial rapid increase in phosphorus, the rate falls almost to a value of zero. This corresponds to almost complete reduction of P_2O_5 from the slag. It will be noted that these experiments appear to indicate a higher rate of phosphorus transfer under conditions of stirring in the metal phase. However, the curves represent only the raw data and the differences are not necessarily significant since the quantities of slag and metal removed during sampling

were not the same for each experiment. The initial conditions were approximately the same in these experiments. Reference to Tables R-2 and R-3 indicates that, although the proportion of slag to metal removed during experiment R-38 (stirred) was slightly greater than during experiment R-39 (unstirred), considerably larger quantities of slag and metal were removed during the latter experiment. The proportions of slag to metal remaining at the end of experiments R-38 and R-39 were 0.28 and 0.24, respectively. Thus, the over-all effect of sampling was to reduce the slag/metal ratio more rapidly under non-stirring conditions and, hence, to decrease the supply of phosphorus from the slag. Similar behaviour is exhibited in experiment $\cdot R$ -36 (stirred) and R-41 (unstirred) and is explained by the same reasoning. After taking into consideration the amount of slag absorbed by the zirconia sleeves as well as the weights of metal and slag removed during sampling, the final proportions of slag to metal were 0.31 and 0.18 for experiments R-36 and R-37, respectively. Thus, the rate of phosphorus transfer would appear to be higher in the stirred experiment.

Mass balance data for experiments R-38 and R-39 are given in Tables R-7 and R-8, respectively. In each case, 200 gm. of iron of average carbon content 4.3 wt. pct. were charged. No samples were taken for carbon analysis prior to slag charging. It was estimated that the carbon content of the saturated iron at 1400°C is approximately 4.95 wt. pct. which corresponds to an increase of 1.4 gm. in the weight of the metal phase. In calculating the slag mass balance, the weight of P_2O_5 equivalent to the weight of phosphorus transferred was calculated from the metal data.

Similar mass balance data are given in Tables R-9 to R-11 for experiments R-36, R-41 and R-37, respectively. Further data is included giving details of the amount of slag absorbed by zirconia sleeves in these experiments. For the purpose of subsequent calculations, estimates of the amount of slag absorbed during time periods between samples, taken in the initial 60 to 120 minutes of each experiment, are given. The estimates are based on the results of an investigation of the rate of slag absorption by zirconia sleeves, the details of which are given in Appendix R-3.

Using the experimental date from Tables R-1 to R-11, the average rate of phosphorus transfer (moles/cm²/sec) and the mole fraction of P₂O₅ in the slag phase ($X_{P_2O_5}$) were calculated for corresponding sample times for each experiment. The mass balance calculations were complicated and extensive and, for these reasons, the method of computation and an example calculation are dealt with in Appendix R-4. Tables R-12 to R-16 give the calculated rates, mole fractions and corresponding logarithmic values for the five experiments. The data for experiments R-38 and R-39 are plotted as log (moles P/cm²/ sec) versus log (mole fraction of P₂O₅) in Figure R-11. Similar graphs are given in Figure R-12 for experiments R-36 and R-41 and Figure R-13 for experiment R-37. The curves are superimposed in Figure R-14.

In Figure R-11, the first point for each experiment at the top right of the graph corresponds to the time of the first sample. Both variables decrease in value with time and consequently the path proceeds diagonally to the left during reduction. The curves exhibit linear behaviour in the initial reaction periods of up to 90 minutes in experiment R-39 and 60 minutes in R-38. Further, it will be seen that the curves, which represent non-stirred and stirred conditions in similar zircon-sleeved crucibles, are superimposed with approximately the same gradient. The linear equation representing both sets of data has been determined by the method of least squares from the experimental data in the linear region, the values of which are denoted by an asterisk in Tables R-12 and R-13. The value for the gradient which is approximately 3 and the intercept are given in Table R-17. The scatter of data which results in deviations from linearity in the later stages of these experiments is probably due to the sensitivity of the calculated values to changes in rate values at low rates of transfer.

The rate behaviour for experiments R-36 and R-41 is shown in Figure R-12. There is an initial region for each curve, up to 60 minutes for experiment R-36 and 180 minutes for R-41, where the curves are superimposed with approximately the same slope. These observations indicate that conditions of stirring in zirconia-sleeved crucibles have no effect on the rate of transfer in the initial stages of the reaction up to 60 minutes. The linear equation representing the combined experiments in the linear region was calculated by the method of least squares from the data in Tables R-14 and R-15. The values for the gradient which is approximately the same as that obtained in zircon-sleeved crucible experiments and the intercept are given in Table R-17.

The behaviour appears to be similar for zircon and zirconiasleeved experiments at 1400°C under conditions of stirring and nonstirring. However, experiments R-36 and R-41 display a much smaller linear region. In these experiments, side effects are involved due to the absorption of slag by the zirconia sleeves. It is assumed that the slag is absorbed linearly with time during the initial period of 60 minutes and at a different rate over the subsequent 60-minute period. This assumption may lead to errors in the calculated values of rate and mole fraction of P₂O₅ in the slag. However, greater importance is assigned to the assumption that phosphorus transfer occurs only across the slag/ metal interface. In the initial stages of the reaction up to 60 minutes, phosphorus transfer across the slag/metal interface would be expected to be dominant. However, after a period of 60 to 90 minutes, the rate of phosphorus transfer across the slag/metal interface has decreased considerably and the sleeve is almost saturated with slag. Reduction of phosphorus from the absorbed slag probably occurs at the sleeve/metal

interface and may even dominate the rate of phosphorus transfer at this stage. The calculated rate of phosphorus transfer is based on the amount of phosphorus transferred to the metal and would therefore include the contribution from the sleeve/metal reaction. Thus, during this period of the experiment, the calculated rate would be higher than the actual rate of transfer across the slag/metal interface. This would account for the deviation of the curves in Figure R-12 away from linearity and to the left of the extrapolated line. The calculation of the concentration of P_2O_5 in the slag phase was based on the same assumption and, consequently, $X_{P_2O_5}$ is underestimated. This would also account for the deviation of the curves in Figure R-12 in the same direction.

The calculated data for experiment R-37 are given in Figure R-13. Linear behaviour is observed for the complete 180-minute period of the experiment at 1500°C and the gradient and intercept, calculated by the method of least squares, are given in Table R-17. The extended region of linearity is accounted for by the fact that the rate of reduction of phosphorus is higher at 1500°C than at 1400°C. Consequently, sleeve/metal reaction probably does not result in a significant contribution to the phosphorus content of the metal during this period of study.

The linear portions of the curves in Figures R-11 to R-13 are superimposed in Figure R-14. It will be seen that the curves for experiments conducted at 1400°C in zircon and zirconia-sleeved crucibles coincide and have approximately the same gradient. Thus, the nature of the sleeve material and the conditions of stirring have no marked effect on the rate versus mole fraction of P_2O_5 relationship.

The curve for experiment R-37 under conditions of stirring at 1500°C is displaced in Figure R-14 with respect to the curves at 1400°C. However, the gradient of the line appears to be temperature independent.

CHAPTER R-5

DISCUSSION

R-5.1 Introduction

In the present investigation the rate of phosphorus transfer from slag to metal was studied during the reduction of synthetic phosphate-bearing blast furnace slags by carbon saturated iron. The rate of transfer under these conditions may be controlled by one or more of four possible steps.

- Mass transfer of P₂O₅ in the slag phase to the slag/ metal reaction interface.
- 2) Chemical reaction at the slag/metal interface.
- Mass transfer of reactants or products in the metal phase to or from the interface.
- 4) Nucleation and evolution of carbon monoxide.

The slowest of these factors will dominate the over-all rate of reduction. However, some of these factors may be justifiably eliminated in the light of experimental conditions and observations. Thus, it was observed that there was considerable agitation of the slag phase due to evolution of carbon monoxide, particularly in the initial reaction period of 60 minutes. This would be expected to result in effective stirring of the slag phase and consequently mass transfer of P_2O_5 in the slag phase to the slag/metal interface may be eliminated. Mass transfer of carbon in the metal to the reaction interface is unlikely to

be a rate controlling factor since the metal is maintained at the carbon saturation level throughout each experiment. Further, Figures R-11 and R-12 show that mechanical stirring in the metal phase did not change the kinetic behaviour of the system which indicates that the over-all rate is not controlled by the mass transfer process in the metal phase.

The rate of evolution of carbon monoxide is generally considered to be controlled by the nucleation process. The possible sites of carbon monoxide nucleation in this system are pores on the surface of refractory sleeves and graphite. In comparison with the dense zircon sleeves, the zirconia sleeves are quite porous and consequently more sites are available for nucleation. There were also much larger areas of metal/graphite interface in the experiments during which the metal phase was stirred by a graphite impeller. If the nucleation of carbon monoxide is important in determining the over-all rate, it would be expected that the stirred experiment with a zirconia sleeve would have a higher rate. Figure R-14 shows that the influence of nucleation of carbon monoxide on the over-all rate is not noticeable.

Thus, by a process of elimination, based on the observations mentioned above, the rate controlling step would appear to be chemical reaction at the slag/metal interface.

R-5.2 Theoretical Considerations

R-5.2.1 Stoichiometric Relation and Reaction Mechanism

The reduction of phosphorus from phosphate-bearing blast

furnace slags may be represented by the relation:

$$(P_2O_5)_{slag} + 5 \underline{C} = 2 \underline{P} + 5 \{CO\}$$
(R.1)

However, this gives no indication of the reaction mechanism which is unknown. It would be unwise to consider phosphorus reduction in terms of a heterogeneous reaction between molecular species which might be inferred from the stoichiometric relation (R. 1). Such a mechanism for a single step reaction would be highly unlikely since it requires the simultaneous rearrangement of six reacting entities in the same locality and, further, the P_2O_5 is present in the slag phase in the form of complex ions. The most likely reduction mechanism would appear to be the formation of "local cells" where electrical charging and discharging of particles would be effected as proposed by Wagner (1956).

R-5.2.2 Reversibility of the Interfacial Chemical Reaction

The final slag phosphorus analyses for experiments R-36 and R-38 were below the lower limit of detection by the photometric technique. The reaction represented by relation (R. 1) is therefore irreversible since carbon monoxide is continuously removed and the phosphate is completely reduced.

If the phosphorus reduction reaction were inherently slow compared with the mass transport processes, the rate would be controlled by chemical reaction at the slag/metal interface. Since the reaction is irreversible the back-reaction may be neglected and the rate of transfer of phosphorus (moles/sec) may be written as:

$$R_{t} = A.k. (X_{P_{2}O_{5}})_{t}^{n} \cdot \begin{bmatrix} a_{C} \end{bmatrix}_{t}^{m}$$

where A = area of slag/metal interface (cm.²)

k = rate constant (mole/cm²/sec.)

 $X_{P_2O_5}$ = mole fraction of P_2O_5 in slag phase

 a_{C} = activity of carbon in metal phase

n and m are constants and represent the orders of the reaction with respect to P_2O_5 in the slag and carbon in the metal phase. It must be emphasised that n and m are not necessarily of integer value or related to the coefficients in the stoichiometric relation (R. 1). The inclusion of the activity term for the metal phase is quite valid. The concentration of P_2O_5 is used instead of activity in equation (R. 2) since, at the present time, there is no information in the literature which gives the activity of P_2O_5 as a function of composition for acid slags.

Carbon saturation was maintained in the iron phase throughout each experiment and, therefore, the value of a_C is unity. Thus equation (R. 2) reduced to:

$$R'_{t} = k. X^{n}_{P_{2}O_{5}}$$
 (moles/cm.²/sec.) (R.3)

or

$$\log R'_{t} = \log k + n \log X_{P_2O_5}$$
 (R.4)

If the rate were controlled by chemical reaction, a logarithmic plot of R_t' versus $X_{P_2O_5}$ would be expected to provide a linear relationship with slope of value n and intercept log k. Under these conditions, stirring in the metal phase would not change the reaction mechanism or

(R. 2)

the reaction rate and consequently the values of k and n would be unaffected. The order of reaction, n, would also be independent of temperature since the reaction mechanism would not be expected to vary in the narrow temperature range studied. However, the rate constant would be temperature dependent and the value of k would increase with temperature. The above mentioned requirements for the case of chemical reaction control are all confirmed in Figure R-14.

The experimental observations, therefore, provide convincing evidence to suggest that the rate of phosphorus reduction is controlled by chemical reaction at the slag/metal interface. The activation energy for the reduction reaction is approximately 100 Kcal/mole and the order with respect to the concentration of P_2O_5 in the slag is approximately 3.

CHAPTER R-6

CONCLUDING REMARKS

R-6.1 Summary

Experiments were conducted at 1400°C in zircon and zirconia sleeved crucibles under conditions of stirring and without stirring in the metal phase. A further experiment at 1500°C was conducted in a zirconia sleeved crucible with metal stirring. Calculated data were plotted logarithmically as rate of transfer of phosphorus versus the mole fraction of P205 in the slag phase. A linear relationship was obtained for each experiment in the initial period up to 60 minutes. Neither sleeve material nor stirring conditions had any significant effect on the rate of transfer at 1400°C or the order of the reaction. The rate constant was found to be temperature dependent whilst the order of the reaction was independent of temperature. These observations were interpreted in terms of chemical reaction control at the slag/ metal interface. The activation energy was found to be approximately 100 Kcal/mole over the temperature range 1400° to 1500°C and the order of the reaction approximately 3 with respect to the concentration of P_2O_5 in the slag.

R-6-2 Suggestions for Further Work

The present work covers one slag composition with the same initial P_2O_5 content and a narrow temperature range. Further investigations could be carried out with varying initial concentrations of P_2O_5 in the slag to provide further information on the controlling steps. In the case of chemical control the log-log plot would be expected to show the same behaviour. Information is also required over a larger temperature range to obtain more precise values for the activation energy. This may prove experimentally difficult where zircon sleeves are used due to slag surface tension effects. However, zirconia sleeves may be quite suitable provided that the rate of slag absorption at the operating temperatures is ascertained. The effect of varying the slag composition on the rate of phosphorus transfer could also be investigated.

STEEL BY SYNTHETIC STEELMAKING SLAGS

THE KINETICS OF DEPHOSPHORISATION OF LIQUID

SECTION 2 S

CHAPTER S-1

INTRODUCTION

In basic steelmaking processes, phosphorus which is initially present in the unrefined metal is removed by reaction with an oxidising basic slag. Close control over the phosphorus level is maintained since its presence may adversely affect the properties of the finished product insofar as it produces brittleness.

The aim of this project was to evaluate the factors controlling the rate of dephosphorisation in steelmaking slag/metal systems under laboratory conditions.

In this section a brief literature review of relevance to dephosphorisation kinetics is made. The laboratory equipment and experimental techniques are described and the results are discussed in terms of rate control by chemical reaction at the slag/metal interface and diffusion in the slag phase. It is concluded that, under the laboratory experimental conditions, the rate of dephosphorisation is dominated by mass transfer in the slag phase except for a very short initial period.

CHAPTER S-2

LITERATURE REVIEW

Several investigations involving phosphorus equilibrium studies in steelmaking slag/metal systems have been reported. (See footnote*). The equilibrium studies of Winkler and Chipman (1946) employed induction heating of the metal phase and radiant heating of the slag phase by means of a suspended carbon arc. These workers reported that under their laboratory conditions equilibrium was established within 15 minutes.

A literature survey indicates that, at the present time, no published work is available pertaining to the kinetics of phosphorus transfer in steelmaking slag/metal systems. It is indeed surprising that no such information is available when phosphorus control in steel refining is so important. In the author's opinion this is, no doubt, a manifestation of the technical difficulties associated with the containment of phosphate-bearing slags under laboratory conditions rather than a lack of interest in the subject.

*Balajiva, et al (1946)

Winkler and Chipman (1946)

Turkdogan and Pearson (1953)

CHAPTER S-3

EXPERIMENTAL CONSIDERATIONS

S-3.1. Introduction

A preliminary investigation of the kinetics of phosphorus transfer in steelmaking slag/metal systems was carried out in a graphite resistance furnace. The major problem was to find a suitable container which would be inert and impervious to the extremely reactive iron oxide slags. Unfortunately, all attempts to overcome this difficulty failed and consequently kinetic studies by this method were abandoned.

To overcome this problem of containment, the advantage of induction heating was exploited. Since the heat source lies within the crucible, a temperature gradient exists through the walls resulting in limited penetration by the slag which freezes, thereby providing its own impervious shell. Water cooling from the induction coil serves to increase this temperature gradient.

S-3.2. Apparatus

S-3.2.1. Power Source

Power was supplied from a 30 KVA, 3,000 c.p.s. Tocco generator to an 8" O.D. water-cooled induction coil made up from 0.5" diameter copper tubing. Figure S-1 shows the furnace construction.

S-3.2.2. Crucibles

The slag/metal systems were contained in commercially manufactured porous magnesia crucibles, 3.5" I.D. x 4.5" O.D. x 4.75" inside height. Magnesia was chosen because of its resistance to chemical reaction with steelmaking slags. The crucibles were packed within the coil with magnesite cement, a high temperature refractory material which provided electrical insulation and support in case of crucible fracture and, at the same time, acted as a heat conductor in order to create a sharp temperature gradient.

S-3.2.3. Graphite Slag-Heater

Since a slag is not heated by induction, the problem of maintaining an isothermal slag/metal system was overcome by the use of an auxiliary slag-heater, Figure S-2. This consisted of an annular graphite crucible, 4" I.D. x 4.5" O.D. x 3" in length, containing approximately 1500 gm. of copper and was situated within the coil directly above the magnesia crucible in order to act as a susceptor, thus heating the slag layer from above.

The susceptor was designed with a 0.75" diameter concentric hole in order to facilitate charging, sampling and temperature measurement by thermocouple immersion. A top covering of insulating brick was used to reduce radiation losses and contact with the atmosphere.

S-3. 2. 4 Furnace Atmosphere

The composition of the atmosphere above the melt was not controlled. However, it was assumed that a reducing atmosphere would be maintained by reaction of the graphite slag-heater with any air which might have penetrated this region.

S-3.3 Experimental Techniques

S-3.3.1 Temperature Measurement

The metal temperature was assumed to be uniform because of the violent inductive stirring and was measured by a Pt/Pt-13 pct. Rh. thermocouple. This was encased in an alumina sheath which was cemented into the crucible wall and protruded approximately 1" into the metal. The temperature of the slag-heater was measured by a Pt - 6 pct. Rh/Pt - 30 pct. Rh. thermocouple encased in alumina and graphite protection tubes immersed in the molten copper.

In experiments where breakdown of one of the couples occurred, temperatures could be checked by immersion in the steel bath or molten copper of a thermocouple protected with a silica sheath, which was used because of its excellent thermal shock properties.

All the thermocouples were connected to a chart recorder and the estimated error in temperature measurement was $\frac{1}{2}$ 5C°.

S-3.3.2 Temperature Control

In order to attain optimum isothermal conditions, the slagheater and the steel bath should be at the same temperature. This depends on the distribution of inductive power between the bath and slag-heater, which is determined by their relative positions within the coil. The gap between them should be large enough to accommodate the slag layer, while leaving sufficient space to prevent contact of the slag and graphite, which would certainly result in reduction of iron oxide in the slag. At the same time, the gap should be as small as possible in order to minimize the temperature gradient across the slag phase in the vicinity of the unheated wall. Thus, the quantities of steel and copper and the dimensions and relative position of the crucible and slag-heater within the coil are extremely important.

Two methods were considered in which isothermal conditions could be attained by adjustment while a run was in progress. The first involved the construction of a crucible and slag-heater unit capable of vertical movement within the coil. Such a unit would need a supporting structure which, if mobile, would not be in close contact with the cooling coil. Thus the advantage of a tremendous temperature gradient between the crucible and the coil would be lost, defeating the original purpose of using induction heating. The possibility of water-cooling the furnace casing was considered and would have required the use of some nonconducting material such as glass tubing to avoid induction heating. It was felt that this was complicating matters unnecessarily at such an early stage in the investigation and attention was focused on the second method because of its simplicity.
The crucible and slag-heater were packed within the induction coil and the required power distribution between them was altered by the use of an external susceptor. This took the form of a water cooled 12" diameter, three-turn coil of 0.5" diameter copper tubing, capable of vertical movement and lying concentrically with the induction coil. This external coil appeared to aggravate temperature control rather than improve it and the technique was abandoned.

Finally, it was decided that a simple packed construction should be used with no allowance being made for temperature adjustments during operation. The optimum dimensions for isothermal conditions could only be determined by trial and error over several experiments and, after being established, were adhered to as far as possible during subsequent runs.

Under optimum conditions, the slag-heater and steel were at the same temperature and it could be safely assumed that the slag/metal system was isothermal. However, a temperature gradient would exist in the slag phase when the temperatures of the slagheater and the steel were not identical. On such occasions, the metal phase was maintained at the intended temperature, since it seemed reasonable to suppose that the temperature of the slag at the reaction interface would be almost the same, and of greater importance, than that measured at the top surface. Operating temperatures in the range 1585° to 1650°C were used and occasionally slag-heater temperatures greater than 1650°C were attained. The Pt - 6 pct. Rh. / Pt - 30 pct. Rh. couple was found to be more reliable at these higher temperatures.

When a run was in progress it was found that little or no adjustment of the power input from the generator was required to maintain the bath at a steady operating temperature. Consequently, if a thermocouple breakdown occurred, the run could generally be continued with occasional temperature checks.

S-3.3.3 Materials

(i) Metal Charge

The iron charge of 2.5 Kg. was made up from 2" diameter mild steel bar and mild steel punchings.

(ii) Phosphorus

Phosphorus was added to the iron phase in the form of ferro-phosphorus (25 wt. pct. P). In order to obtain an initial 0.4 to 0.5 wt. pct. P in the melt, approximately 40 to 50 gm. of ferrophosphorus were charged.

(iii) Slags

Steelmaking slags were prepared from the component oxides, the major components being Fe_2O_3 , CaO and SiO₂. Other components, calcium phosphate (3 CaO. P_2O_5), MgO, CaF₂ and Al₂O₃, were used for fluxing purposes. Preparation of the slags involved weighing out the appropriate components which were then thoroughly mixed in an agate ball mill for 12 hours. The slag mix was then prefused using a carbon electrode arc furnace. This technique involved melting a slag button in the powder mix without physical contact from either the electrodes or container crucibles thus eliminating contamination. It was found that several "falling" slags had been prepared and on cooling the fused buttons tended to disintegrate into fine powders. However, powdered slags were required for charging purposes and any lumpy material was broken up with a pestle and mortar.

It was intended that a metal/slag ratio of 3:1 would be used, with a charge of approximately 800 gm. of slag. In fact, the quantities of slag ranged from 400 to 850 gm.

S-3.3.4 Sampling

(i) Metal Samples

A suction sampling technique was employed which involved the use of a 1/8" O.D. silica tube attached to an aspirator bulb. Metal samples in the form of thin rods were obtained.

(ii) Slag Samples

Slag samples were obtained by dipping a cold steel rod into the slag phase for a few seconds. Difficulty was encountered in obtaining such samples during most experiments and consequently analytical data on the variation of slag composition with time could not be established.

S-3.3.5 Analysis

Metal samples were analysed for phosphorus by the photometric method of Adelt and Gruendler (1948), in which the molybdenum blue complex is developed. (See Appendix S-1.)

Slag phosphorus analysis was carried out by the same method. Slags were also analysed for total iron by the method of reduction with stannous chloride and titration with potassium dichromate solution.

S-3.3.6 Experimental Procedure

At the start of an experiment, an alumina thermocouple sheath was cemented into the crucible wall and the crucible and thermocouple were carefully rammed into position within the coil with magnesite cement. After charging the cold metal, the slag-heater containing copper was placed on top of the crucible and rammed into position with more cement. Finally, refractory bricks were placed on top of the slag-heater for insulation.

The generator was switched on and the metal and susceptor were heated to the required temperature within one hour. The powdered slag was then slowly charged through a funnel into the furnace, taking approximately one hour to complete. During this time a portion of the slag was absorbed by the crucible to form a shell of slag around the melt.

After power input adjustments had been made to regulate the

temperature of the metal, a slag sample was taken whenever possible in order to determine the initial iron content of the slag. A weighed amount of ferro-phosphorus, which was contained in a steel capsule attached to the end of a welding rod, was charged by immersion in the molten iron. As soon as the capsule had melted the rod was removed and the clock was started. This was taken as zero time for the reaction to commence since it was assumed that rapid inductive stirring would quickly produce a homogeneous melt.

Metal samples were taken frequently for periods of up to 35 minutes which was presumed to be ample time for attainment of equilibrium since Winkler and Chipman (1946) had found that equilibrium was attained within 15 minutes. The power supply was switched off and the assembly was subsequently dismantled and samples of solidified slag were taken for analysis whenever possible.

Many operating difficulties were experienced with these experiments. Where slags of high basicity were used, experiments had to be undertaken at high temperatures in order to melt the slags and this led to frequent thermocouple breakdown. The system could be operated at about 1600°C, in experiments where slags of low basicity or higher iron oxide contents were employed. However, the extremely corrosive action of the slags frequently resulted in breakdown of the thermocouple or greater penetration of the crucible wall. Difficulties in slag sampling were associated with these problems. In several experiments it was found that the slag was of a doughy consistency and would not adhere to a cold steel rod. On other occasions the high meniscus of the steel interface, due to inductive stirring, tended to float the slag to the wall leaving the central region clear of slag. This behaviour was often the result of a substantial loss of slag phase by crucible penetration. Under these conditions, a slag sample could not be obtained since the sampling area was restricted by the diameter of the orifice in the susceptor.

It was often impossible to obtain a final slag sample after dismantling the furnace. Such occasions involved "falling" slags which had penetrated the crucible wall during an experiment. The slag and the crucible wall had disintegrated on cooling so that it was impossible to separate them from each other or from the powdered magnesite cement packing. An example of the effects of the slag/ metal system on the crucible at the end of the experiment for which penetration was well defined is shown in Figure S-2. It will be noted that the slag phase penetrated up to 0. 1" around the metal phase. Although penetration is somewhat greater in the region of the slagcrucible interface, the interface is still discernible.

CHAPTER S-4

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EXPERIMENTAL RESULTS

Details of the quantities of materials used and the operating temperatures of the melt and the slag-heater are given in Table S-1. The initial phosphorus content of the iron is also included and is calculated on the basis of the ferro-phosphorus (25 wt. pct. P) additions to the melt. The initial synthetic slag compositions, by weight percent, and also the Vee-ratio, V_r , (i.e. CaO/SiO₂ ratio in wt. pct.) are given in Table S-2. Iron contents of slags are given in Table S-3 for experiments where it was possible to take slag samples for chemical analysis. The calculated initial iron contents of the synthetic slag mixes are compared with the total iron content in the molten slag directly after slag charging has been completed and at the end of the experiment. The latter samples were obtained either in the liquid state or from the solid slag which formed two phases, solid and "falling" powder slags. Table S-4 lists the phosphorus contents of samples obtained from molten slags at the end of experiments where samples were available, the corresponding metal phosphorus analyses, and the observed dephosphorisation ratio.

The phosphorus analyses of metal samples are listed with the corresponding sampling times in Tables S-5 to S-7 for a series of ten experiments. These data are plotted as wt. pct. phosphorus in the

metal versus time in Figures S-3 to S-7. The data for six of these experiments, namely #S-9, S-18, S-19, S-20, S-24 and S-25, have been used to calculate the mole fraction of phosphorus in and the rate of removal of phosphorus from the metal at corresponding sample times. (See Appendix S-2.) The calculations are given in Tables S-8 to S-13. Graphs of log (rate of transfer, moles P/cm²/sec.) versus log (mole fraction, X_P) are given for each of the six experiments in Figures S-8 and S-9. The curves are superimposed in Figure S-10. The data from the remaining four experiments are discussed in Section S-5.6.

CHAPTER S-5

DISCUSSION

S-5.1 Introduction

The rate of dephosphorisation of steel by slag/metal reaction may be controlled by one or more of three possible factors:

- Mass transfer of phosphorus in the metal phase to the reaction interface
- (ii) Chemical reaction at the slag/metal interface
- (iii) Mass transfer of the reaction product in the slag phase away from the interface

In the present studies, induction heated melts were employed and it may be safely assumed that the resulting vigorous electromagnetic stirring of the metal phase precluded any possibility of diffusion control in the metal. The purpose of this study, therefore, was to determine the relative importance of mass transfer in the slag phase and chemical reaction at the interface in controlling the rate of dephosphorisation.

S-5.2 Stoichiometric Relations

The dephosphorisation of liquid steel by a basic slag may be represented by the over-all stoichiometric relation

$$2 P + 5 'O' + 3 (CaO) = (Ca_3 (PO_4)_2)$$
 (S.1)

or more simply by the separate relations

$$2 P + 5 'O' = (P_2O_5)$$
 (S. 2)

and 2
$$(P_2O_5) + 3 (CaO) = (Ca_3 (PO_4)_2)$$
 (S. 3)

where terms which are underlined and those in parentheses refer to the components in the metal and slag phases, respectively.

In relations (S. 1) and (S. 2) the phase containing the reactant oxygen is not defined since the actual mechanism of the reaction is unknown. It will suffice to state that the oxygen which is involved may be provided either as dissolved oxygen in the metal phase or by FeO in the slag phase since the oxygen concentrations in each phase are interdependent:

$$(FeO) \doteq Fe + 'O'$$
 (S.4)

It will be seen that CaO is involved in relations (S. 1) and (S. 3). However, its function would appear to be that of stabilizing the P_2O_5 product by the formation of a 3 CaO P_2O_5 compound. In other words, the CaO acts as a "sink" for the removal of product and relation (S. 3) may be considered as secondary.

S-5.3 Possible Reaction Mechanisms

Since the actual mechanism of dephosphorisation is unknown, it is worthwhile considering the possible reactions which could be involved.

S-5.3.1 Homogeneous Reaction

In this case, the oxidation of phosphorus by oxygen, both dissolved in the metal, would result in the creation of a new phase:

 $2 \underline{P} + 5 \underline{O} = \left\{ P_2 O_5 \right\} gas$

This would appear to be unlikely since many atoms would be involved in the reaction and nucleation process. Even a step-wise buildup to the product is unlikely to result in extensive oxidation since it must be remembered that reaction in this manner without the participation of lime is likely to be reversible. The dissociation of some intermediate product would probably occur before further oxidation is achieved.

S-5.3.2 Heterogeneous Reaction

(i) Ordinary Chemical Mechanism

In this case two phases would be involved; namely, the slag and the metal. Such a reaction could probably be represented by:

 $2 P + 5 'O' = (P_2O_5)$ slag.

However, the possibility of two phosphorus and five oxygen atoms meeting and reacting at the interface is, from an energy aspect, highly unlikely if not impossible.

(ii) Electrochemical Reaction Mechanism

If an electrochemical reaction were involved in the oxidation and transfer of phosphorus from the metal to the slag phase, a system of local cells, as proposed by Wagner (1956), could be formed at the slag/metal interface between the reacting species. This would allow the individual reacting atoms or ions to cross the interface in order to effect the charging and discharging process and thus maintain an over-all electrical neutrality. This appears to be the most likely mechanism which would be involved in the oxidation reaction.

S-5.4 Theoretical Considerations for Chemical Reaction Control

If the dephosphorisation reaction were inherently slow compared with the rates of supply of reactants and removal of products, the rate of dephosphorisation would be controlled by chemical reaction at the slag/metal interface. Under these conditions relation (S. 2) may be considered as irreversible when sufficient lime is available at the slag/metal interface to react with P_2O_5 in relation (S. 3). It may be supposed that the rate dependence for relation (S. 2) is of the form

$$n_{P} = A.k.X_{P}^{m}.X_{O}^{n}$$
 (S.5)

where

 $n_{\rm P}$ is the rate of phosphorus transfer (moles P/sec.) A is the area of the reaction interface (cm.²) k is the rate constant (moles/cm²/sec.) X_i is the mole fraction of component i m and n are the orders of reaction with respect to the phosphorus and oxygen components.

The initial conditions are:

$$\begin{array}{c} x_{P} = x_{P_{i}} \\ x_{O} = x_{O_{i}} \end{array} \right\} \qquad t = 0$$

and the conditions at time t:

$$\begin{cases} X_{P} = X_{P} \\ X_{O} = X_{O} \end{cases}$$
 $t = t$

However, phosphorus and oxygen are removed stoichiometrically in relation (S. 2) and it can be shown (see Appendix S-3) that

$$X_{O} = \alpha + \Theta X_{P}$$
 (S.6)

where α and Θ are constants. Substituting equation (S. 6) in (S. 5):

$$n_{\rm P} = A.k.X_{\rm P}^{\rm m} (\ll + \Theta X_{\rm P})^{\rm n}$$
 (S.7)

The constants m and n in equations (S. 5) and (S. 7) are not related in any way to the coefficients in the corresponding stoichiometric equation (S. 2) and are not necessarily of integer value. As a consequence, it will be seen from equation (S. 7) that the observed order of a reaction does not necessarily have to be an integer.

Since FeO in the slag is associated with the provision of oxygen in relation (S. 2), it would be expected that an increase in FeO content of the slag would result in an increase in the reaction rate in equations (S. 5) and (S. 7). These equations have been proposed on the assumption that relation (S. 2) is irreversible; i. e. that sufficient lime is available at the slag/metal interface. Thus it would be expected that the observed rate of dephosphorisation increases with increasing lime content of the slag up to a certain level.

It follows that the initial P_2O_5 content of the slag would also affect the rate of dephosphorisation since it would decrease the amount of available lime. Hence, the greater the initial P_2O_5 content of the slag, the lower would be the rate of dephosphorisation. It would also be expected that the rate of dephosphorisation would increase with increasing temperature. However, since a change in the reaction mechanism is unlikely over the narrow range of temperatures studied, the orders m and n would remain constant and any rate changes would result from the temperature dependence of the rate constant K.

S-5.5 Theoretical Considerations for Mass Transfer

Control in the Slag Phase

If equilibrium for the dephosphorisation reaction at the slagmetal interface is attained rapidly, then the rate of the reaction may be determined by mass transport processes. Thus the rate of supply of the reactants to or the removal of product from the reaction interface may be the rate limiting step. However, in view of the vigorous electromagnetic stirring in the metal phase, it would appear that, if the rate of reaction were mass transport controlled, the slow step would be transport of the reactant or product in the slag phase.

Wagner (1956) notes that the rate of transport of a species in a liquid phase is dependent on diffusion and convection. The rate of transport, $j_{i(x)}$ (moles/cm²/sec.), of species i in the x direction may be written

$$j_{i(x)} = -D_{i} \left(\frac{\partial C_{i}}{\partial x} \right) + C_{i}u(x)$$
 (S. 8)

where D_i is the diffusion coefficient of i (cm²/sec.)

 C_i is the concentration of species i (mole/cm³)

 u_x is the flow velocity in the x direction.

The first term on the right represents the contribution to transport by diffusion down a concentration gradient while the second represents the convection term. Wagner states that under most conditions significant concentration differences are found only in the vicinity of the interface. Thus behaviour in the bulk liquid may be ignored and only the boundary layer conditions are of importance. When the concentration distribution in the boundary layer is unknown, an "effective" boundary layer thickness, S_i , may be defined by

$$\left(\frac{\partial C_{i}}{\partial x}\right)_{x=0} = \frac{C_{i}(B) - C_{i}(I)}{S_{i}}$$
(S. 9)

where $C_{i(B)}$ and $C_{i(I)}$ are the concentrations of species i in the bulk and at the interface, respectively. At the interface $u_x = 0$ and so combining equations (S. 8) and (S. 9) yields

$$j_{i(x)} = \frac{D_{i}}{\delta_{i}} \begin{pmatrix} C_{i(I)} - C_{i(B)} \end{pmatrix}$$
(S.10)

This equation gives the transport rate/unit area for an element of the interface and the total transport rate, n_i , is calculated as $j_{i(x)} dA$. If there are local variations in the value of δ_i , then the total transport rate may be written as

$$n_i = A \cdot \frac{D_i}{S_i} \left(C_{i(I)} - C_{i(B)} \right)$$
 (S.11)

where S_i is then an average boundary layer thickness.

If several species are involved, then several transport processes must be considered. In the case of the dephosphorisation reaction it will be seen from the stoichiometric relations (S. 2) to (S. 4) that, in the slag phase, the transport of FeO and CaO to the interface and transport of Ca_3 (PO₄)₂ away from the interface are involved. In view of the complexity of slag structures, these are more likely to be in the form of ionic species or ionic complexes. However, since the mechanism is not known, a series of rate equations may be expressed in terms of molecular diffusion in the slag phase:

$$\dot{n}_{FeO} = \frac{A.D_{FeO}}{S_{FeO}} \cdot \left(C_{FeO(I)} - C_{FeO(B)} \right)$$
 (S.12)

$$\hat{n}_{CaO} = \frac{A \cdot D_{CaO}}{S_{CaO}} \left(C_{CaO(I)} - C_{CaO(B)} \right)$$
(S. 13)

$$\hat{n}_{Ca_{3}(PO_{4})_{2}} = \frac{A \cdot D_{Ca_{3}(PO_{4})_{2}}}{S_{Ca_{3}(PO_{4})_{2}}} \left(C_{Ca_{3}(PO_{4})_{2(I)}} - C_{Ca_{3}(PO_{4})_{2(B)}} \right)$$
(S. 14)

By the stoichiometry of relations (S. 2) to (S. 4) and under steady state conditions, the rate of removal of phosphorus from the metal phase, n_{p} , may be expressed in terms of the rates of supply of reactants and removal of products in the slag phase at the interface:

$$n_{\rm P} = 5/2 n_{\rm FeO}$$
 (S. 15)

$$\dot{n}_{\rm P} = 3/2 \, \dot{n}_{\rm CaO}$$
 (S. 16)

$$n_{\rm P} = 1/2 n_{\rm P_2O_5}$$
 (S. 17)

$$n_{\rm P} = 1/2 n_{\rm Ca_3(PO_4)_2}$$
 (S. 18)

The actual rate of phosphorus transfer is dominated by the slowest step among relations (S. 12) to (S. 14).

The concentration terms in relations (S. 12) to (S. 14) indicate that the rates of supply of FeO and CaO to and the removal of P_2O_5 or $Ca_3(PO_4)_2$ from the interface and hence the rate of dephosphorisation will be increased by high FeO and CaO and low $Ca_3(PO_4)_2$ contents in the bulk slag phase. However, the composition of the slag influences its liquidus temperature and its viscosity. Thus, an increase in CaO content or Vee-ratio increases the viscosity, whereas an increase in FeO or phosphate content of the slag decreases the viscosity, (Kozakevitch, 1950). It would therefore be expected that the diffusion coefficients, D_i , and the effective boundary layer thickness, S_i , would be influenced by slag composition. Furthermore, viscosity is temperature dependent and decreases with increasing temperature. Thus, the rate of dephosphorisation would be expected to increase with lower CaO, high FeO and phosphate contents and temperature. The conditions are quite complex since this conclusion contradicts the concentration gradient considerations and is further complicated by the fact that the slag composition changes during dephosphorisation.

S-5.6 Interpretation of Experimental Data

Experiments S-9, S-18, S-19, S-20, S-24 and S-25 are plotted in Figures S-3, S-4 and S-5. All show considerable dephosphorisation, little scatter of experimental points and are characterised by a high rate of dephosphorisation during the first five minutes. Sufficient

experimental points are available, particularly in the initial reaction period, to calculate the individual rates of phosphorus transfer.

However, experiments S-2 and S-10 in Figure S-6, and S-14 and S-23 in Figure S-7 show little dephosphorisation. In experiment S-2 there is a considerable scatter of analytical data throughout the reaction period and, since this was a preliminary trial, probably reflects the uncertainties at that stage in the development of the experimental technique and chemical analysis. Samples taken during the first few minutes in experiments S-10, S-14 and S-23 are somewhat dubious and indicate that mixing in the metal phase was not achieved rapidly. For this reason and also because insufficient data were available, precise calculations of the rate of dephosphorisation during the initial five-minute period could not be made. Furthermore, experiments S-10 and S-14 were typified by high Vee-ratios and low slag and metal temperatures. Under such conditions, it is possible that the slag temperature may have been lower than the liquidus temperature and could account for the small amount of dephosphorisation. Experiment S-14 also had an exceptionally small slag charge of 450 gm compared with the remainder, as shown in Table S-1.

It would therefore appear that experiments S-2, S-10, S-14 and S-23 may be justifiably discarded and, for the purpose of this discussion, attention is directed towards experiments S-9, S-18, S-19, S-20, S-24 and S-25. The quantities of metal, slag and ferro-phosphorus used in each experiment were approximately the same and, consequently, the extent of dephosphorisation may be directly compared. Further it may be noted from Table S-2 that the initial Fe_2O_3 contents of the slags lie within the range 26 \pm 2 wt. pct. for these experiments. Unfortunately, the iron content of the slags cannot be considered as unimportant since the data given in Table S-3 indicate that the iron contents decrease during dephosphorisation. Although the data are incomplete, experiments S-20 and S-25 indicate that there is only a slight decrease from the calculated iron content of the synthetic slag mixture to that immediately prior to dephosphorisation. Experiments S-18 and S-25 further show that there is a considerable decrease in iron content during dephosphorisation. This may also be noted for the remaining experiments where solid slag samples were obtained after their completion.

Relations (S. 2) and (S. 4) may be combined and the dephosphorisation reaction represented by the relation:

$$P + 5/2 (FeO) = 1/2 (P_2O_5) + 5/2 Fe$$
 (S.19)

The observed decrease in the iron content of the slags may then be accounted for by oxidation of phosphorus in the metal phase. (See Appendix S-4).

The experimental curves in Figures S-3, S-4 and S-5 show that little dephosphorisation occurs after the first five minutes of reaction and, presumably, indicates that equilibrium has been attained. However, if the rate of dephosphorisation is chemical reaction controlled, it would be expected that the phosphorus content of the metal at equilibrium would be dependent on the initial P_2O_5 concentration in the slag. Comparison of experiments S-18 (Figure S-3) and S-19 (Figure S-4) shows that the initial wt. pct. P_2O_5 is definitely unimportant in its effect on the final phosphorus level in the metal after a period of 30 minutes. Experiments S-9 (Figure S-3) and S-20 (Figure S-4) appear to support this view if the temperature differences of less than 20 C° from the conditions of S-18 and S-19 were considered to be insignificant. This would, therefore, indicate that the equilibrium was not reached over this time period.

Final phosphorus slag analyses were obtained only for experiments S-24 and S-25 (Table S-4). The observed dephosphorisation ratios are seen to be lower than would be expected from the equilibrium studies of Winkler and Chipman (1946) for which certain slags having approximately the same composition are listed. This indicates that the reaction was far from equilibrium in experiments S-24 and S-25 and lends further support to the conclusion that the reaction was irreversible.

In Figure S-8, log/log plots are given for the rate of phosphorus transfer (moles/cm²/sec.) versus mole fraction of phosphorus in the metal, X_p , in experiments S-9 and S-18 and S-19 and S-20. Similar graphs are shown for experiments S-24 and S-25 in Figure S-9. The initial point for each experiment corresponds to the average rate after approximately 1 minute of dephosphorisation and is located at the top right of each graph. Subsequent points correspond to the calculated values at progressively later stages in the experiments and it will be seen that the slope of each curve varies with time.

For purposes of comparison, the curves are superimposed in Figure S-10 where they fall into two distinct groups. These consist of experiments S-9, S-18, S-19 and S-20 (from Figure S-8) in GroupA and S-24 and S-25 (from Figure S-9) in Group B. Reference to Table S-2 indicates that, although the initial Fe₂O₃ concentrations are approximately the same, both groups may be classified according to their initial slag compositions:

Group	P ₂ O ₅ (wt. pct.)	Vr	CaO (wt. pct.)	T°C (metal)	
A	0 - 8	2.85 - 3.96	46 - 48	1620 - 1650	
В	0	1.075, 1.36	30.4, 38	1580, 1600	

In order to reduce the complexity of the treatment, it is assumed that the physical properties of the metal and the temperature of the slag near the interface are the same for both groups. This seems reasonably justifiable since the slag temperature away from the interface varies considerably with the temperature of the slag heater.

In Group A experiments (Figure S-8), the initial dephosphorisation rate for a given mole fraction, X_p , in the metal is lower for experiments S-9 and S-18 for which the initial slag contained P_2O_5 .

This observation indicates that interfacial reaction plays an important role in the initial stages. However, after this short period, the initial P_2O_5 content of the slag no longer has an important influence on the dephosphorisation rate.

Group A experiments (Figure S-8) have initial gradients with values in the range 2 to 5 which would correspond to the order of the reaction with respect to phosphorus in the metal phase. An accurate estimate cannot be made of these gradients since data are available for only two or three points in the early stages of the experiments. In the later stages, the gradients increase to the range 15 to 20. A somewhat similar behaviour is shown in Figure S-9 for Group B experiments. Since there is a large excess of iron oxide in the slag phase, there should be no drastic change in the oxygen content of the slag and metal phases during the reaction and on this basis m should be approximately constant. In addition, it is clear that the rate of phosphorus transfer is strongly dependent on the phosphorus content of the metal phase. This strong dependence is not compatible with the electrochemical mechanism discussed previously for which m should be small and constant.

In Figure S-10, the initial rates of transfer are higher for Group B than A at corresponding phosphorus concentrations. This implies that the higher the CaO content, or Vee-ratio, of the slag, the lower the rate of dephosphorisation and is contrary to any assumption

of chemical reaction control. Also the temperature dependence observed for the two groups of experiments is the reverse of that expected for chemical reaction control.

Such phenomena can only be explained by considering the relationship between the Vee-ratio and the melting point and viscosity of the slags. Since no viscosity data are available for these particular slags, reference has been made to corresponding compositions in the ternary CaO-SiO₂-FeO system (at 1400°C) reported by Kozakevitch (1950). Estimates of the liquidus temperatures of synthetic slags used in the present investigation have been made by comparison with the data given for slags of similar composition by Margot-Marette et al (1964). The following slag compositions were considered:

Slag	II (#8)	II (#11)	III (e)	II (#5)	III (b)	III (d)
Vr	2.8	4.0	4.06	1.8	2.2	1.77
CaO	47.5	53.2	43.48	35.5	38.8	31.36
SiO ₂	17.0	13.3	10.70	19.0	17.3	17.67
FeOt	15.0	20.0	21.78	25.0	17.2	20.47
MnOt	12.0	5.0	11.1	12.0	12.8	22.24
MgO	6.5	6.5	8.15	6.5	8.5	4.47
Al ₂ O ₃	2.0	2.0	2.06	2.0	2.7	3.00
P ₂ O ₅	0.0	0.0	1.18	0.0	1.6	1.82
RO	35.5	33.5	45.82	45.5	43.8	50.97
Liquidus T°C	1625	1618	1600	1403	1550	1428
	Group A			Group B		
Compare	S-18,	S-9	S-9	S-25	S-25	S-24
with	S-19, S-20					

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It will be seen that the composition of these slags include MnO. However, Margot-Marette et al consider the compositions in terms of a pseudo-ternary system, CaO-SiO₂-RO, where RO represents the sum of the remaining oxides. Comparison of slag II (#8) with slags S-19 and S-20 (Table S-2) shows that they are of similar composition. The composition of slag S-18 is also similar although it contains 4 wt. pct. P_2O_5 . Slag S-9 lies in the composition range of slags II (#11) and III (e) although the 8.0 wt. pct. P_2O_5 concentration is considerably higher. The liquidus temperatures of slags in Group A would, therefore, appear to be in the region of 1600°C.

The lowest basicity ratios included in the investigation by Margot-Marette et al were slightly higher than those of Group B slags. Comparison of slags II (#5) and III (b) with S-25 and slag III (d) with S-24 shows that they are of similar lime content. Presumably, Group B slags have liquidus temperatures in the range 1403° to approximately 1550°C or even lower.

The properties of slags of initial compositions given in Table S-2 may therefore be estimated as approximately

Group	Vr	Liquidus, °C	Viscosity	
А	2.85 - 3.96	1600 - 1625	A » B	
В	1.075, 1.36	1403 - 1550	(CaO-SiO ₂ -FeO)	

Additions of MgO, P_2O_5 and Al_2O_3 to Group A slags act as fluxing agents but would not be expected to reduce the viscosity to a level comparable with that of Group B. In all experiments, the FeO contents of the slags decrease during dephosphorisation and would be expected to result in an increase in slag viscosity although this would be counteracted to some extent by the fluxing effect of the reaction product.

The more fluid slags in Group B correspond to a higher rate and greater extent of dephosphorisation regardless of their low lime contents. This suggests that the rate of dephosphorisation is dominated by the rate of mass transfer within the slag phase. Apart from a very short initial period, comparison of the initially phosphatebearing with phosphate-void slags of Group A also supports this view. If molecular diffusion were too slow to account for the rate of transfer, an alternative mechanism could be convection which was referred to in equation (S. 8). However, convection would not appear to be of great importance since the temperature of the slag-heater was generally higher than that of the metal phase and such conditions would not encourage natural convection. The possibility of gas agitation of the slag due to carbon monoxide evolution would also be of little importance since the melts were low in carbon.

Thus, in summary, the results of this investigation indicate that the rate of phosphorus transfer between mild steel and synthetic basic slags is controlled by mass transfer in the slag phase except during the very short initial period.

CHAPTER S-6

CONCLUDING REMARKS

S-6.1 Summary

A series of experiments were conducted with mild steel and synthetic basic slags under conditions of inductive stirring in the metal phase and little or no agitation in the slag phase. Measurements of the rate of dephosphorisation of the metal by oxidising slags of high and low basicity were made and the behaviour was assessed in terms of chemical reaction at the slag/metal interface and mass transfer in the slag phase. Comparison of dephosphorisation rates for phosphate-bearing and phosphate-void slags of similar lime content and Vee-ratio indicated chemical reaction control for a very short initial period. From experiments conducted under similar conditions, with slags of high and low Vee-ratio, it was concluded that phosphorus transfer after the initial period was controlled by mass transfer within the slag phase.

S-6.2 Suggestions for Further Work

It is suggested that further experiments be conducted in order to determine the variation of the rate of phosphorus transfer with initial phosphorus content of the metal. The development of a satisfactory slag sampling technique would be necessary to gain a knowledge of the variation of slag composition with time. An analytical treatment of equations of type (S. 14) could then be effected, thus providing further information on the mechanism of control by diffusion.

The initial rates of dephosphorisation in experiments S-9 and S-18 where initially phosphate-bearing slags were employed were considerably lower than those in which comparable slags initially void of phosphorus (S-19 and S-20) were used. This suggests that if the slag phase were effectively stirred, dephosphorisation could be very high and achieved very quickly. Thus, if a satisfactory slag agitation technique were developed, the rate law for chemical reaction control of dephosphorisation could be studied.

APPENDIX V-1

A COMPARISON OF THE LEVITATION DATA OF

SHIRAISHI (1966) WITH THAT OF THE PRESENT STUDY

The full lines B and D in Figure V-14 respectively correspond to the lines drawn in Figure V-10 in accordance with equation (V. 5. 3) obtained in the present investigation. The experimental points are those reported by Shiraishi (1966) and details of the water vapour/hydrogen ratios for these data are included in the figure. The gradient of line S has been given the value expected from the temperature dependence of log K reported by Shiraishi:

log
$$\left[\text{wt. } \% \ \underline{O} \right] = \frac{-7159}{\text{T}} + \log \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right) + 3.23$$
 (i)

and is drawn through the region where the data are most numerous. It will be seen that the gradient of the line S is not as strongly dependent on temperature as lines B and D of the present investigation. Further, line S represents data corresponding to several water vapour/hydrogen ratios. This is contrary to the form of equation (i) and suggests that the gradient of line S does not represent the true temperature dependent behaviour of oxygen in liquid iron for Shiraishi's work.

Lines 1 to 5, with the same gradient as lines B and D, have been drawn through the most reasonable data from the five groups of results corresponding to particular gas compositions. As would be expected, the oxygen contents represented by these lines increase with increasing water vapour/hydrogen ratio at corresponding temperatures. In general, the experimental data are better represented by lines 1 to 5 than line S. Two points which correspond to line 2 appear to have extremely high oxygen concentrations since they are even situated above line 4 for which the water vapour/hydrogen ratio is approximately 30 pct. higher.

Consideration of equation (V. 5. 2) for a particular droplet temperature indicates that K is constant and consequently:

$$\left(\frac{p_{H_2O}}{p_{H_2}}\right) \propto \text{wt. } \% \underline{O}$$
(ii)

Line 4 is drawn through the greatest number of points. If this were assumed to be the most reliable base line for representing the data by water vapour/hydrogen ratios, the actual positions of lines 2 and 3 agree well with those expected from a consideration of equation (ii). Thus, the majority of the experimental points display good agreement within themselves. However, line 5 is too high by approximately 0.1 and line 1 by 0.08 logarithmic units.

It may be concluded that six of the 16 experimental values reported by Shiraishi are somewhat dubious. The remaining data give values of K which are situated along the lower 95 pct. confidence limit of the present work (Figure V-9), and in reasonably close agreement with respect to temperature dependence.

APPENDIX R-1

THE EFFECTS OF PHOSPHATE BEARING SLAGS

ON SOME CRUCIBLE MATERIALS

Several crucible materials were tested for their ability to contain iron and steelmaking slag/metal systems.

(i) Graphite Crucibles

In reduction experiments the most obvious choice of crucible material appeared to be graphite since carbon saturation would be maintained in the metal phase. However, reaction between the phosphate bearing slags and the crucible wall resulted in the evolution of gaseous phosphorus at 1400°C. Although the loss of phosphorus from the slag/metal system would not prevent the analysis of phosphorus transfer experiments, it is undesirable and would provide a serious complication especially if a radio-tracer technique were to be employed.

Further experiments were therefore conducted in order to determine whether phosphorus contamination of the furnace and laboratory could be avoided. The crucible was furnished with a chimney and condenser system which is shown schematically in Figure R-1.1. The design of the crucible was modified and consisted of two eccentric wells one of which was used for sampling and the other to contain the slag and metal. The chimney consisted of a machined graphite section in the hot



Figure R-1.1 Schematic diagram of crucible and cold trap used for condensation of phosphorus vapour region of the furnace which was connected by means of a "Swagelok" fitting to a steel tube. The lower end of the graphite tube was located in the top of the reaction vessel and was tapered in order to provide a gas-tight seal. The upper end of the steel tube was connected by flexible tubing to a glass bulb immersed in liquid nitrogen where escaping phosphorus vapour could be condensed.

Although the phosphorus trap was successful, it was found that the connections within the furnace were not gas-tight and it was considered doubtful whether even accurate machining of the tapered connections would prevent the leakage of phosphorus. Investigations in this direction were consequently discontinued.

(ii) Silica Crucibles

A series of experiments were carried out using vitreous silica crucibles, 45 mm. O.D. by 1 mm. wall by 3". Since silica softens at iron-making temperatures, the crucibles were supported inside closely fitting graphite crucibles.

A simple phosphorus bearing silica saturated slag was chosen with the aim of eliminating crucible attack. Reference to "Phase Diagrams for Ceramists" (1964) shows that the 3CaO. P_2O_5 -SiO₂ system has a low melting point eutectic at a temperature of 1550°C and composition of approximately 10 mole pct. or 2 wt. pct. SiO₂. The expected saturation level at 1600°C is only slightly above this concentration.

The powder components 3CaO. P_2O_5 and SiO₂ were mixed to

give ${\rm SiO}_2$ contents of 1, 2, 6, 9, 12 and 20 wt. pct. and the powders were compressed into pellet form. Pellet charges of 25 gm. were melted in SiO₂ crucibles at 1600°C, and it was found that no crucible attack occurred with the 6 and 9 wt. pct. SiO₂ slags after one hour. Higher concentrations were of a doughy consistency whilst lower SiO₂ contents caused crucible corrosion. However, when further experiments were carried out using carbon saturated iron and the 9 wt. pct. SiO₂ slag, a vigorous reaction was observed and the crucible was penetrated within 15 minutes. The same crucible arrangement with an inner sleeve of 2 mm. wall thickness did not alleviate this problem. It appears from the work of Schverdtfeger and Engell (1963) that a loss of P₂O₅ from a SiO₂ saturated 3CaO. P₂O₅-SiO₂ slag is accompanied by an increase in the SiO₂ saturation level. This would account for the SiO₂ crucible dissolving in the slag during these reduction experiments.

(iii) Zircon Refractories

Preliminary experiments using graphite crucibles lined with zircon (ZrO₂. SiO₂) sleeves showed no sleeve attack. Carbon saturation was maintained in the metal phase by direct contact with the graphite crucible.

The reaction vessel was first designed so that the bottom end of the sleeve was located slightly below the slag/metal interface in order to prevent slag/crucible reaction and to expose the metal phase to the graphite wall. This would facilitate radio-activity measurements in the

Slag	Composition (by weight)					
No.	CaO	MgO	SiO2	Al ₂ O ₃	P205*	FeO
A	30	10	40	20	5	
В	38	-	42	20	5	-
С	23 .		62	15	5	
D	30	8	62		5	
. Е	50	5	45	3 - A - A	5	
F	28	14	26	-	7	24

* The compositions of all slags except F represent the percentages by weight excluding the P_2O_5 content which represents a 5 wt. pct. addition to the slags.

TABLE R-1.1 The Composition of Synthetic Slags.

event of radio P-32 isotope being used, since the graphite crucible wall would act as a window for the radiation and the risk of absorption by zircon would be eliminated. However, a tendency for the slags to wet the sleeves, both inside and outside, prevented their use and the longer sleeves described in Section R-3.3.4 had to be used.

A series of experiments were carried out using the phosphate bearing slags listed in Table R-1. L carbon saturated iron and long zircon sleeves. After one hour at 1600°C, it was found that Slags A, B, C and D had wet the zircon sleeves, climbed out and reacted with the graphite supporting crucibles. Slag E under the same conditions badly attacked the sleeve material. At a lower temperature of 1400°C, Slag D remained unmelted and Slag A was contained without climb and with only slight reaction with the sleeve at the slag/metal interface. Subsequently, kinetic experiments were successfully carried out using zircon sleeves and a slag of composition A at 1400°C.

(iv) Zirconia Refractories

Further tests were carried out to determine whether zirconia (ZrO₂) sleeves could be employed for reduction experiments. These indicated that there was no chemical reaction with the slag. A sharp interface between the sleeve and slag phase was observed (Figure R-7) and the slag layer could be parted from the sleeve without difficulty. A more detailed investigation, involving mass balance considerations, showed that the sleeve did in fact absorb a considerable amount of slag. However, a correction was made for slag absorption and successful experiments were carried out at 1400°C and 1500°C using Slag A.

(v) Magnesia Crucibles

It was intended that steelmaking experiments, involving phosphorus transfer from iron to a synthetic steelmaking slag, would be undertaken using the carbon resistance furnace. Commercially produced recrystallised magnesia crucibles were to be used as reaction vessels. However, a synthetic Slag F, Table R-1. 1, and Armco iron were heated in a magnesia crucible at 1600°C for one hour to determine whether significant crucible attack would occur. It was found that the slag completely penetrated the crucible wall and flowed down the supporting refractories. The crucible remained uncracked and apparently unattacked. However, the porosity of these crucibles rendered them useless for further steelmaking investigations.
APPENDIX R-2

A RADIO-TRACER TECHNIQUE FOR PHOSPHORUS

TRANSFER STUDIES IN IRON AND STEELMAKING

SLAG/METAL SYSTEMS

Radio-isotopes have been used to study a variety of physical and chemical processes. Gamma-emitting isotopes are particularly suitable since the electromagnetic gamma radiation may be detected at relatively large distances from the radiation source. This facilitates the experimental measurement of radiation intensity, especially under high temperature conditions where it is essential that the detecting instrument is located in a cool region at some distance from the source.

The electron radiation from beta-emitting isotopes is more susceptible than gamma-radiation to absorption and, from a practical standpoint, its measurement is restricted insofar as the detector must be located very close to the radiation source. However, betaemitters give rise to Bremsstrahlung, a secondary gamma-radiation, which is produced when beta particles are slowed down in passing through their own carrier material or through some external absorber. Bremsstrahlung consists of a characteristic radiation, due to excitation of the electron shells surrounding the atomic nuclei of the absorber, which is superimposed on a continuous spectrum resulting from the interaction of the beta particles with the atomic nuclei. The intensity of this secondary radiation is proportional to the atomic number of the absorber and the energy of the continuous spectrum ranges from the maximum energy of the beta-radiation to zero.

Phosphorus has one important radio-isotope, P-32, which is a pure beta-emitter and may be obtained by neutron irradiation of the stable isotope P-31:

 $\stackrel{31}{\stackrel{n}{\xrightarrow{}}} \stackrel{n}{\longrightarrow} \stackrel{32}{\stackrel{n}{\xrightarrow{}}} \stackrel{32}{\longrightarrow} \stackrel{32}{\xrightarrow{}} \stackrel{32}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{} } \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}} \stackrel{\beta}{\xrightarrow{}}$

P-32 has a maximum beta-decay energy, $E_{max} = 1.7$ Mev and a radioactive half-life, $t\frac{1}{2} = 14.3$ days. The presence of this isotope in iron gives rise to Bremsstrahlung radiation.

The possible application of Bremsstrahlung to the kinetics of dephosphorisation of liquid iron was suggested by Dibbs (1960) and could also be applied to the reduction of phosphorus in simulated blast furnace slag/metal systems. In a conventional study it is necessary to either "freeze" or take samples at various stages from the slag/ metal system in order to analyse for phosphorus. In principle, the radio-tracer technique could be employed to determine the phosphorus content of the metal throughout an experiment by continuously monitoring the Bremsstrahlung emitted from the iron phase. This is an advantage in itself and, further, eliminates the necessity for conventional sampling, which disturbs the temperature and mass of the system, and time-consuming chemical analysis.

Dibbs (1960) demonstrated the feasibility of this technique by conducting experiments in the solid state at room temperature. The arrangement consisted of an alumina crucible containing pelletised iron powder (density 6 gm/cm^3) above which was placed a compressed pellet of lime corresponding to the slag phase. Both phases contained a known amount of P-32 and the total beta activity was maintained at 250 μ c. which was taken as 100 pct. activity. (1 μ c. = 3.7 x 10⁴ disintegrations/sec.). A series of pellets was employed in which the beta activity in the metal phase was varied from 0 to 100 pct. whilst the corresponding activity in the slag phase was 100 to 0 pct. A scintillation detector was placed axially, 18" below the base of the crucible in order to measure the Bremsstrahlung count rate. A linear relationship was obtained between the count rate and the beta activity in the metal (or the slag), the count rate being 150 cpm at 0 pct. and 1000 cpm at 100 pct. beta activity in the metal. This indicated that the Bremsstrahlung count rate was linearly proportional to the phosphorus concentration in the metal.

The major problems in applying this technique to high temperature studies are experimental difficulties associated with the containment of phosphorus within the crucible. The escape of P-32 into the furnace atmosphere would be a health hazard and would also result in a contamination which would interfere with further radioactivity measurements. If the problem of phosphorus containment can be surmounted, the P-32 tracer technique appears to be quite feasible. P-32 could be introduced into the slag phase in the form of calcium phosphate $(3CaO. P_2O_5)$ since the irradiation of this compound does not result in the formation of appreciable amounts of calcium or oxygen radioisotopes. Harvey (1962) showed that the activity of a neutron irradiated sample may be calculated from:

$$-\frac{\mathrm{dX}}{\mathrm{dt}} = \mathrm{N} \, \boldsymbol{o} \cdot \mathrm{F} \, \lambda \, \mathrm{t}$$

where t is the time for irradiation of N atoms with radiation crosssection, σ , by a neutron flux, F. X is the number of disintegrations and λ is the decay constant of the radio-isotope. This equation may be used to calculate the radio-activity of a calcium phosphate sample which has been irradiated in the McMaster University nuclear reactor which has a flux of $F = 6.7 \times 10^{12}$ neutrons/cm²/sec. To obtain a P-32 activity of 5 µc. in a sample containing 1 gm. of phosphorus requires irradiation for 12.6 sec. This results in an activity of 0.05 µc. for the beta-emitter Ca-45 and 2 µc. for the beta-emitter 0 - 19. However, 0 - 19 has a short half life of 19 sec., compared with 14.3 days for P-32, and its activity falls to one thousandth of this level within 5.5 hours. Thus, the interference from Ca and oxygen isotopes would be less than 1 pct. after 5.5 hours.

APPENDIX R-3

THE DETERMINATION OF THE RATE OF SLAG ABSORPTION

BY ZIRCONIA SLEEVES AT 1400°C

Three experiments were undertaken in order to determine the rate of absorption of slag by zirconia sleeves under conditions simulating those for phosphorus reduction studies. The same experimental procedure was employed and the weights of slag and sleeve were approximately the same as in the kinetic experiments. However, the carbon saturated iron was replaced by approximately the same weight of copper in order to prevent slag/metal reaction since carbon does not dissolve in copper.

The sleeves were weighed prior to the experiments and, after the slag was charged, the temperature was maintained at 1400°C for periods of 20, 60 and 360 minutes. The reaction vessel was subsequently withdrawn from the furnace, broken open and the sleeve weighed after chipping away any adhering slag.

The results are given in Table R-3.1. and the amount of slag absorbed by zirconia is given as a function of time in Figure R-3.1. The error bars represent the uncertainty in estimating the weight of slag absorbed and is due to adhesion of some slag and the loss of some chips of zirconia when the slag was being removed. It will be observed (complete curve) that most of the slag is absorbed within the first 60

Experiment	#R-31	#R-32	#R-33
Operating temp. °C	1400	1400	1400
Time at temp. (mins.)	20	60	360
Wt. copper phase (gm)	171.65	179.2	178.8
Wt. slag phase (gm)	60.93	62.13	61.55
Initial sleeve wt. (gm)	208.2	211.2	205.0
Final sleeve wt. (gm)	211.3	220.3	218.1
Wt. slag absorbed by sleeve (gm)	3. 1 <u>+</u> 0. 5	9.1±0.5	13.1 <u>+</u> 1.0

TABLE R-3.1 Experimental conditions and results for the investigation of the rate of slag absorption by zirconia sleeves.



minutes (approximately 10 gm.) and the bulk of the remainder within the next 60-minute period.

For simplicity in calculating the rate of absorption in subsequent mass transfer calculations, it may be assumed that there is a linear rate of absorption of 10 gm. of slag in the first 60 minutes followed by a linear rate of absorption of 4 gm. of slag in the following 60-minute period. It will be seen (broken line) that the approximation is in good agreement with the observed behaviour for the first period and is reasonable for the remaining period.

APPENDIX R-4

METHOD OF COMPUTATION OF THE AVERAGE RATE

OF PHOSPHORUS TRANSFER AND THE MOLE

FRACTION OF P205 IN THE SLAG

(i) The Average Rate of Phosphorus Transfer

The calculation of the average rate of phosphorus transfer is complicated by the fact that metal is removed during sampling and, in the experiments where zirconia sleeves were used, the absorbed slag may contribute to phosphorus transfer at the metal/sleeve interface. However, in these calculations it was assumed that phosphorus reduction in all experiments occurred only at the slag/metal interface, i.e. there is no reaction at the metal/sleeve interface.

The total weight of phosphorus, $(W_P)_{t_n}$, transferred to the metal phase at sampling time, t_n , can be calculated from the initial weight of the metal phase (Tables R-7 to R-11) and the phosphorus analyses and weight of metal removed as samples (Tables R-2 to R-6). Thus, weight of phosphorus transferred = weight of phosphorus in metal + weight of phosphorus in samples:

$$(W_P)_{t_n} = (W_M)_{t_n}$$
. $\frac{wt. pct. P}{100} + \leq t_n t_n \left(W_s. \frac{wt. pct. P}{100} \right)_t$

where W_{M} = weight of metal phase W_{s} = weight of metal sample.

Sample No.	Time (min.)	Metal* Phase (gm)	<u>P</u> (gm)* Metal Phase	P (gm)* in Sample	Total <u>P</u> (gm) Samples
-	0	201.4	-	-	-
1	3	197.09	0.0453	0.0010	0.0010
2	7	192.29	0.1115	0.0023	0.0033
3	15	190.10	0.2414	0.0028	0.0061
4	30	184.73	0.3953	0.0115	0.0176
5	60	179.67	0.5480	0.0154	0.0330
6	90	174.24	0.6604	0.0206	0.0536
7	120	169.48	0.7627	0.0214	0.0750
8	150	163.27	0.7837	0.0298	0.1048
9	180	157.56	0.8036	0.0291	0.1339
10	210	149.62	0.7930	0.0421	0.1760
11	240	140.99	0.7895	0.0483	0.2243
12	300	135.03	0.7967	0.0352	0.2595
13	360	129.43	0.7895	0.0342	0.2937

* Calculated from data in Tables R-4 and R-9.

TABLE R-4.1 Example Calculation of Average Rate of Phosphorus Transfer for Experiment #R-36.

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Sample No.	Total <u>P</u> (gm) Trans- ferred	P (gm) Trans- ferred △t*	Rate x 10 ³ (gm/min.)	Average** Rate (gm/min.)	Average ⁺ Rate, R' (mole/cm ² / sec)	Log R'
-	-	-	-			_
: 1	0.0463	0.0463	15.43	16.28	8.14	7.9106
2	0.1148	0.0685	17.12	16.86	8.43	7.9258
3	0.2475	0.1327	16.59	13.81	6.91	7.8395
4	0.4129	0.1654	11.03	8.315	4.16	7.6191
5	0.5810	0.1681	5.603	5.018	2.51	7.3997
6	0.7140	0.1330	4.433	4.278	2.14	7.3304
7	0.8377	0.1237	4.123	2.908	1.45	7.1614
8	0.8885	0.0508	1.693	1.663	0.832	8.9201
9	0.9375	0.0490	1.633	1.342	0.671	8.8267
10	0.9690	0.0315	1.050	1.272	0.636	8.8035
11	1.0138	0.0448	1.493	1.100	0.550	8.7404
12	1.0562	0.0424	0.7066	0.578	0.289	8.4609
13	1.0832	0.0270	0.4500	-	-	-

* During period between samples.

$$** \times 10^{3}$$

 $+ \times 10^{7}$

TABLE R-4.1 (Continued)

The total weight of phosphorus transferred in the time interval t_{n-1} to t_n is then:

$$(W_{P})_{t_{n}} - (W_{P})_{t_{n-1}}$$
 (gm)

and the rate of transfer in the time interval t_{n-1} to t_n :

$$R_{t_{n-1},t_{n}} = \frac{(W_{P})_{t_{n}} - (W_{P})_{t_{n-1}}}{t_{n} - t_{n-1}} \qquad (gm./min)$$

The average rate of transfer at time, t_n , is then:

$$R_{t_n} = \frac{R_{t_{n-1},t_n} + R_{t_n,t_{n+1}}}{2}$$
 (gm./min)

The average specific rate of transfer across a slag/metal interface of area A (cm^2) may be calculated by a simple conversion:

$$R_{t_n} = \frac{R_{t_n}}{60 \times 31 \times A} \qquad (moles P./cm^2/sec)$$

A sample calculation of the average rate of phosphorus transfer for experiment R-36 is given in Table R-4.1.

(ii) The Mole Fraction of P2O5 in the Slag Phase

The mole fraction of P₂O₅ in the slag phase was obtained by mass balance considerations since slag analyses were not available. It was assumed that the slag was homogeneous throughout the reaction period and is justified in the initial stages up to 60 minutes since vigorous agitation of the slag phase due to gas evoluation was observed. The calculations are complicated by the fact that slag was removed during metal sampling and slag was absorbed by zirconia crucibles. It was further assumed for all experiments that phosphorus transfer occurred only across the slag/metal interface. The rate of slag absorption was taken to be linear as discussed in Appendix R-3.

The initial composition and weight of synthetic slag are known and the weight of phosphorus transferred can be calculated for the metal phase. The initial conditions may be written as:

t = O:
$$P_i$$
 = wt. pct. phosphorus in slag
 W_i = wt. of slag (gm.)
 w_i = wt. of phosphorus in slag (gm.)
t = t_1: m_1 = wt. of phosphorus transferred (gm.)
 $\equiv M_1$ gm. P_2O_5 in slag
 A_1 = wt. of slag absorbed by sleeve (in the case
of zirconia sleeves) (gm.)

L₁ = wt. of slag removed during sampling (gm.)

The weight of slag prior to sampling at t₁:

$$W_1 = W_i - M_1$$

and its phosphorus content:

$$w_1 = w_i - m_1$$

The phosphorus content (wt. pct.) of the slag at t₁:

$$P_{1} = \frac{w_{1}}{W_{1}} \cdot 100$$

This is, in fact, an over-estimate for experiments with zirconia crucibles since the average phosphorus content of the absorbed slag will lie in the range P_1 to P_i . However, the correction results in differences

of less than 1 pct. in the values for the phosphorus concentrations and is not included in the calculation.

The weight of slag available for further reaction after the sample at t_1 has been taken is:

$$W_1 = W_1 - L_1 - A_1$$

and the weight of available phosphorus in the slag phase:

$$w'_1 = W'_1 P_1$$

 $t = t_2$: $m_2 = wt$. of phosphorus transferred (gm.) $\equiv M_2$ gm. P_2O_5 in

slag

 $A_2 = wt.$ of slag absorbed by sleeve (gm.)

L₂ = wt. of slag removed during sampling (gm.)

The computation cycle is repeated:

$$W_2 = W_1 - M_2$$

 $W_2 = W_1 - M_2$

and the phosphorus concentration is calculated to be:

$$P_2 = \frac{w_2}{W_2} \cdot 100$$

The cycle is repeated for all experimental data.

Having obtained the values of wt. pct. phosphorus in the slag phase, the corresponding values of wt. pct. P_2O_5 may be calculated. The mole fraction, $X_{P_2O_5}$, is then obtained from the relation:

$$x_{P_2O_5} = \frac{\underbrace{(wt. pct. P_2O_5)}_{142}}{\leqslant \frac{wt. pct. i}{M_i}}$$

where i represents the component oxides in the slag phase.

Sample Time (Min)	P* Transferred (gm)	(P2O5) [‡] Removed (gm)	Wt. Slag (gm)	Wt. P in Slag (gm)	Wt. Pct. P in Slag	Wt. Slag + Sample (gm)	Wt. Slag × Absorbed (gm)
0 3 7 15 30 60 90 120 150 180 210 240 300 360	0.046 0.068 0.133 0.165 0.168 0.133 0.124 0.051 0.049 0.032 0.045 0.045 0.042 0.027	$\begin{array}{c} 0.11\\ 0.16\\ 0.30\\ 0.38\\ 0.38\\ 0.30\\ 0.28\\ 0.17\\ 0.11\\ 0.07\\ 0.10\\ 0.10\\ 0.10\\ 0.06\\ \hline 2.52\end{array}$	67.04 66.93 64.49 62.31 59.65 55.31 48.09 44.55 44.05 43.77 43.34 42.68 41.97 41.49	1.394 1.348 1.231 1.063 0.862 0.634 0.419 0.266 0.213 0.163 0.129 0.082 0.039 0.011	2.08 2.01 1.91 1.71 1.44 1.14 0.871 0.597 0.483 0.373 0.298 0.192 0.093 0.026	1.78 1.28 0.88 1.46 1.92 1.26 0.33 0.17 0.36 0.56 0.61 0.42 0.16	0.50 0.60 1.40 2.50 5.00 2.00 - - - - - -
	4 Contraction of the second second	2.56		EGCNT24 Stable			

* Calculated for time period between samples (see TABLE R-4.1)

 \neq P₂O₅ = 2.29 x (P transferred to metal in Column 2)

+ See TABLE R-4

x See TABLE R-9

TABLE R-4.2

Example Calculation of the Mole Fraction of P_2O_5 in the Slag for Experiment R-36.

Sample Time (Min)	Wt. Slag * (gm)	Wt. P [*] in Slag (gm)	Wt. Pct. P ₂ O ₅	Mole Fraction $XP_2O_5.10^2$	Log X _{P2O5}
0 3 7 15 30 60 90 120 150 150 180 210 240 300 360	64.65 62.61 60.03 55.69 48.39 44.83 44.22 43.88 43.41 42.78 42.07 41.55 41.33	- 1.299 1.196 1.027 0.802 0.552 0.390 0.264 0.212 0.161 0.127 0.081 0.038 0.019	4.76 4.60 4.37 3.91 3.29 2.61 1.99 1.36 1.106 0.853 0.682 0.439 0.213 0.595	2.10 2.03 1.93 1.73 1.45 1.15 0.88 0.60 0.49 0.376 0.301 0.194 0.094 0.027	$ \begin{array}{r} \overline{2.322} \\ \overline{2.308} \\ \overline{2.286} \\ \overline{2.238} \\ \overline{2.161} \\ \overline{2.061} \\ \overline{3.944} \\ \overline{3.778} \\ \overline{3.690} \\ \overline{3.575} \\ \overline{3.479} \\ \overline{3.288} \\ \overline{4.973} \\ \overline{4.431} \\ \overline{4.431} \end{array} $

* After removal of slag during sampling and due to absorption by sleeve

TABLE R-4.2 (continued)

During the phosphorus reduction experiments, it is assumed that only P_2O_5 is removed from the slag phase and that the relative proportions of the components CaO, SiO₂, Al₂O₃ and MgO remain unchanged. The initial P_2O_5 content of the slag was calculated to be 4.76 wt. pct. and the value decreases during reduction. For slags of composition A (Table R-1) the relationship between wt. pct. concentrations and mole fraction for values up to 4.76 wt. pct. P_2O_5 was found to be:

(wt. pct.
$$P_2O_5$$
) = 2.27 x 10² $X_{P_2O_5}$

This is an approximation since the relation between the concentration terms is not strictly linear. However, the maximum difference is less than 3 pct. of the actual concentration value and the approximation approaches the corrected values at higher concentrations, i.e. corresponding with the early stages of the experiments. This is considered to be an extremely close approximation compared with the assumption of slag absorption.

An example calculation of the mole fraction of P_2O_5 in the slag for experiment R-36 is given in Table R-4.2.

APPENDIX S-1

DETERMINATION OF PHOSPHORUS IN

STEEL BY A PHOTOMETRIC METHOD*

Summary of Method

After dissolution of the sample in acid, an aliquot is treated with sodium sulphite and ammonium molybdate-hydrazine sulphate solutions. A phospho-molybdenum complex is formed which is reduced by hydrazine sulphate to form the molybdenum blue complex suitable for photometric measurements.

Reagents

1.	Acid Mixture:	H ₂ O	l vol.
		HNO ₃	l vol.
		HC10 ₄ (conc. 70%)	2 vol.

2. Sodium Sulphite Solution:

150g Na_2SO_3 . 7 H_2O in 1 litre H_2O , or 75g Na_2SO_3 in 1 litre H_2O .

Prepare fresh solution daily.

- <u>Reduction Mixture</u>: Dilute 25 ml. of Sol. (a) with H₂O to 80 ml., add 10 ml. of Sol. (b) and dilute to 100 ml. Solution unstable, prepare fresh solution daily.
 - a. Molybdate Solution: Add 600 ml. H₂SO₄ (1:1) into
 200 ml. H₂O, cool, dissolve 20g ammonium molybdate, and dilute to 1 litre.

*Adelt and Gruendler, Arch. Eisenhuttenwesen, (1948), 19, 21-24

b. Hydrazine Sulphate Solution: Dissolve 1.5g
 hydrazine sulphate in 1 litre H₂O.

Procedure

Dissolve 0. 250g sample in a 100 ml. erlenmeyer flask in 15 ml. of reagent (1) and evaporate to copious white fumes.

After cooling, transfer to a 50 ml. volumetric flask, and fill to mark.

Transfer 10 ml. aliquot to a 100 ml. volumetric flask, add 10 ml. reagent (2) and boil for 20 to 30 seconds.

Add 20 ml. reagent (3) and heat on water bath at $\sim 85^{\circ}$ -90°C for 20 minutes.

After cooling, dilute to 100 ml. and mix.

The blue color of the phosphorus-molybdate complex has now been developed and is stable for about 2 hours.

Measure the color intensity using filter 6 on the Unicam color photometer against a blank. (Either distilled water, or blank solution produced from the reagents without initial sample.)

It is advisable to carry one or two standard samples through the reagent treatment to check the method.

It has been found that the photometer reading multiplied by . 6 gives wt. pct. P.

APPENDIX S-2

CALCULATION OF MOLE FRACTION OF PHOSPHORUS IN THE METAL PHASE AND THE CORRESPONDING AVERAGE RATE OF

PHOSPHORUS TRANSFER

Tables S-8 to S-13 list the sampling times and corresponding phosphorus analyses of the metal for the specified experiments and these were taken from Tables S-5 to S-7. The mole fraction, X_p , of phosphorus in the metal is also tabulated and was calculated from the expression:

$$X_{p} = \left(\frac{\text{wt. pct. P}}{\text{atomic wt. P}}\right) \left| \left(\frac{\text{wt. pct. Fe}}{\text{atomic wt. Fe}}\right) \right|$$
$$= \frac{\text{[wt. pct. P]}}{\frac{56}{31 \times 100}}$$
$$= 1.805 \times 10^{-2} \text{[wt. pct. P]}$$

which assumes dilute solution conditions.

The average rate of phosphorus transfer was obtained in the following manner. The initial weight of metal phase was computed for each experiment in Table S-1 as the total weight of the metal and ferrophosphorus charged. It was assumed that the weight of metal charge remained constant throughout an experiment; i. e. sampling losses were neglected since the total effect of samples with weights as great as 5 gm. would lead to an error of less than 2 pct. in estimating the weight of the bulk phase (approximately 2500 gm.). The phosphorus content (gm.) at any sampling time, t'_n , was then calculated and the weight of phosphorus transferred during the period between sampling times t_n and t_{n+1} was found by difference. The rate of transfer (moles P/cm²/sec) in the period t_n to t_{n+1} was then calculated from the expression:

$$Rate_{t_n-t_{n+1}} = \frac{(P \text{ gm. transferred})}{31} \cdot \frac{1}{A} \cdot \frac{1}{(t_{n+1}-t_n)}$$

where A is the area of slag/metal interface, assumed equal to the cross sectional area of the crucible, and t is measured in seconds.

The average rate of transfer at any sampling time t_n is finally calculated from the expression:

(Average rate)_{t_n} = $\frac{\text{Rate}(t_{n-1}-t_n) + \text{Rate}(t_n-t_{n+1})}{2}$

APPENDIX S-3

THE RELATIONSHIP BETWEEN THE MOLE

FRACTIONS OF PHOSPHORUS AND OXYGEN

The mole fraction of a component j in a solution, A, of k components may be defined as

$$X_j = \frac{n_j}{\xi n_A}$$

where n_j is the number of moles of component j and ξn_A is the total number of moles of k components in solution A.

The phosphorus concentration at times zero and t are respec-

$$X_{P_i} = \frac{{}^{n_{P_i}}}{\xi_{n_A(t=o)}}$$
 and $X_P = \frac{{}^{n_{P_i}}}{\xi_{n_A(t=t)}}$

If it is assumed that the total number of moles in solution does not change appreciably during phosphorus transfer, then the number of moles of phosphorus transferred

$$n_{P_i} - n_P = (X_{P_i} - X_P) \leq n_A.$$
 (i)

If the same reasoning is applied to phase B in which the oxygen is available for reaction (S. 2), the number of moles of oxygen which react is

$$n_{O_i} - n_O = (X_{O_i} - X_O) \leq n_B.$$
 (ii)

Since oxygen and phosphorus react stoichiometrically in relation (S. 2)

$$2(n_{P_i} - n_{P}) = 5(n_{O_i} - n_{O})$$

It follows from equations (i) and (ii) that

$$2(X_{P_i} - X_P) \leq n_A = 5(X_{O_i} - X_O) \leq n_B.$$
 (iii)

Rearranging (iii)

$$X_{O} = X_{O_{i}} - 2/5 - \frac{\xi n_{A}}{\xi n_{B}} (X_{P_{i}} - X_{P})$$

This reduces to $X_0 = a + 0.X_P$

where the constants

APPENDIX S-4

MASS BALANCE FOR CHANGE

IN THE IRON CONTENT OF THE

SLAG DUE TO DEPHOSPHORISATION

Complete details of slag iron analyses prior to and at the end of dephosphorisation are only provided for Experiment S-25 in Table S-3 and consequently a precise estimate of the mass balance could only be made in this case.

Total weight of metal charged	=	2560 gm. (Table S-1)
Decrease in P content	=	0.372 wt. pct. (Table S-7)
Weight of P transferred	=	$2560 \ge \frac{0.372}{100}$ gm.

~ 9.5 gm.

From relation (S. 19)

	l gm.P	=	4.5 gm. Fe (in slag)
9.	5 gm.P	=	43 gm. Fe (in slag)
Weight of slag charge	ed [:]	=	850 gm. (Table S-1)
Assume slag absorbe	d ,	~	300 gm. (Table S-1)
Initial weight of slag		\sim	550 gm.
Initial Fe content		=	15.9 wt. pct. (Table S-3)
Initial weight of slag	Fe	=	$550 \ge \frac{15.9}{100}$ gm.

~ 88 gm.

Weight of reacted iron (slag)	=	43 gm.
Final wt. of iron (slag)	=	45 gm.
Weight slag (final)	\sim	(550 - 43 + 9.5) gm.
	=	517 gm.
Final Fe content (slag)	=	$\frac{45}{517}$ x 100 wt. pct.
	=	8.7 wt. pct. (estimated)
Final Fe (slag) analysis	=	8.9 wt. pct. (Table S-3)

A less precise estimate was made for Experiment S-18 by the same procedure with satisfactory results:

Final Fe content (slag)	=	13.3 wt. pct. (estimated)
Final Fe analysis	÷	12.05 wt. pct. (Table S-3)

It may reasonably be concluded that, for the experiments under consideration, the decrease in iron content of the slag is accounted for by the dephosphorisation reaction.

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Qrder	Free Mole Fraction	Energy Wt. Pct.	Enth Mole Fraction	Wt. Pct.	Entr Mole Fraction	wt. Pct.	System for Obtaining Property
Zero	$\ln \chi_i^o$	log f _i =O	н ^Е °	J ^{E°} i	s ^{E^o} i	& E ^o i	l-i binary
First	€ ⁽ⁱ⁾ _i	e (i) i	ນ (i) i	h (i) i	σ (i) i	s (i) s i	l-i binary
	€ ^(j) _i	e (j) i	$\gamma_{i}^{(j)}$	h (j) i	$\sigma_{i}^{(j)}$	s (j) i	l-i-j ternary
Second	$\rho_{i}^{(i)}$	r (i) r i	$\lambda_{i}^{(i)}$	1 (i) i	$\mathcal{T}_{i}^{(i)}$	p (i) p i	l-i binary
•	P ^(j) _i	r (j) r i	$\lambda_{i}^{(j)}$	1 (j) 1 i	$\mathcal{T}_{i}^{(j)}$	p (j) p i	l-i-j ternary
	$\rho_{i}^{(j,k)}$	r (j,k) r i	$\lambda_{i}^{(j,k)}$	1 (j,k) i	$\mathcal{T}_{i}^{(j,k)}$	p (j, k) p i	l-i-j-k quaternary



Summary of Interaction Parameters (after Lupis and Elliott, April 1966).

Expt.	Saturator Unit T [°] C	Vapour [*] Pressure pH ₂ O (mm)	Observed ^{**} Pressure (mm) pH ₂ O (corr.)	Difference [#] in pH ₂ O (Pct.)	Flow Rate (1. p. m.)
1/9	28.4	29.02	29.08	+ 0.21	1. 3
1/10	28.4	29.02	28.50	- 1.8	4.5
1/4	36.2	45.05	44.77	- 0. 62	1. 12
1/7	36.2	45.05	43.96	- 2.42	5. 59
1/18	40.8	57.72	58.21	+ 0.85	0.62
1/16	40.85	57.87	56.26	- 2.78	2.05
1/17	40.8	57.72	58.74	+ 1.77	2.08
1/15	49.0	88.02	87.37	- 0.74	0, 35
1/11	48.15	84.31	83.05	- 0, 31	0.54
1/12	48.9	87.58	86.01	- 1.68	4. 2

* Taken from water vapour pressure/temperature tables.

** Calculated from experimental observations corrected to N. T. P.

Difference between observed and theoretical values.

TABLE V-2 Water Vapour Pressure Data for the Saturator Unit.

Analysis Wt. Pct.	Armco Iron	Ferrovac - "E" - F 82
С	0. 012	0.003
Mn	0.017	0.001
S	0.025	0.005
Р	0.005	0.003
0	0.075	<0.006
Si		0.00096

TABLE V-3 Analysis of Armco Iron and Ferrovac - "E".

		Average			
Master	First A	Analysis	Second A	'Wt. Pct.	
Alloy	End (a)	End (b)	End (a)	End (b)	v
17	0.094	0.094	0.094	0.091	0.093
2V	0.188	0.181	0.184	0.183	0.184
3V	0.280	0.266	0.275	0.269	0.272
4V	0.362	0.367	0.364	0.371	0.366
5V	-		0.447	0.446	0.446
6V	0.530	0.542	0.533	0.528	0.533
7V	0.602	0.615	0.610	0.618	0.611
8V	0.704	0.707	0.697	0.697	0.701
9V	0.787	0.797		0.784	0.789
10V	-	0.844	0.849	9.846	0.846
11V	0.104	0.105			0.105
12V	0.102	0.108			0.105
13V	0.438	0.428			0.430
14V	0.426	0.433			0.433
15V	0.814	0.821			0.817
16V	0.794	0.797			0.795
17V	1.066				
18V	1.088				
19V	1.072				

* Corrected against calibration curves obtained for chemical standards.

<u>TABLE V-4</u> Spectrographic Analyses of Iron-Vanadium Master Alloys.

	Experimental Conditions				Master*	Levitated*	
Experiment	H ₂		H ₂ O/H ₂ **		Alloy	Sample	
	Min.	°C	Min.	°C	Wt. Pct. V	Wt. Pct. V	
2/1-1V	5	1550	5	1550	0.093	0.092	
2/2-1V	5	1550	5	1730	0.093	0.094	
2/3-1V	10	1730		-	0.093	0.093	
2/4-10V	5	1550	5	1600	0.846	0.829	
2/5-10V	5	1600	. 5	1730	0.846	0.833	
2/6-10V	10	1730	-	-	0.846	0.839	

* Spectrographic analysis corrected against calibration curves obtained for chemical standards.

** $\left(\frac{pH_2O}{pH_2}\right) = 4.54 \times 10^{-2}$

TABLE V-5 The Effect of Heat Treatment on the Vanadium

Content of Levitated Samples.

Expt. *	Time (min.)	Wt. Pct. O
3/5-A	1	0.022
3/4-A	2	0.023
3/3-A	5	0.021
3/2-A	10	0.024
3/1-A	15	0.024
3/7-A	15	0.021

* Gas flow rate: 1 l. p. m. H₂.

TABLE V-6The Effect of Time at Temperature on the
Solution of Oxygen in Armco Iron Samples
Levitated at 1685°C and Constant Oxygen
Potential.

Expt. **	Flow Rate 1. p. m.	Wt. Pct. O
3/6-A	0.5	0.022
3/3-A	1	0.021
3/8-A	2	0.021
3/9-A ·	2	0.020
3/10-A	4	0.021
3/11-A	4	0.025
3/12-A	4	0.024

** Time at temperature: 5 min.

TABLE V-7The Effect of Flow Rate on the Solution
of Oxygen in Armco Iron Samples Levi-
tated at 1685°C in Water Vapour/
Hydrogen Atmospheres.

Expt.	Metal T [°] C	$_{\rm T^{o}C}^{\rm Bath}$	$\left(\frac{pH_2O}{pH_2}\right)_{x \ 10^2}_{corr.}$	Wt. Pct. <u>O</u>	к	log K	Flow Rate l. p. m.	Melt Technique
15/24-A 17/6-A 17/7-A 17/8-A	1450 '' ''	42.2 "' "'	8.80 8.99 "	0.0076 0.005 0.005 0.005 0.006	11.6 18.0 18.0 15.0	1.063 1.255 1.255 1.176	1.6 2.5 "	$N_2 \rightarrow H_2/H_2O$
15/18-A 15/19-A 15/20-A 15/21-A	1500 '' ''	42 . 2 '' ''	8.79 8.80 "	0.0103 0.0078 0.0083 0.0095	8.53 11.3 10.6 9.27	0.931 1.052 1.025 0.967	1.6 1.2 1.3 1.5	$N_2 \rightarrow H_2/H_2O$
15/5-A 15/7-A 15/17-A 18/6-A 24/1-A 24/4-A 25/1-A 25/10-A	1550 "' "' "' "' "'	42. 3 '' 42. 2 '' 31. 7 '' 24. 7 ''	9.02 " 8.79 9.02 4.83 " 3.18	0.0119 0.0136 0.0118 0.014 0.008 0.007 0.004 0.004	7.59 6.64 7.45 6.44 6.04 6.82 7.96 7.96	0.880 0.822 0.872 0.809 0.781 0.834 0.901 0.901	1.5 1.4 1.0 1.3 1.0 1.0 1.0 1.2	$N_{2} \rightarrow H_{2_{11}} \rightarrow H_{2}/H_{2}O$ $N_{2} \rightarrow H_{2_{11}}/H_{2}O$ $He \rightarrow H_{2_{11}}/H_{2}O$ $Ar \rightarrow H_{2}/H_{2}O$

TABLE V-8

Experimental Data, Techniques and Calculated Values of the Equilibrium Constant, K, at 1450°, 1500° and 1550° C.
Expt.	$Bath T^{\circ}C$	$ \begin{pmatrix} pH_2O \\ pH_2 \end{pmatrix} \times 10^2 \\ corr. $	Wt. Pct. O	K	log K	Flow Rate l. p. m.	Melt Technique	Experimental Modifications
17/1-A 17/2-A 17/3-A 17/4-A 17/5-A 18/3-A 18/4-A	42. 3 " " " " 42. 2 " "	9.08 9.10 9.09 "' " 9.02	0.015 0.015 0.016 0.015 0.014 0.015 0.015	6.05 6.07 5.68 6.05 6.49 6.01 6.01	0.782 0.783 0.754 0.782 0.812 0.779 0.779	1.0 	N ₂ → H ₂ /H ₂ O "' "' "'	Sample dropped into mould. Reaction tube with side arms.
21/1-A 21/2-A 21/3-A 21/4-A 21/6-A 21/7-A 21/8-A 21/9-A 22/1'-A 22/1'-A 22/5-F 22/6-F. 22/7-F	31.6 "" "" "" 31.7 "" ""	4.83 "" "" 4.81 "" 4.87 "" " "	0.008 0.010 0.007 0.009 0.010 0.007 0.009 0.007 0.007 0.010 0.008 0.008	6.04 4.83 6.90 5.37 4.83 6.87 5.35 6.87 6.97 4.86 6.10 6.10	0.781 0.684 0.839 0.730 0.684 0.837 0.728 0.837 0.843 0.843 0.687 0.785 0.785	1.0 "" "" "" "" "" 1.2 ""	$N_{2} \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2} \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2} \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2}/H_{2}O$	Ferrovac "E" samples.

<u>TABLE V-9</u> Experimental Data, Techniques and Calculated Values of the Equilibrium Constant, K, at 1600°C.

Expt.	Bath T [°] C	$\left(\frac{\text{pH}_2\text{O}}{\text{pH}_2}\right)_{\text{corr.}} \times 10^2$	Wt. Pct. O	K	log K	Flow Rate 1. p. m.	Melt Technique	Experimental Modifications
15/11-A 15/12-A 15/13-A 18/5-A 18/7-A 18/8-A	42.3 42.2 ''	8.99 8.77 " 9.02	0.0282 0.0272 0.0253 0.030 0.026 0.029	3. 19 3. 22 3. 47 3. 01 3. 47 3. 11	0.504 0.508 0.540 0.478 0.540 0.493	1.0 ''' ''' '''	$N_2 \rightarrow H_2 \rightarrow H_2 / H_2 O$ $N_2 \rightarrow H_2 / H_2 O$ $H_2 / H_2 O$ $H_2 / H_2 O$	Reaction tube with side arms.
21/10-A 21/11-A 21/12-A 22/2-F 22/3-F 22/4-F	31.7 "" "" ""	4.81 '' 4.87 ''	0.013 0.012 0.014 0.014 0.014 0.014 0.015	3.70 4.01 3.44 3.48 3.48 3.25	0.568 0.603 0.536 0.542 0.542 0.542 0.512	. 1. 0 	$N_2 \rightarrow H_2/H_2O$ $He \rightarrow H_2 \rightarrow H_2/H_2O$ $He \rightarrow H_2/H_2O$ $He \rightarrow H_2/H_2O$	Ferrovac "E" samples.
23/3-A 23/4-A 23/5-A 23/6-F 23/7-F 23/8-F	31.7 "" ""	24.94 "' 24.86 "'	0.086 0.087 0.084 0.087 0.080 0.090	2.90 2.86 2.97 2.86 3.11 2.76	0.462 0.457 0.473 0.456 0.492 0.441	4.0 4.2 4.0 7.0 6.0 6.0	$Ar \rightarrow H_2 \rightarrow Ar/H_2/H_2O$	Ar-19.6% H ₂ mix- ture. Ar-19.6% H ₂ mix- ture. Ferrovac ''E'' samples.

TABLE V-10Experimental Data, Techniques and Calculated Values of the EquilibriumConstant, K, at 1700°C.

Expt.	Metal T [°] C	Bath T [°] C	$\left(\frac{pH_2O}{pH_2}\right) \times 10^2$	Wt. Pct. O	к	log K	Flow Rate 1. p. m.	Melt Technique
15/8-A 15/9-A 15/10-A 26/1-A 24/17-A 24/18-A	1650 '' '' '' ''	42. 3 " 40. 6 31. 7 31. 7	8.99 " " 8.10 4.83 "	0.0202 0.0218 0.0203 0.018 0.010 0.013	4.45 4.12 4.43 4.50 4.83 3.72	0.648 0.615 0.646 0.653 0.684 0.570	1.0 "' " " "	$N_2 \rightarrow H_2 \rightarrow H_2/H_2O$ H_2/H_2O H_2/H_2O H_2/H_2O
15/15-A 17/9-A 27/1-A 27/2-A 24/32-A	1750 '' '' ''	42. 2 '' 40. 6 '' 31. 7	8.77 8.99 8.09 11 4.84	0.0303 0.033 0.029 0.033 0.020	2.90 2.72 2.79 2.46 2.42	0.462 0.435 0.446 0.390 0.383	1.0 '' '' ''	$N_{2} \rightarrow H_{2} \rightarrow H_{2}/H_{2}O$ $N_{2} \rightarrow H_{2}/H_{2}O$ " $H_{2}/H_{2}O$
23/1-A 23/2-A	1800 ''	31.7 ''	24. 94 ''	0.112 0.125	2.23 2.00	0.348 0.300	4.0 4.2	$Ar \rightarrow H_2 \rightarrow H_2O/H_2O$

TABLE V-11 Experimental Data, Techniques and Calculated Values of the Equilibrium Constant, K, at 1650°, 1750° and 1800° C.

Temp. °C	$\frac{1}{T} \ge 10^4 (^{\circ} \text{K}^{-1})$	No. Values log K	log K Mean	Standard Deviation
1450	5.977	4	1, 187	0.091
1500	5.640	4	0.994	0.055
1550	5. 486	. 8	0.851	0.045
1600	5.339	19	0.773	0.051
1650	5.200	6	0.636	0.039
1700	5.068	18	0.510	0.047
1750	4.943	5	0.423	0.035
1800	4.824	_2	0.324	0.024
		66		

TABLE V-12Mean Values and Standard Deviationsof log K at Each Temperature for DataGiven in Tables V-8 to V-11.

Temp. Range °C	Gradient - $\frac{\Delta H^{0}}{4.575}$	Intercept. $\frac{\triangle S^{\circ}}{4.575}$	No. Pts.	Correlation Coeff.	
1450-1800	8674 <mark>+</mark> 263*	-3.876 <u>+</u> 0.102 ⁺	66	0.97	

 $\log K = -\frac{\Delta H^{\circ}}{4.575} \cdot \frac{1}{T} + \frac{\Delta S^{\circ}}{4.575}$

* Error on 1 σ .

+ 95% Confidence Limits.

TABLE V-13 The Effect of Temperature on the

Equilibrium Constant, K.

Expt.	Bath T ^O C	$\left(\frac{pH_2O}{pH_2}\right) \times 10^{2^*}$	Wt. Pct. <u>O</u>	к'	log K'	% <u>v</u>	Melt Technique
24/2-11V 24/3-11V 24/5-13V 24/6-13V 24/6-13V 24/7-13V 24/9-15V 24/10-15V	31, 7 "" "" "" ""	4.83 " 4.88 " " "	0.007 0.006 0.008 0.010 0.008 0.011 0.012	6.90 8.05 6.10 4.88 6.10 4.44 4.06	0.839 0.906 0.785 0.688 0.785 0.647 0.609	0. 105 0. 105 0. 430 0. 430 0. 430 0. 430 0. 817 0. 817	He \rightarrow H ₂ /H ₂ O "' Ar \rightarrow H ₂ /H ₂ O "'
25/2-11V 25/4-13V 25/5-13V 25/6-16V 25/8-17V 25/9-17V	24.7 '' '' ''	3. 18 "' "' "'	0.006 0.007 0.005 0.008 0.009 0.008	5.31 4.55 6.37 3.98 3.54 3.98	0.725 0.658 0.804 0.600 0.549 0.600	0.105 0.430 0.430 0.797 1.066 1.066	Ar→H ₂ /H ₂ O '' '' ''

TABLE V-14 Experimental Data, Techniques and Calculated Values of the Apparent Equilibrium Constant, K¹, at 1550°C.

Expt,	Bath T [°] C	$\left(\frac{pH_2O}{pH_2}\right) \times 10^2$	Wt. Pct. O	K,	log K [']	% <u>V</u>	Flow Rate l. p. m.	Melt Technique
16/1-2V 16/2-4V 26/12-12V 26/13-12V	42. 2 '' 40. 6 ''	9.08 " 8.12 "	0.018 0.020 0.016 0.018	5.05 4.54 5.07 4.51	0.703 0.657 0.705 0.654	0.184 0.366 0.105 0.105	1.0 '' ''	$N_2 \rightarrow H_2/H_2O$ Ar $\rightarrow H_2/H_2O$
21/13-3V 21/14-3V 21/19-4V 21/20-4V 22/8-7V 22/9-7V 22/13-8V 24/8-15V 24/11-15V	31,7 11 11 11 11 11 11 11 11	4.81 "' "' 4.87 "' "' 4.88 "'	0.009 0.010 0.009 0.009 0.012 0.011 0.015 0.012 0.013	5.35 4.81 5.35 5.35 4.06 4.42 3.25 4.06 3.76	0.728 0.682 0.728 0.728 0.609 0.645 0.512 0.609 0.575	0.272 0.272 0.366 0.366 0.611 0.611 0.701 0.817 0.817	1.5 1.2 1.0 "" " 1.2 1.2 1.0 ""	$N_{2} \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2}/H_{2}O$ $He \rightarrow H_{2}/H_{2}O$

TABLE V-15 Experimental Data, Techniques and Calculated Values of the Ap-

parent Equilibrium Constant, K¹, at 1600°C.

Expt.	Bath T ^o C	$\left(\frac{pH_2O}{pH_2}\right) \times 10^{2^*}$	Wt. Pct. O	к'	log K	% <u>V</u>	Melt Technique
20/2-5V 26/2-11V 26/3-11V 26/4-14V 26/5-14V	42.2 40.6 "'	8.96 8.10 "'	0.030 0.019 0.018 0.025 0.025	2.99 4.27 4.50 3.24 3.24	0.476 0.630 0.653 0.511 0.511	0.446 0.105 0.105 0.433 0.433	$N_2 \rightarrow H_2/H_2O$ Ar \rightarrow H_2/H_2O ''
24/19-11V 24/20-11V 24/21-13V 24/12-15V 24/23-16V 24/13-17V 24/14-17V	31.7 "" "" "" ""	4.83 11 4.84 4.88 4.88 4.88 4.88 11	0.011 0.012 0.015 0.016 0.015 0.018 0.019	4.40 4.03 3.22 3.05 3.22 2.71 2.57	0. 643 0. 605 0. 508 0. 484 0. 508 0. 433 0. 410	0.105 0.105 0.430 0.817 0.794 1.066 1.066	

TABLE V-16 Experimental Data, Techniques and Calculated Values of the Apparent Equilibrium Constant, K['], at 1650°C.

Expt.	Bath T ^o C	$\left(\frac{pH_2O}{pH_2}\right) \times 10^{2^*}$	Wt. Pct. O	к'	log K	% <u>V</u>	Melt Technique
20/4-3V 20/5-5V 20/3-7V 20/7-7V 20/8-9V	42. 2 '' '' ''	8.94 "' " 8.79	0.032 0.034 0.037 0.039 0.039	2.79 2.63 2.42 2.25 2.25	0.446 0.420 0.383 0.353 0.353	0.272 0.446 0.611 0.611 0.789	N ₂ → H ₂ /H ₂ O "' "'
26/14-12V 26/15-12V 26/11-16V	40.6 ''	8.12 " 8.10	0.025 0.028 0.041	3.25 2.90 1.98	0.512 0.462 0.296	0. 105 0. 105 0. 795	Ar→ H ₂ /H ₂ O ''
21/15-3V 21/16-3V 21/17-4V 21/18-4V 22/10-7V 22/12-8V	31.7 "" "" "	4.81 "" "" 4.87 "	0.014 0.014 0.016 0.015 0.018 0.019	3. 44 3. 44 3. 01 3. 21 2. 70 2. 56	0.536 0.536 0.478 0.506 0.432 0.409	0.272 0.272 0.366 0.366 0.611 0.701	$N_2 \rightarrow H_2/H_2O$ $He \rightarrow H_2/H_2O$ $He \rightarrow H_2/H_2O$

TABLE V-17 Experimental Data, Techniques and Calculated Values of the Apparent Equilibrium Constant, K¹, at 1700°C.

Expt.	Bath T ^o C	$\left(\frac{\text{pH}_2\text{O}}{\text{pH}_2}\right)_{\text{x 10}} \times 10^{2*}$	Wt. Pct. O	к'	log K ¹	% <u>v</u>	Melt Technique
20/10-5V 20/11-9V	42.2	8.79 ''	0.041 0.049	2.14 1.80	0.331 0.254	0.447 0.789	N ₂ → H ₂ /H ₂ O
26/16-12V 26/17-12V 26/18-14V 26/19-14V 26/7-16V 26/8-17V 26/10-17V	40.6 "" "" "" ""	8.12 "" "" 8.10 ""	0.031 0.033 0.034 0.039 0.043 0.045 0.048	2.62 2.46 2.39 2.08 1.88 1.80 1.69	0. 418 0. 391 0. 378 0. 318 0. 275 0. 255 0. 227	0.105 0.105 0.433 0.433 0.795 1.066 1.066	Ar→ H ₂ /H ₂ O '' '' '' ''
24/26-11V 24/29-13V 24/30-16V 24/31-16V 24/15-17V 24/16-17V	31.7 "" "" ""	4.84 "' "' 4.88 "'	0.020 0.019 0.024 0.026 0.028 0.030	2.42 2.55 2.01 1.86 1.74 1.63	0.383 0.406 0.304 0.269 0.241 0.211	0.105 0.430 0.795 0.795 1.066 1.066	Ar→ H ₂ /H ₂ O '' '' ''

TABLE V-18 Experimental Data, Techniques and Calculated Values of the Ap-

parent Equilibrium Constant, K['], at 1750°C.

Metal T [°]	Intercept [*] log K	Slope+ e (V) O	Correlation Goeff.	No. Pts.
1550	0. 852 + 0. 100	-0.268 <u>+</u> 0.032	-0.89	21
1600	0.768±0.096	-0.244 ± 0.034	-0.80	32
1650	0.634 <u>+</u> 0.068	-0.208 <u>+</u> 0.024	-0.91	18
1700	0.514 <u>+</u> 0.086	-0.189±0.030	-0.76	32
1750	0.424 <u>+</u> 0.053	-0.179 ± 0.016	-0.94	20

* 95% Confidence Limits.

+ Error on lo.

<u>TABLE V-19</u> Statistical Details for the Effect of Vanadium on the Apparent Equilibrium Constant, K¹, where

 $\log K' = \log K + e \binom{(V)}{O} \cdot [wt, \% \underline{V}].$

т°с	т ^о к	<u>8670</u> T	log K	$\Delta \log K$
1440 1450 1460	1713 1723 1733	5.064 5.034 5.005	1. 158	+ 0.030 - 0.029
1490 1500 1510	1763 1773 1783	4.920 4.892 4.865	1.016	+ 0. 028
1540 1550 1560	1813 1823 1833	4.784 4.758 4.732	0.882	+ 0.026 - 0.026
1590 1600 1610	1863 1873 1883	4.656 4.631 4.606	0.755	+ 0.025 - 0.025
1640 1650 1660	1913 1923 1933	4.534 4.511 4.487	0.635	+ 0. 023
1690 1700 1710	1963 1973 1983	4.419 4.396 4.374	0.520	+ 0. 023
1740 1750 1760	2013 2023 2033	4.309 4.288 4.267	0.412	+ 0.021 - 0.021
1790 1800 1810	2063 2073 2083	4.205 4.184 4.164	0.308	+ 0.021

<u>TABLE V-20</u> The Uncertainty in the Value of log K Due to $\frac{+}{10}$ C^o where log K = $\frac{8670}{T}$ - 3.88.

Group	$\left(\frac{pH_2O}{pH_2}\right) \times 10^2$	Error in $\log\left(\frac{pH_2O}{pH_2}\right)$
A	3.18±0.00	± 0. 000
В	4.12±0.03	<u>+</u> 0. 003
с	8.10±0.01	± 0. 0006
D	9.00±0.20	± 0. 01
Е	24. 90 <u>+</u> 0. 05	± 0. 001

TABLE V-21 The Variation of Water Vapor/Hydrogen Ratios for Experimental Data in Figure V-10.

Expt.	Wt. Pct. Q	Experimental Conditions
19/1-A	0.079	Untreated sample.
19/2-A	0.081	Untreated sample.
19/3-A	0.073	Melted in N ₂ ; quenched after 3 sec.
19/4-A	0.053	Melted in N ₂ ; quenched after 30 sec.
19/5-A	0.028	Melted in N ₂ for 30 sec.; cooled in H_2O/H_2 for 10 sec.; quenched.

TABLE V-22

Initial Variation of the Oxygen Content of Armco Iron Prior to Equilibration under Controlled Water Vapour/Hydrogen Atmospheres.

Author	log K	Temperature Range
Present work	$\frac{8670}{T}$ - 3.88	1450-1800
Shiraishi (1966)	$\frac{7159}{T}$ - 3.23	1470-1750
Tankins et al (1964	$\frac{6817}{T}$ 3. 13	1550-1700
Matoba and Kuwana (1965)	$\frac{7480}{T}$ - 3.421	1550-1663
Sakao and Sano (1960)	$\frac{7040}{T}$ - 3.224	1550-1650
Floridis and Chipman (1958)	$\frac{7050}{T} - 3.20$	1550-1600
Averin et al (1955)	$\frac{9440}{T}$ - 4.536	1550-1700
Chipman and Dastur (1949)	$\frac{7050}{T}$ - 3.17	1560-1760

TABLE V-23

Comparison of the Temperature Dependence of log K for the Present Work with Previous Data.

· · · · · · · · · · · · · · · · · · ·			
Author	Technique	Atmosphere	Concentration*
Larche' (1968)	Levitation	co ₂ /co	644
Gokcen (1956)	Crucible	co ₂ /co	743
Present Work Tankins et al (1964)	Levitation Crucible	н ₂ 0/н ₂ н ₂ 0/н ₂	644 1130
Sunderland (1968) Donderlinger (1968)	Levitation Crucible	H ₂ S/H ₂ H ₂ S/H ₂	2100 2700

* Calculated for 1600°C and gas ratios of

$$\left(\frac{CO_2}{CO}\right) = 5.641 \times 10^{-2}, \left(\frac{H_2O}{H_2}\right) = 36.58 \times 10^{-2}, \left(\frac{H_2S}{H_2}\right) = 7.0 \times 10^{-4}$$

TABLE V-24A Comparison of Oxygen and Sulphur Concentrations in Ironfor Levitation and Crucible Experiments ConductedUnder CO_2/CO , H_2O/H_2 , and H_2S/H_2 Atmospheres.

Metal T [°] C	Expt. e (V) O	$\varepsilon_{O}^{(V)} = \varepsilon_{V}^{(O)}$	Calculated e (O) v
1550	-0.268	-56.2	-0.863
1600	-0.244	-51.2	-0.788
1650	-0.208	-43.6	-0.672
1700	-0.189	-39.7	-0.613
1750	-0.179	-37.6	-0.581

 $M_V = 50.95$ $M_{Fe} = 55.85$ $M_O = 16.00$ $\mathcal{E}_{O}^{(V)} = 230 \frac{M_{V}}{M_{Fe}} = \frac{(V)}{O} + \frac{M_{Fe} - M_{V}}{M_{Fe}}$ $= 209.8 e_{O}^{(V)}$

 $\mathcal{E}_{V}^{(O)} = 230 \frac{M_{O}}{M_{Fe}} e_{V}^{(O)} + \frac{M_{Fe}^{-M_{O}}}{M_{Fe}}$ = 65.9 e_{V}^{(O)} + 0.7

TABLE V-25	Values of the	Free	Energy	Interaction
	Parameters	$\epsilon_{o}^{(v)}$, $\epsilon_v^{(0)}$, and e $\binom{(O)}{V}$

	e (V) =	$\frac{h \binom{(V)}{O}}{4.575 \text{ T}} - \frac{s \binom{(V)}{O}}{4.575}$		
Temp. Range °C	Gradient = $\frac{h^{(V)}}{\frac{O}{4.575}}$	Intercept = $-\frac{s}{4.575}^{(V)}$	No. Pts.	Correlation Coeff.
1550-1750	-1740 <u>+</u> 277	0.6886±0.0116	5	+0.99

TABLE V-26 The Effect of Temperature on the Free

Energy Interaction Parameter, $e \begin{pmatrix} V \\ O \end{pmatrix}$.

% V Temp. °C	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0. 7	0.8	0.9	1. 0
1550	0.970	0.941	0.885	0.832	0.783	0.736	0.692	0.651	0.613	0.576	0.542
1600	0.973	0.946	0.895	0.847	0.802	0.759	0.718	0.679	0.643	0.608	0.575
1650	0.975	0.952	0.905	0.861	0.820	0.780	0.742	0.706	0.672	0.639	0.608
1700	0.978	0.957	0.915	0.875	0.837	0.801	0.766	0, 733 [.]	0.701	0.670	0.641
1750	0.980	0.962	0.924	0.889	0.854	0.821	0.790	0.759	0.730	0.702	0.674

TABLE V-27 The Activity Coefficient of Oxygen in Iron-Vanadium

Oxygen Alloys.

All experiments employed

- 1. Carbon saturated iron
- 2. Carbon crucible
- 3. Slag A (*)

Expt. #	T°C	Sleeve	Stirring Conditions	Sleeve ID cm	Area cm ²
R-38	1400	Zircon	Stirring ~100 rpm	3.95	12.25
R-39	1400	Zircon	No stirring	3.85	11.64
R-36	1400	Zirconia	Stirring ~100 rpm	3.70	10.75
R-41	1400	Zirconia	No stirring	3.70	10.75
R-37	1500	Zirconia	Stirring ~100 rpm	3.70	10.75

(*)

Analysis of Slag A

Component	Wt. Pct.
CaO	28.6
MgO	9.5
SiO ₂	38.1
Al2O3	19.1
P205	4.76
	100.06

TABLE R-1

Experimental Conditions for Phosphorus Reduction from Synthetic Blast Furnace Slags

Sample #	Time (Min)	[P] Wt. Pct.	Sample Metal (gm)	Slag Removed (gm)
1	*	-	1.88	
2	3	0.062	0.50	1.00
3	7	0.096	2.10	0.90
4	15	0.170	1.16	0.97
5 6	30	0.261	1.09	1.94
7	60	0.328	1.74	0.97
8	90	0.391	2.06	1.48
9	120	0.416	1.49	0.76
10	150	0.447	1.93	0.42
11	180	0.454	2.01	0.40
12	210	0.473	1.52	0.42
13	240	0.466	1.85	0.43
14	300	0.504	1.66	0.98
15+	305	≺0.02		0.73
Total	•	•	20.99	11.40

* Sample prior to slag addition

+ Slag Sample

TABLE R-2

Sampling Details and Analysis for Experiment #R-38 at 1400°C

	and the second se			
Sample #	Time (Min)	[P] Wt. Pct.	Sample Metal (gm)	Slag Removed (gm)
1	3	0.021	3.74	4.83
2	7	0.043	2.25	1.98
3	15	0.116	6.66	1.51
4	30	0.201	2.92	1.78
5	60	0.274	5.17	2.73
6	90	0.323 -	5.04	1.24
7	120	0.343	3.16	1.99
8	150	0.363	5.48	0.89
9	180	0.396	8.22	3.60
10	210	0.403	4.74	0.76
11	240	0.396	6.03	2.25
12	270	0.403	3.10	1.22
13	300	0.409	4.73	0.80
Total			61.24	25.58

TABLE R-3 Sampling Details and Analysis for Experiment #R-39 at 1400°C

		and the second se		
Sample #	Time (Min)	[P] Wt. Pct.	Sample Metal (gm)	Slag Removed (gm)
1	3	0.023	4.31	1.779
2	7	0.058	4.80	1.275
. 3	15	0.127	2.19	0.877
4	30	0.214	5.37	1.457
5	60	0.305	5.06	1.925
6	90	0.379	5.43	1.265
7	120	0.45	4.76	0.334
8	150	0.48	6.21	0.174
9	180	0.51	5.71	0.361
10	210	0.53	7.94	0.562
11	240	(0.56)	8.63	0.610
12	300	0.59	5.96	0.417
13	360	0.61	5.60	0.164
14*	365	<0.02	-	0.635
Total			71.97	11.835

* Slag sample

TABLE R-4

Sampling Details and Analysis for Experiment #R-36 at 1400°C

Sample #	Time (Min)	[P] Wt. Pct.	Sample Metal (gm)	Slag Removed (gm)
. 1	3	0.036	0.45	1.49
2	7	0.069	1.18	1.28
3	15	0.115	1.03	0.71
4	30	0.210	0.48	2.51
5	60	0.267	1.01	2.14
6	120	0.342	1.71	0.70
7	180	0.366	2.01	1.68
8	240	0.396	2.95	2.05
9	300	0.420	1.97	1.42
Total			12.79	13.98

TABLE R-5

\$

Sampling Details and Analysis for Experiment #R-41 at 1400°C

Sample	Time	[P]	Sample	Slag Removed
No.	(mins.)	Wt. Pct.	Metal (gm)	(gm)
	1	0.047	3 17	0.62
· · · · · · · · · · · · · · · · · · ·	T.	0.047	,5, 11	0, 02
2	8	0.144	3.56	0.63
3	15	0.255	3.33	1.04
4	30	0.368	3.48	0.29
5	60	0.41	3.60	0.16
. 6	120	0.44	3.06	0.22
7	180	0.45	5.18	0.17
Total			25. 38	3. 13

TABLE R-6 Sampling Details and Analysis for Experiment #R-37 at 1500°C.

1		IN (gm)	OUT (gm)
(i)	Metal:		
	Weight of metal bath Weight of metal samples	201.4	180 20, 99
	Total weight	201.4	200.99
(ii)	Slag:		
	Weight of slag phase Weight of slag removed Weight of P2O5 ≡ P transferred*	60.86	47.0 11.40 2.14
	Total weight	60.86	60.54

(iii) Assume no slag absorbed by zircon crucible.

* Calculated from metal data.

TABLE R-7 Mass Balance for Experiment #R-38.

		IN (gm)	OUT (gm)
(i)	Metal:		
	Weight of metal bath Weight of metal samples	201.4	140 61. 24
	Total weight	201.4	201.24
(ii)	Slag:		
	Weight of slag phase	58.56	32.0
	Weight of slag removed		25.58
	Weight of $P_2O_5 \equiv P$ transferred*		1.73
	Total weight	58.56	59.31

(iii) Assume no slag absorbed by zircon sleeve.

* Calculated from metal data.

TABLE R-8 Mass Balance for Experiment #R-39.

방의 일을 넣고 말했다. 한 중 가지 않는 것을 잡았는 것을 했다.	IN (gm)	OUT (gm)
(i) Metal:		
Weight of metal bath Weight of metal samples	201. 4	129.27 71.97
Total	201.4	201.24
(ii) Slag:		
Weight of slag phase	67.04	40.53
Weight of slag removed	물 강화 한 것이야지.	11.84
Weight of $P_2O_5 \equiv P$ transferred*		2.48
Total weight	67.04	54.85
Weight loss	12.	19
(iii) Zirconia sleeve:		
Weight of sleeve	239	251
Weight gain = slag absorbed	12	

(iv) Slag absorbed = 12.0 gm:

Assume 10.0 gm slag absorbed after 60 mins. Assume 2.0 gm slag absorbed in next 30 mins.

* Calculated from metal data.

Time ^x (mins.)	Slag ⁺ (gm)
3	0.5
7	0.6
15	1.4
30	2.5
60	5.0
90	2.0
Total	12.0

- x Sample times during experiment #R-36.
- + Calculated weight of slag absorbed prior to corresponding sample time in period between samples.

TABLE R-9 Mass Balance for Experiment #R-36.

	영금 이 없다. 영상 방송 방송 방송 방송 방송 방송 방송 방송	IN (gm)	OUT (gm)
(i)	Metal:		
	Weight of metal bath Weight of metal samples	201.4	188 12.79
	Total weight	201.4	200.79
(ii)	Slag:		
	Weight of slag phase	62.30	32.42
	Weight of slag removed		13.98
	Weight of $P_2O_5 \equiv P$ transferred*		1.90
	Total weight	62.30	48.30
	Weight loss	14.	. 00
(iii)	Zirconia sleeve:		
	Weight of sleeve	242	256
	Weight gain ≡ slag absorbed	14	

(iv) Slab absorbed = 14.0 gm:

Assume 10.0 gm slag absorbed after 60 mins. Assume 4.0 gm slag absorbed in next 60 mins.

* Calculated from metal data.

$Time^{X}$	Slag ⁺
(mins.)	(gm)
3	0.5
7	0.6
15	1.4
30	2.5
60	5.0
120	4.0
Total	14.0

- x Sample times during experiment #R-41.
- + Calculated weight of slag absorbed prior to corresponding sample time in period between samples.

TABLE R-10 Mass Balance for Experiment #R-41.

		IN (gm)	OUT (gm)
(i)	Metal:		
	Weight of metal bath Weight of metal samples Total weight	201 . 4 201 . 4	176 25.38 201.38
(ii)	Slag:		
	Weight of slag phase Weight of slag removed Weight of $P_2O_5 \cong P$ transferred*	54.31	39.38 3.13 2.00
	Total weight	54.31	44.51
		9.	8
(iii)	Zirconia sleeve:		
	Weight of sleeve	235	245
	Weight gain ≡ slag absorbed	. 10	

(iv) Slab absorbed = 10.0 gm:

Assume 10.0 gm slag absorbed after 60 mins.

* Calculated from metal data.

Time ^x (mins.)	Slag ⁺ (gm)
4	. 0.7
8	0.6
15	1.2
30	2.5
60	5.0
Total	10.0

x Sample times during experiment #R-37.

+ Calculated weight of slag absorbed prior to corresponding sample time in period between samples.

TABLE R-11 Mass Balance for Experiment #R-37.

Time (Min)	Average Rate (mole/cm ² /sec) x 10 ⁷	Mole Fraction $XP_2O_5.10^2$	Log (Rate)	Log XP205
0 * 3 * 7 * 15 * 30 * 60 * 90 120 150 150 180 210 240 300	18.09 12.76 7.71 6.60 3.59 1.84 1.24 0.778 0.526 0.355 0.286 0.607 -	2.10 1.90 1.79 1.55 1.24 1.01 0.782 0.690 0.576 0.551 0.481 0.410 0.392	$ \overline{6.257} \overline{6.106} \overline{7.887} \overline{7.820} \overline{7.551} \overline{7.266} \overline{7.093} \overline{8.891} \overline{8.721} \overline{8.550} \overline{8.456} \overline{8.783} - - $	$ \overline{2.322} \overline{2.279} \overline{2.253} \overline{2.190} \overline{2.094} \overline{2.003} \overline{3.893} \overline{3.839} \overline{3.761} \overline{3.741} \overline{3.682} \overline{3.612} - - - - - - $

TABLE R-12

Calculated Values of Average Rate of Phosphorus Transfer and
 Mole Fraction of P2O5 in the Slag for Experiment #R-38

Time (Min)	Average Rate (mole/cm ² /sec) x 10 ⁷	Mole Fraction $X_{P_2O_5, 10^2}$	Log (Rate)	Log X _{P2} O5
0 3 7 15 * 30 * 60 * 90 * 120 150 150 180 210 240 270 300	5.77 6.63 6.59 3.51 1.73 0.951 0.535 0.690 0.474 0.085 0.035 0.035 0.067	$\begin{array}{c} 2.10\\ 2.03\\ 1.95\\ 1.68\\ 1.36\\ 1.08\\ 0.886\\ 0.805\\ 0.722\\ 0.586\\ 0.570\\ 0.557\\ 0.557\\ 0.529\end{array}$	$ \begin{array}{r} - \\ \overline{7.761} \\ \overline{7.822} \\ \overline{7.819} \\ \overline{7.546} \\ \overline{7.237} \\ \overline{8.978} \\ \overline{8.728} \\ \overline{8.728} \\ \overline{8.839} \\ \overline{8.676} \\ \overline{9.928} \\ \overline{9.549} \\ \overline{9.549} \\ \overline{9.826} \\ - \end{array} $	$ \overline{2.307} \overline{2.289} \overline{2.225} \overline{2.135} \overline{2.034} \overline{3.947} \overline{3.906} \overline{3.859} \overline{3.756} \overline{3.756} \overline{3.746} \overline{3.746} \overline{3.746} \overline{-} $

TABLE R-13

Calculated Values of Average Rate of Phosphorus Transfer and Mole Fraction of P_2O_5 in the Slag for Experiment #R-39

Time (Min)	Average Rate (mole/cm ² /sec) x 10 ⁷	Mole Fraction X _{P2O5} .10 ²	Log (Rate)	Log XP2O5	
0 3 * 7 * 15 * 30 * 60 * 90 120 150 150 180 210 240 300 360	- 8.14 8.43 6.91 4.16 2.51 2.14 1.45 0.832 0.671 0.636 0.550 0.289 -	$\begin{array}{c} 2.10\\ 2.03\\ 1.93\\ 1.73\\ 1.45\\ 1.15\\ 0.88\\ 0.60\\ 0.49\\ 0.376\\ 0.301\\ 0.194\\ 0.094\\ 0.027\end{array}$	7.911 7.926 7.839 7.619 7.400 7.330 7.161 8.920 8.827 8.804 8.740 8.460	$ \begin{array}{r} - \\ \overline{2.308} \\ \overline{2.286} \\ \overline{2.238} \\ \overline{2.161} \\ \overline{2.061} \\ \overline{3.944} \\ \overline{3.778} \\ \overline{3.690} \\ \overline{3.575} \\ \overline{3.479} \\ \overline{3.288} \\ \overline{4.973} \\ \overline{-} \\ \end{array} $	

TABLE R-14Calculated Values of Average Rate of Phosphorus Transfer and
Mole Fraction of P2O5 in the Slag for Experiment #R-36

Time (Min)	Average Rate (mole/cm ² /sec) x 10 ⁷	$\begin{array}{c} \text{ge Rate} \\ \text{cm}^2/\text{sec} \end{pmatrix} \qquad \text{Mole Fraction} \\ 10^7 \qquad \qquad$		Log X _{P2O5}	
0 3 * 7 * 15 * 30 * 60 * 120 * 180 *	- 10. 19 7. 02 6. 02 4. 09 1. 56 0. 812 0. 437	2.10 1.98 1.87 1.71 1.37 1.16 0.796 0.673	$ \frac{\overline{6.008}}{7.846} \overline{7.780} \overline{7.612} \overline{7.193} \overline{8.910} \overline{8.640} $	$ \overline{2.296} \overline{2.272} \overline{2.234} \overline{2.137} \overline{2.062} \overline{3.901} \overline{3.828} $	
240 300	0.433 0.381	0.516 0.382	8.636	3.712	

TABLE R-15Calculated Values of Average Rate of Phosphorus Transfer and
Mole Fraction of P2O5 in the Slag for Experiment #R-41

Time (Min)	Average Rate (mole/cm ² /sec) x 10 ⁷	Mole Fraction $XP_2O_5.10^2$	Log (Rate)	Log (XP2O5)	
0 4 8 * 15 * 30 * 60 * 120 * 180 *	17.97 19.77 11.32 4.26 0.888 0.305 0.150	2.10 1.93 1.57 1.15 0.696 0.508 0.369 0.325	$ \overline{6.255} \overline{6.296} \overline{6.054} \overline{7.629} \overline{8.948} \overline{8.484} \overline{8.176} $	$ \overline{2.285} \overline{2.197} \overline{2.062} \overline{3.843} \overline{3.706} \overline{3.567} \overline{3.511} $	

 $\frac{\text{TABLE R-16}}{\text{Mole Fraction of } P_2O_5 \text{ in the Slag for Experiment } \#\text{R-37}}$

ype	n	Log k	k
con 1400	3.17	1. 52	0.33
conia 1400	2.72	2.60	0.04
conia 1500	3.10	0.04	1.10
	con 1400 conia 1400 conia 1500	con14003.17conia14002.72conia15003.10	con14003.17Ī. 52conia14002.722.60conia15003.100.04

Average value of k at $1400^{\circ}C = 0.185$

TABLE R-17

Values of the Order of Reaction, n, and the Rate Constant, k, for the Present Studies

	Operating Temp.		Initial	Wt. Slag	Ferro*	Initial P
	1	°C	Wt. Metal	Charged	Phosphorus	Content
Expt.	Melt	Susceptor	(gm.)	(gm.)	Charged (gm.)	(Wt. Pct.)
S-2	1600	1645	2500	~690	50	0.490
S-9	1650	1620	2520	850	40	0.391
S-10	1610	1610	2570	750	40	0.383
S-14	1585	1580	2530	450	40	0.390
S-18	1640	1665	2530	~700	35	0.341
S-19	1640	1665	2540	~700	40	0.388
S-20	1620	1620	2530	~800	45	0.437
S-23	1580	1600	2550	710	45	0.434
S-24	1580	1590	2520	850	45	0.438
S-25	1600	1620	2515	850	45	0.439

* Ferrophosphorus contains 25 wt. pct. P.

 \sim 300 gm. slag absorbed by crucible.

Operating times: ~ 60 min. (40 min. - 67 min.) to heat up and

adjust T°C.

 \sim 30 min. to add slag.

~30 min. to adjust temp. to melt slag, etc.

TABLE S-1 Experimental Conditions.
Expt.	P205	CaO	SiO2	Fe203	MgO	A1203	Vr
S-2	-	32.6	30.2	21.0	16.3		1.075
S-9	8.0	47.5	12.0	24.8	5.6	1.9	3.96
S-10	-	48.4	16.3	30.8	2.5	2.2	3.16
S-14	4.0	46.0	16.0	27.0	5.0	2.0	2.88
S-18	4.0	46.0	16.0	27.0	5.0	2.0	2.88
S-19		48.0	16.0	28.0	6.0	2.0	3.0
S-20	444	48.0	16.0	28.0	6.0	2.0	3.0
S-23	7.0	28.0	26.0	24.0	14.0	-	1.075
S-24		30.4	28.3	26.1	15.2	-	1.075
S-25	-	38.0	28.0	26.0	8.0	-	1.36

TABLE S-2 Initial Synthetic Slag Composition (Weight Percent).

	Synthetic Slag Calculated	Molten Slag Initial	Molten Slag Final	Soli Final V	d Slag Wt. % Fe	Molten Slag Final
Expt.	Wt. % Fe	Wt. % Fe	Wt. % Fe	Solid	Powder	Wt. % P
S-18	18.9		12.05	7.55	-	-
S-19	19.6	-		6.50	10.30	-
S-20	19.6	18.85	-	6.30	10.60	-
S-24	18.2	- 10 - 10 -			-	0.77
S-25	18.2	15.90	8.90	-	-	0.85

TABLE S-3 Iron Contents of Slags.

	Metal % P	Slag % P	Dephosphorisation Ratio (Wt. %P ₂ O ₅)	Expected Equilibrium	Winkler et al 1946
Expt.	Final	Final	[Wt. %P]	Ratio	Sample & T°C
S-24	0.087	0.77	20.3	50-84	E-30-5/1573°C
					E-30-7/1656°C
S-25	0.067	0.85	29.1	130-160	E-37-8/1622°C
					E-37-13/1590°C

TABLE S-4 Dephosphorisation Data.

Expt	. S-2	Expt	. S-9	Expt.	S-10	Expt.	S-14
Time	P	Time	P	Time	P	Time	P
(min:sec)	(Wt. pct.)						
0:00	0.490	0:00	0.391	0:00	0. 383	0:00	0, 390
2:00	0.356	1:00	0.307	1:20	0.275	1:00	0.308
2:30	0.372	3:00	0.251	3:00	0.235	3:00	0.323
3:30	0.344	5:00	0.216	5:00	0.259	5:00	0.313
5:30	. 0. 370	9:00	0.203	7:00	0.250	7:00	0.298
6:30	0.304	13:00	0.197	9:00	0.246	11:00	0.284
10:30	0.276	17:00	0.185	11:00	0.228	15:00	0.284
12:30	0.294	21:00	0.175 .	13:00	0.252	19:00	0.280
17:30	0.240	25:00	0.196	15:00	0.225	23:00	0.267
22:30	0.252			17:00	0.231	27:00	0.264
27:30	0.280			19:00	0.234	31:00	0.275
				- 21:00	0.215		
	영화 영화			23:00	0.222		
•				25:00	0.241		
				27:00	0.211		
				29:00	0.239		

TABLE S-5 Phosphorus Analyses of Metal Samples from Experiments S-2, S-9, S-10 and S-14.

Expt.	S-18	Expt.	S-19	Expt.	S-20
Time	P	Time	P	Time	P
(min:sec)	(Wt. pct.)	(min:sec)	(Wt. pct.)	(min:sec)	(Wt. pct.)
0:00	0.341	0:00	0.388	0:00	0.437
1:00	0.287	1:00	0.280	0:30	(0.218)
3:00	0.206	2:00	0.237	1:10	0.305
5:00	0.189	3:00	0.199	2:00	0.244
7:00	0.185	5:00	0.188	4:00	0.211
9:00	0.186	7:00	0.187	7:00	0.196
11:00	0.173	11:00	0.183	10:00	0.191
15:00	0.168	15:00	0.173		21 28 1
20:00	0.171	20:00	0.172		
25:00	0.167	25:00	0.167		
30:00	0.174	30:00	0.167		
35:00	0.162	35:00	0.161		

TABLE S-6Phosphorus Analyses of Metal Samples fromExperiments S-18, S-19 and S-20.

Expt	. S-23	Expt	S-24	Expt	. S-25
Time	P	Time	Р	Time	P
(min:sec)	(Wt. pct.)	(min:sec)	(Wt. pct.)	(min:sec)	(Wt. pct.)
0:00	0.434	0:00	0.438	0:00	0.439
0:30	0.462	0:45	0.357	1:00	0.360
2:30	0.390	1:30	0.285	1:40	0.298
5:00	0.366	2:40	0,210	2:40	0.220
9:00	0.342	4:00	0.206	4:00	0.167
15:00	0.342	6:00	0. 142	6:00	0.122
20:00	0.342	10:00	0.110	10:00	0.106
30:00	0.366	15:00	0.105	15:00	0.083
		20:00	0.097	20:00	0.092
		25:00	0.091	30:00	0.067
		30:00	0.087		

TABLE S-7 Phosphorus Analyses of Metal Samples from Experiments S-23, S-24 and S-25.

		P in	Wt. P	Rate ** 2	Avg. Rate		X _n , mole	
Time	% P in	Metal	Transferred	(mole/cm ² /	(mole/cm ² /	Log	fraction,	
(min.)	Metal	(gm)*	(gm)	sec) x 10'	sec) x 10'	(avg. rate)	$\times 10^3$	Log Xp
0	0.391	10.00		-		-	-	-
1	0.307	7.86	2.14	185	123. 5	5. 092	5,53	3.743
3	0.251	6.43	1. 43	61.7	50.5	6.703	4.52	3.655
5	0.216 ·	5.53	0.90	38.9	23.0	6. 362	3.89	3. 590
9	0.203	5.20	0, 33	7.11	5.28	7. 723	3.66	3. 564
13	0.197	5.04	0.16	3.46	4.99	7. 698	3.55	3. 550
17	0.185	4.74	0, 30	6.49	6.34	7.802	3.33	3. 522
21	0.175	4.48	0.26	6.17	. Milit – Milit		-	1.
25	0.196	-			한 한 비원	• •	199 - - 991	-

* Calculated for 2560 gm. metal.

** Crucible I. D. = 3. 5"; Mole Wt. P = 31.

TABLE S-8Calculated Rate of Phosphorus Transfer andMole Fraction of Phosphorus in Metal forExperiment S-9.

Time (min.)	% P in Metal	P in Metal (gm)*	Wt. P Transferred (gm)	Rate ** (mole/cm ² / sec) x 10 ⁷	Avg. Rate (mole/cm ² / sec) x 10 ⁷	Log (avg. rate)	X _p , mole fraction, x 10 ³	Log X
	0.241	0.75						P
0	0. 541	0.15			-	_		_
1	0.287	7.36	1.39	120	105.5	5. 022	5, 17	3.714
3	0.206 ·	5.28	2.08	90.0	54.4	6.736	3.71	3.569
5	0.189	4.85	0.43	18.7	11.5	6.060	3.41	3. 532
7	0,185	4.75	0.10	4.35	1.74	7.240	3,33	3. 522
9	0,186	4.77	-0.02	-0.867	6.68	7. 825	3,35	3. 525
11	0.173	4.44	0.33	14.2	8. 53	7.931	3.12	3.494
15	0.168	4.31	0.13	2.82	0.716	8.855	3.03	3.481
20	0.171	4.39	-0.08	-1.38	0.261	8. 416	3.08	3. 489
25	0.167	4.28	0.11	1.90		-	3.01	3.479
30	0.174	4.46	-0.18	-3.11	1.05	7.020	3.14	3. 497
35	0.162	4.16	0.30	5.20	-	-	-	

* Calculated for 2565 gm. metal.

** Crucible I. D. = 3. 5"; Mole Wt. P = 31.

<u>TABLE S-9</u> Calculated Rate of Phosphorus Transfer and Mole Fraction of Phosphorus in Metal for Experiment S-18.

Time	% P in	P in Metal	Wt. P Transferred	Rate $**$ (mole/cm ² /	Avg. Rate $(mole/cm^2/$	Log	X _p , mole fraction.	
(min.)	Metal	(gm)*	(gm)	sec) x 10 ⁷	sec) x 10^7	(avg. rate)	x 10 ³	Log Xp
0	0.388	10.00	-	-	-		-	-
1	0.280	7.22	2.78	241	167.9	5. 227	5.05	3. 703
2	0.237	6.11	1.11	96.2	90.6	6.956	4.27	3.630
3	0.199	5.13	0.98	84.9	48.6	6. 687	3.59	3.555
5	0.188	4.85	0.28	12.2	6.71	7.827	3.39	3. 530
7	0.187	4.82	0.03	1.30	1.73	7.239	3.37	3. 528
11	0.183	4.72	0.10	2.17	3.89	7. 590	3.30	3. 518
15	0.173	4. 46	0.26	5.63	2. 98	7.474	3.12	3. 494
20	0.172	4.44	0.02	0.346	1.30	7. 114	3.10	3. 491
25	0.167	4.31	0.13	2.25	1.12	.7. 051	3.01	3. 479
30	0.167	4.31	0.00	0.00	1.39	7. 142	3.01	3. 479
35	0.161	4.15	0.16	2.77	하고 아무런 것	-	-	2-11-1-

* Calculated for 2580 gm. metal.

** Crucible I. D. = 3. 5"; Mole Wt. P = 31.

TABLE S-10 Calculated Rate of Phosphorus Transfer and Mole Fraction

of Phosphorus in Metal for Experiment S-19.

Time	% P in	P in Metal	Wt. P Transferred	Rate ** (mole/cm ² /	Avg. Rate (mole/cm ² /	Log	X _p , mole fraction,	
(min.)	Metal	(gm)*	(gm)	sec) x 107	sec) x 10 ⁷	(avg. rate)	x 10 ³	Log X _p
0	0. 437	11.25	-	-	-		-	-
1.1	0.305	7.85	3.40	267	209.4	5. 321	5.50	3.740
2	0.244	6.28	1, 57	151	94.0	6.973	4.40	3.644
4	0.211	5.43	0.85	36.8	23.9	6.378	3.80	3. 580
7	0.196	5.05	0.38	11.0	7.38	7.868	3.53	3. 548
10	0.191	4.92	0.13	3.76	-		-	-

* Calculated for 2575 gm. metal.

** Crucible I. D. = 3. 5"; Mole Wt. P = 31.

TABLE S-11 Calculated Rate of Phosphorus Transfer and Mole Fraction of Phosphorus in Metal for Experiment S-20.

		P in	Wt. P	Rate **	Avg. Rate		X _n , mole	1
Time	% P in	Metal	Transferred	$(mole/cm^2/$	(mole/cm ² /	Log	fraction,	
(min.)	Metal	(gm)*	(gm)	sec) x 10^7	sec) x 10'	(avg. rate)	$\times 10^3$	Log Xp
0	0.439	11.25	-	-			-	
0.75	0.357	9.16	2.09	241	227.5	5.357	6.43	3.808
1.50	0.285	7.31	1.85	214	178.6	5. 252	5.14	3.711
2.67	0.210	5.39	1. 92	143	94.4	6.975	3.78	3. 578
4	(0.206)	-	-	-	-		-	-
6	0.142	3.64	1.75	45.6	31.8	6. 502	2.56	3. 408
10	0.110	2.82	0.82	17.8	10.0	6.000	1.98	3. 297
15	0.105	2.69	0.13	2.25	2.84	7. 454	1.89	3. 276
20	0.097	2.49	0.20	3.46	3.11	7. 493	1.75	3. 243
25	0.091	2.33	0.16	2.76	2.25	7. 352	1.64	3.215
30	0.087	2, 23	0.10	1.73	-	-	-	-

* Calculated for 2565 gm. metal.

** Crucible I. D. = 3. 5"; Mole Wt. P = 31.

TABLE S-12Calculated Rate of Phosphorus Transfer and Mole Fractionof Phosphorus in Metal for Experiment S-24.

		P in	Wt. P	Rate **	Avg. Rate		X _p , mole	
Time	% P in	Metal	Transferred	(mole/cm ² /	(mole/cm ² /	Log	fraction,	
(min.)	Metal	(gm)*	(gm)	sec) x 10'	sec) x 10'	(avg. rate)	$\times 10^{3}$	Log Xp
0	0.439	11.25		-			-	-
1	0.360	9.22	2.03	176.0	191.0	5. 281	6.49	3.812
1. 67	0.298	7.63	1. 59	207.0	190.1	5. 279	5.37	3.730
2.67	0.220	5.63	2.00	173.0	130.1	5. 116	3.96	3. 598
4	0.167	4.28	1.35	87.4	68.7	6.837	3.01	3. 478
6	0.122	3.12	1.16	50.2	29.5	6. 470	2.20	3. 342
10	0.106	2.71	0.41	8.85	7.46	7.873	1.91	3. 281
15	0.092	2.36	0.35	6.06	4.86	7. 687	1.66	3.220
20	0.084	2.15	0.21	3, 65	2.68	7. 429	1.51	3. 180
30	0.076	1.95	0.20	1.72	-			-

* Calculated for 2560 gm. metal.

** Crucible I. D. = 3. 5"; Mole Wt. P = 31.

TABLE S-13 Calculated Rate of Phosphorus Transfer and Mole Eraction

of Phosphorus in Metal for Experiment S-25.



Fig. V-I. THE EFFECT OF OXYGEN ON THE APPARENT EQUILIBRIUM CONSTANT,K'.



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0 1 7

FIG. V-2 A GENERAL VIEW OF THE APPARATUS USED FOR OXYGEN SOLUTION EXPERIMENTS



FIG. V-3 THE LEVITATION COIL AND REACTION CHAMBER



FIGURE V-4. THE REACTION CHAMBER.



FIGURE V-5. THE GAS SYSTEM.



THE FORMER

THE COIL (schematic)

FIGURE V-6.



THE EFFECT OF OXYGEN CONTENT OF PURE IRON ON THE EQUILIBRIUM CONSTANT K' FOR THE REACTION $H_2 + Q = H_2 O$ AT 1550, 1650, 1750 °C.









CONSTANT K' FOR THE REACTION H2+ OFe-V = H2O AT 1600 & 1700°C.



FOR THE REACTION $H_2 \div O_{Fe-V} = H_2O$ AT 1550, 1650, 1750 °C.

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Fig. V-15. THE EFFECT OF THERMAL DIFFUSION ON THE EQUILIBRIUM CONSTANT K AT 1700 °C.



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FIGURE V-18. CALCULATED VALUES OF EXCESS ENTHALPY AND ENTROPY FOR SOLUTION OF OXYGEN IN IRON-VANADIUM ALLOYS.



FIGURE V-19. CORRELATION OF FREE ENERGY AND ENTHALPY PARAMETERS AT 1600°C



FIGURE V-20. CORRELATION OF FREE ENERGY AND ENTHALPY PARAMETERS AT 1600°C (MOLE FRACTION SCALE)



FIG. R-1 THE GRAPHITE HEATING ELEMENT, CRUCIBLE AND DRIVE SHAFT



FIGURE R-2. THE CARBON RESISTANCE FURNACE.



s sharkara char ar share shi shi shukara sevili bahor tar 2.1015 shifu shi ta sa sa

FIG. R-3 THE DRIVE SHAFT AND POWER LEADS LOCATED IN THE BASE OF THE FURNACE



FIG. R-4 GENERAL VIEW OF FURNACE AND AUXILIARY EQUIPMENT



FIG. R-5 THE FURNACE SHOWING LOCATION OF SIDE-PORTS


FIGURE R-6. TEMPERATURE PROFILE OF CARBON RESISTANCE FURNACE.











FIGURE R-II. RATE OF PHOSPHORUS TRANSFER VERSUS MOLE FRACTION OF P205 IN SLAG AT 1400 °C.



FIGURE R-12. RATE OF PHOSPHORUS TRANSFER VERSUS MOLE FRACTION OF P_2O_5 IN SLAG AT 1400°C.



FIGURE R-13. RATE OF PHOSPHORUS TRANSFER VERSUS MOLE FRACTION OF P205 IN SLAG AT 1500 ° C



FIGURE R-14. RATE OF PHOSPHORUS TRANSFER VERSUS MOLE FRACTION OF P205 IN SLAG AT 1400° & 1500° C.



SCALE-INCHES

FIGURE S-I INDUCTION FURNACE USED FOR STEEL DEPHOSPHORISATION STUDIES











WITH TIME.







