SOLUBILITY OF NITROGEN
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LIQUID IRON ALLOYS

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By

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ABSTRACT:

An investigation has been made concerning the solubility of nitrogen in pure liquid iron, iron-carbon and iron-aluminium alloys. A technique involving levitation melting and a rapid quench device has been used. The experimental data obtained have been expressed in terms of the interaction coefficients proposed by Wagner and Lupis and Elliott. The data have also been used to test the formalisms developed recently by Darken and Chipman. A simple model for liquid metal solutions in which the solutes may be considered "interstitial" has been developed and tested using the results of the present study and published data for a number of ternary solutions.

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CHAPTER 1

INTRODUCTION

From the first iron droplets formed in the bosh of the blast furnace, to the final casting of the finished steel product, liquid iron, throughout many of its various stages of refinement, is in contact with nitrogen from the atmosphere. The droplets in the bosh of the blast furnace are exposed under reducing conditions to essentially one atmosphere partial pressure of nitrogen, and it seems likely that the liquid metal is saturated with nitrogen at this stage. As the droplets fall into the well of the furnace their carbon content increases and the temperature decreases. Both effects result in a decreasing solubility of nitrogen. The iron tapped from the blast furnace generally contains about 0.006 wt. pct. nitrogen, however it has fallen to 0.004 wt. pct. by the time the metal reaches the mixer, which suggests that the metal in the furnace is supersaturated with respect to nitrogen.

The iron tapped from the furnace contains considerable quantities of carbon, phosphorus, sulphur, silicon and manganese all of which, with the exception of manganese, decrease the solubility of nitrogen in liquid iron. During the conversion to steel, the bulk of these impurities are removed and this allows the solubility of nitrogen in the melt to increase. The extent of this increase will depend on the type of process used. In a traditional air-blown converter, the gas entering the molten metal through the tuyeres contains 79 pct. by volume of nitrogen. The oxygen in the gas reacts to form oxides and hence the gas passing through the metal is essentially pure nitrogen, except during the carbon reaction when carbon monoxide is also present. The variation in the nitrogen content of the metal in the course of the basic process is shown in Fig. 1, (1). While the silicon and manganese are being oxidised, the gas passing through the metal is almost pure nitrogen but the low temperature and high carbon content keep the nitrogen solubility at a low level. Towards the end of this period the temperature rises and continues to rise during the oxidation of carbon. The nitrogen content however remains at a low level and may actually decrease slightly since the nitrogen passing through the metal now has a much lower partial pressure due to the presence of carbon monoxide. The boil becomes less vigorous when the carbon content of the melt reaches about 1 wt. pct. At this stage the carbon monoxide content of the gas decreases rapidly, the partial pressure of nitrogen increases and since the carbon content of the metal is greatly reduced, the concentration of nitrogen in the melt increases rapidly during the final minutes of the "carbon blow".

In the basic Bessemer process an "after blow" is required to remove the phosphorus. During this period the nitrogen content of the metal continues to rise due to the increased temperature, the low carbon content of the melt, and the fact that the partial pressure of nitrogen is almost unity. At the end of the "after blow", the nitrogen content of the metal is in the region of 0.015 to 0.025 wt pct.

In the acid Bessemer process where there is no phosphorus removal, the converter is turned down immediately after the carbon flame drops and the final nitrogen content of acid Bessemer steels remains fairly low (around 0.01 wt. pct.). It is important that the converter is turned down as quickly as possible since the nitrogen content of the melt rises rapidly after the carbon has been oxidized; a delay of a few seconds will significantly alter the nitrogen content of the steel. It has been estimated that the rate of nitrogen dissolution is of the order of 0.005 wt. pct. for each minute of blowing time after carbon oxidation has ceased. (1).

The lowest nitrogen contents in converter steels (0.003 to 0.006 wt. pct.) are obtained by either eliminating or minimising the nitrogen in the blowing gas. This can be accomplished by bottom blowing with oxygen-steam or oxygen-carbon dioxide gas mixtures or by enriching the air with oxygen up to a practical limit of 40 pct. by volume. These procedures reduce both the time required for a given blow and also the partial pressure of nitrogen in the gases passing through the metal, thereby reducing the final nitrogen content of the melt. In side blown air converters, nitrogen dissolution is reduced by blowing air tangentially over the slag surface through tuyeres in the side of the vessel. The nitrogen content of the metal is kept at a low level, since nitrogen from the gas phase cannot easily penetrate the slag layer above the metal. However, the overall refining rates are greatly decreased and this process has never been widely accepted. On the other hand, top blown converter processes such as the L.D. (Linz-Donawitz), have become popular during the past ten years. In these processes commercially pure oxygen is blown into the melt through water cooled copper lances. In this manner high rates of production are achieved and the nitrogen content of the steel generally does not exceed 0.005 wt. pct.

In the conventional open-hearth process, the oxygen required for refining is obtained mainly from slag-metal reactions rather than gas-metal reactions and the metal is therefore protected from the nitrogen in the atmosphere by a slag layer in a similar manner to the side blown converter. A considerable quantity of nitrogen may enter the metal with the scrap charged but this is effectively flushed out by the carbon monoxide bubbles during the carbon oxidation and nitrogen contents as low as 0.002 wt. pct. are obtained at tap. Nitrogen may be absorbed during the tapping operation and also from additions made to the ladle in finishing the steel.

As a consequence, open-hearth steels generally have a nitrogen content in the range 0.004 to 0.007 wt. pct.

Steels prepared in the electric arc furnace usually have higher nitrogen contents than those obtained from the open-hearth process since some of the nitrogen in the atmosphere above the melt is ionized by the arc. Nitrogen in this form is in a more active state and will dissolve much more readily in the liquid metal. In addition, the carbon boil is less intense than in the open-hearth and thus the flushing action of carbon monoxide bubbles on dissolved nitrogen is less effective in this process. Many of the additions used in making high alloy steels in the electric arc furnace often contain considerable quantities of nitrogen. Frequently these additions raise the solubility of nitrogen in liquid iron and the nitrogen contents of steels prepared in this manner are generally in the region of 0.005 to 0.010 wt. pct.

Oxygen dissolved in liquid iron inhibits the dissolution of nitrogen in the metal due to the presence of a surface active layer of oxygen which poisons the sites available for the entry of nitrogen. (2). In general, after the refining process steels have a high oxygen content, and nitrogen absorption during tapping, when the liquid metal is exposed to the atmosphere, is not great. However, when a steel has been thoroughly deoxidized the metal does not have this protection. Usually when the steel is poured from the ladle into the mould the nitrogen absorbed may be considerable. This absorption of nitrogen is not encountered when deoxidized additions are made to the mould rather than the ladle, but the advantage of this procedure is frequently offset by the high incidence of inclusions in the solidified ingot. In the production of rimming steels, the metal is only partially deoxidized so the rate of nitrogen absorption during pouring is reduced. In addition, some of this nitrogen will be flushed out by the evolution of carbon monoxide during the freezing process.

Although the solubility of nitrogen in iron base alloys is in general small, the effects of nitrogen on the properties of steel may be quite profound. For most purposes nitrogen in finished steels is undesirable particularly in the low carbon grades, since on cooling to room temperature the solubility limit of nitrogen in the steel may be exceeded and this can lead to embrittlement and loss of ductility of the steel on ageing. On the other hand, nitrogen improves the work hardening properties and machinability of steels. In combination with aluminium, as AlN, it can cause intergranular fracture in cast steels. However, if the AlN is precipitated in a finely divided form, it can lead to improvements in mechanical properties. In some stainless steels nitrogen is actually necessary as an alloying element in order to stabilize the austenite phase and hence nitrogen pick up in the electric arc furnace is not always a disadvantage. (3).

In the light of the above discussion, it is clearly desirable that one should be able to predict the solubility of nitrogen in liquid iron alloys under a variety of steelmaking conditions. To do this, information is required concerning the interaction between nitrogen and the various alloying elements which may be present in liquid iron. There have been a number of investigations of these effects in recent years and the interactions between nitrogen and many elements dissolved in liquid iron are now known to a high degree of precision at steelmaking temperatures. Unfortunately, several elements which are of importance in steelmaking have proved difficult to deal with using the standard experimental techniques for this type of investigation. Two of these elements are carbon and aluminium. Carbon is always present to some extent in the metal and aluminium is the element most commonly used for deoxidation purposes.

In this investigation a new technique has been devised to study nitrogen solubilities which incorporates levitation melting together with a rapid-quenching device. Using this technique, the solubility of nitrogen has been determined in the following systems:

a) Pure liquid iron over the temperature range 1530° - 1780°C.

b) Iron-carbon alloys for the composition range 0 - 5 wt. pct. C and the temperature range 1450° - 1750°C.

c) Iron-aluminium alloys up to the solubility limit of aluminium nitride and for the temperature range 1550° - 1750°C.

The experimental data obtained from this investigation have been expressed in terms of the interaction coefficients proposed by Wagner (5) and Lupis and Elliott (6). The data have also been used to test the formalisms developed recently by Darken (9,10) and Chipman (67). A model for liquid metal solutions in which the solutes may be considered "interstitial" has been developed. The prediction powers of this model have been examined using the results of the present study together with published data for a number of ternary solutions.

CHAPTER 2

THERMODYNAMICS OF METALLIC SOLUTIONS

2.1 Lupis and Elliott formalism.

2.1.1 Introduction. Chipman (4) has shown that for a solvent 1 containing solutes 2, 3, ---- the activity coefficient γ_2 of solute 2 is a function of the other solutes present and may be expressed approximately by the relation

$$\gamma_2 = \gamma_2^2 \times \gamma_2^3 \times \gamma_2^4 \times --- \qquad (2.1)$$

Where γ_2^2 is the activity coefficient of solute 2 in the binary solution 1 - 2 containing a mole fraction X_2. γ_2^3, γ_2^4, ---- represent the effects of solutes 3, 4, ---- on the activity coefficient of 2. In this case, the reference state for the activity coefficient is based on Henry's law, so that the coefficient becomes equal to unity for an infinitely dilute solution.

Wagner (5) has shown that the partial molar free energy of a solute, or alternatively the logarithm of the activity coefficient of the solute, can be expressed in terms of a Taylor series.

If the series for $\ln \gamma_i$ is expanded about the point $X_i = 0$, the following expression is obtained:

$$\mathrm{Ln}\ \gamma_i = \mathrm{Ln}\ \gamma_i^o + X_i\left(\frac{\partial \ln \gamma_i}{\partial X_i}\right) + X_j\left(\frac{\partial \ln \gamma_i}{\partial X_j}\right) + \tfrac{1}{2}X_i^2\left(\frac{\partial^2 \ln \gamma_i}{\partial X_i^2}\right) + \tfrac{1}{2}X_j^2\left(\frac{\partial^2 \ln \gamma_i}{\partial X_j^2}\right) + X_iX_j\left(\frac{\partial^2 \ln \gamma_i}{\partial X_i\ \partial X_j}\right) + \text{----} \qquad (2.2)$$

where the derivatives are evaluated at infinite dilution with respect to the solutes. In this expression, the reference state for the activity coefficient of i is taken as pure i and γ_i^o is the value of the activity coefficient at infinite dilution.

The partial differential coefficients are explicit expressions of the various orders of contribution for the interaction effects of the added solutes on the activity coefficient of the primary solute. Using the convention of Lupis and Elliott (6), first and second order free energy interaction parameters may be defined as follows:

$$\varepsilon_i^i = \left(\frac{\partial \ln \gamma_i}{\partial X_i}\right)_{X_i = 0}$$

First order self interaction parameter

$$\varepsilon_i^j = \left(\frac{\partial \ln \gamma_i}{\partial X_j}\right)_{X_i = X_j = 0}$$

First order interaction parameter representing the effect of j on the activity coefficient of i.

$$\left.\begin{aligned} \rho_i^i &= \tfrac{1}{2}\left(\frac{\partial^2 \ln \gamma_i}{\partial X_i^2}\right) \quad X_i = 0 \\ \rho_i^j &= \tfrac{1}{2}\ \frac{\partial^2 \ln \gamma_i}{\partial X_j^2} \quad X_i = X_j = 0 \\ \rho_i^{i,j} &= \left(\frac{\partial^2 \ln \gamma_i}{\partial X_i \partial X_j}\right) \quad x_i = x_j = 0 \end{aligned}\right\} \text{Second order interaction parameters.}$$

Third and higher order interaction parameters may be defined in a similar manner.

Restricting the discussion to second order effects, an interaction model for a ternary solution can be defined as follows:

$$\begin{aligned} \text{Ln}\ \gamma_i = \ln \gamma_i^o + X_i \varepsilon_i^i + X_j \varepsilon_i^j + X_i^2 \rho_i^i \\ + X_j^2\ \rho_i^j + X_i X_j\ \rho_i^{i,j} \end{aligned} \qquad (2.3)$$

If the reference state chosen is the infinitely dilute solution, then the first term in the above expression becomes zero.

Since the excess partial molar free energy of mixing F_i^E is defined by the relation

$$F_i^E = F_i - F_{id} \qquad (2.4)$$

where F_i is the partial molar free energy of mixing and F_{id} is the ideal partial molar free energy of mixing then

$$F_i^E = RT\ \ln a_i - RT\ \ln X_i = RT\ \ln \gamma_i \qquad (2.5)$$

Hence by multiplying expression (2.2) or (2.3) throughout by "RT" an expansion for the excess partial molar free energy is obtained. i.e.

$$F_i^E = RT\ \ln \gamma_i^o + RT \sum_{j=z}^{m} \varepsilon_i^j X_j + --- \qquad (2.6)$$

For steelmaking purposes it is more convenient to express concentrations in terms of weight pct. and to choose the 1 wt. pct. solution as standard state for defining activities. Expression (3) now becomes

$$\mathrm{Log}\, f_i = e_i^i\,(\%i) + e_i^j\,(\%j) + \cdots \qquad (2.7)$$

where the interaction parameters e_i^i and e_i^j are defined by

$$e_i^i = \frac{\partial\, \mathrm{Log}\, fi}{(\partial\, \%\, i)}\ , \qquad e_i^j = \frac{\partial\, \mathrm{Log}\, fi}{(\partial\, \%\, j)}$$

2.1.2 Free energy, enthalpy and entropy interaction parameters. Lupis and Elliott (4) have extended the treatment of Wagner (5) to include excess partial entropy and enthalpy functions.

The first order entropy interaction parameter is defined as

$$\sigma_i^j = \left(\frac{\partial S_i^E}{\partial X_j}\right)_{X_1 \rightarrow 1} \qquad (2.8)$$

where

$$S_i^E = -\left(\frac{\partial F_i^E}{\partial T}\right)_p \qquad (2.9)$$

and the enthalpy interaction parameter as

$$\eta_i^j = \left(\frac{\partial H_i^E}{\partial X_j}\right)_{X_i \rightarrow 1} \qquad (2.10)$$

where

$$H_i^E = \left(\partial(F_i^E/T) \big/ \partial\left(\frac{1}{T}\right)_P\right) \qquad (2.11)$$

and

$$H_i^E = H_i^M$$

$$\frac{\partial\left(\frac{H}{T}\right)}{\partial\left(\frac{1}{T}\right)}$$

If second and higher order terms are omitted then:

$$S_i^E = S_i^{E^o} + \sum_{j=2}^{m} \sigma_i^j X_j \qquad (2.12)$$

and

$$H_i^M = H_i^{M^o} + \sum_{j=2}^{m} \eta_i^j X_j \qquad (2.13)$$

where the superscript zero denotes the state of infinite dilution.

Since $F_i^E = H_i^M - TS_i^E$ (2.14)

combining equations (2.6), (2.12), (2.13) and (2.14):

$$RT \ln \gamma_i^o + RT \left[\varepsilon_i^2 X_2 + --- \varepsilon_i^j X_j + --- + \varepsilon_i^m X_m \right]$$
$$= H_i^{M^o} + \eta_i^2 X_2 + ---- + \eta_i^j X_j + -- + \eta_i^m X_m$$
$$- T \left[S_i^{E^o} + \sigma_i^2 X_2 + --- + \sigma_i^j X_j + --- + \sigma_i^m X_m \right] \qquad (2.15)$$

and consequently

$$RT \varepsilon_i^j = \eta_i^j - T \sigma_i^j \qquad (2.16)$$

i.e.

$$\varepsilon_i^j = \frac{1}{R} \left[\frac{\eta_i^j}{T} - \sigma_i^j \right] \qquad (2.17)$$

From this expression it can be seen that if $\sigma = 0$, then ε_i^j is directly proportional to 1/T, while if $\eta = 0$, the free energy parameter ε_i^j is independent of temperature and equal to $-\frac{\sigma}{R}$.

Sometimes a more convenient way of expressing these quantities is in terms of "extra" excess quantities.

$$RT \; (\ln \gamma_i - \ln \gamma_i^o) = F_{i(j)}^{ex} \qquad (2.18)$$

$F_{i(j)}^{ex}$ is the "extra" excess free energy of i created by the addition of the solute j.

This extra excess free energy may be separated into enthalpy and entropy terms.

$$\frac{F^{ex}_{i(j)}}{RT}{}_j = \frac{1}{R}{}_j \left[\frac{H^{ex}_{i(j)}}{T} - S^{ex}_{i(j)} \right] \tag{2.19}$$

$$= X_i \varepsilon^i_i + X_j \varepsilon^j_i + X_i^2 \rho^i_i + X_i X_j \rho^{j,i}_i + X_j^2 \rho^j_i + ---$$

if Henry's law applies $\varepsilon^i_i = \rho^i_i = 0$ and if only first order interactions are considered equation (2.19) becomes

$$\varepsilon^j_i = \frac{1}{RX_j} \left[\frac{H^{ex}_{i(j)}}{T} - S^{ex}_{i(j)} \right] \tag{2.20}$$

which is equivalent to equation (2.17) where

$$\eta^j_i = \frac{H^{ex}_{i(j)}}{X_j} \quad \text{and} \quad \sigma^j_i = \frac{S^{ex}_{i(j)}}{X_j} \tag{2.21}$$

To include the more general case where second order terms are not ignored the "extra" terms for free energy, enthalpy and entropy may be divided into first and second order contributions

$$H^{ex} = H^{ex}_1 + H^{ex}_2 \tag{2.22}$$

$$S^{ex}_i = S^{ex}_1 + S^{ex}_2 \tag{2.23}$$

Using equation (2.19) and assuming Henry's law is obeyed and that the second order cross interaction term may be neglected, Gluck and Pehlke(7) have shown:

$$\varepsilon^j_i + X_j \rho^j_i = \frac{1}{RX_j} \left[\frac{\left[H^{ex}_1 + H^{ex}_2 \right]}{T} - \left(S^{ex}_1 + S^{ex}_2 \right) \right] \tag{2.24}$$

This equation may be separated as follows

$$\varepsilon^j_i + X_j \rho^j_i = \frac{1}{RX_j} \left[\frac{H^{ex}_1}{T} - S^{ex}_1 + \frac{H^{ex}_2}{T} - S^{ex}_2 \right] \tag{2.25}$$

and written in two parts

$$\varepsilon_i^j = \frac{1}{RX_j}\left[\frac{H_1^{ex}}{T} - S_1^{ex}\right] = \frac{1}{R}\left[\frac{\eta_i^j}{T} - \sigma_i^j\right]$$

$$\rho_i^j = \frac{1}{RX_j^2}\left[\frac{H_2^{ex}}{T} - S_2^{ex}\right]$$

or
$$\rho_i^j = \frac{1}{R}\left[\frac{\lambda_i^j}{T} - \pi_i^j\right] \qquad (2.26)$$

Where λ_i^j and π_i^j are the corresponding second order enthalpy and entropy interaction parameters respectively.

Similar expressions may also be derived on the basis of the one wt. pct. solution as standard state.

i.e.
$$e_i^j = \frac{1}{2.3\,R}\left[\frac{h_i^j}{T} - s_i^j\right] \qquad (2.27)$$

$$r_i^j = \frac{1}{2.3\,R}\left[\frac{l_i^j}{T} - p_i^j\right] \qquad (2.28)$$

2.1.3 Interaction parameter relationships. Using the definition of the partial molar free energy $F_i = \left(\frac{\partial F}{\partial X_i}\right)_{X_j ---}$, and the Maxwell relations of thermodynamics Wagner (5) has shown that for an infinitely dilute solution:

$$\varepsilon_i^j = \varepsilon_j^i \qquad (2.29)$$

This expression has been termed the reciprocity relationship.

Schenck, Frohberg and Steinmetz (8) have shown that the first order free energy interaction parameter based on a mole fraction scale is related to the corresponding parameters on a wt. pct. scale by the following equation:

$$\varepsilon_i^j = 230 \frac{M_j}{M_1} e_i^j + \frac{M_1 - M_j}{M_1} \qquad (2.30)$$

where M_1 and M_j are the atomic weights of the solvent 1 and the solute j respectively. Combining equations (2.29) and (2.30) gives:

$$e_j^i = e_i^j \frac{M_j}{M_i} + 0.434 \times 10^{-2} \frac{M_i - M_j}{M_i} \qquad (2.31)$$

Lupis and Elliott (6) have derived the following relationships for first and second order free energy, enthalpy and entropy parameters.

(i) Second order free energy interaction parameters.

$$\rho_i^j = \frac{230}{M_1^2} \left[10^2 M_j^2 r_i^j + M_j (M_1 - M_j) e_i^j \right] + \frac{1}{2} \left(\frac{M_1 - M_j}{M_1} \right)^2 \qquad (2.32)$$

(ii) First order enthalpy interaction parameters.

$$\eta_i^j = 100 \frac{M_j}{M_1} h_i^j \qquad (2.33)$$

(iii) Second order enthalpy interaction parameters.

$$\lambda_i^j = \frac{10^2}{M_1^2} \left\{ 10^2 M_j^2 \ell_i^j + M_j (M_1 - M_j) h_i^j \right\} \qquad (2.34)$$

(iv) First order entropy interaction parameters.

$$\sigma_i^j = 100 \frac{M_j}{M_1} s_i^j - R \frac{M_1 - M_j}{M_1} \qquad (2.35)$$

(v) Second order entropy interaction parameters.

$$\pi_i^j = \frac{10^2}{M_1^2} \left\{ 10^2 M_j^2 p_i^j + M_j (M_1 - M_i) s_i^j \right\} - \frac{R}{2} \left(\frac{M_1 - M_j}{M_1} \right)^2 \qquad (2.36)$$

It is also possible to derive a number of reciprocal relationships of the type $\mathcal{E}^{i}_{j} = \mathcal{E}^{j}_{i}$ between the various parameters and this has also been done by Lupis and Elliott (6).

2.2 Darken Formalism.

A somewhat different approach to the treatment of metallic solutions has been followed by Darken (9, 10). Darken suggests that a binary metallic solution may be divided into three regions -- two terminal regions and a central region. In each terminal region the second derivative of the molal excess energy with respect to mole fraction is substantially constant; Darken refers to this function as the excess stability. i.e. the excess stability is constant in the terminal regions. In the central region the stability may vary strongly and may often exhibit a pronounced maximum which often occurs at compositions where compounds might be expected to form.

Reviewing the available data, Darken (9) has shown that expressions of the type

$$\ln \gamma_1 = \alpha X_2^2 \quad \text{and} \quad \ln \gamma_2 = \alpha X_1^2 \qquad (2.37)$$

represent the data at finite concentrations up to surprisingly high solute concentrations.

Using the Gibbs-Duhem equation

$$X_1 \, d \log \gamma_1 + X_2 \log d \gamma_2 = 0 \qquad (2.38)$$

and assuming the activity coefficient of the solvent may be represented as $\text{Log } \gamma_1 = \alpha X_2^2$

On substituting
$$x_1\, d\,(\alpha x_2^2) + x_2\, d \log \gamma_2 = 0$$

i.e.
$$d \log \gamma_2 = - \frac{x_1}{x_2} \cdot \alpha \cdot d(x_2^2)$$

Integrating
$$\text{Log}\, \gamma_2 = \alpha \int \frac{x_2 - 1}{x_2} \cdot d(x_2^2)$$

i.e.
$$\text{Log}\, \gamma_2 = \alpha (x_2^2 - 2x_2) + I'$$

or
$$\text{Log}\, \gamma_2 = \alpha x_1^2 + I \qquad (2.39)$$

Darken emphasized that I is in general not zero and demonstrated this fact by comparing his own experimental data for $\text{Log}\, \gamma_{Fe}$ VS x_{Si}^2 which were linear in nature up to 0.6 atomic pct. Si, with the experimental data of Schwerdtfeger and Engel (11) for $\text{Log}\, \gamma_{Si}$ VS x_{Fe}^2 which again followed a linear relationship up to 0.6 atomic pct. Si. While the two linear portions of the curves had identical slopes, the second line had a non-zero intercept.

In general equation (2.39) holds only over a limited concentration range. It may be written in a more convenient form
$$\text{Log}\, \gamma_2/\gamma_2^o = \alpha_{12}(x_1^2 - 1) = \alpha_{12}\left[(1 - x_2)^2 - 1\right]$$
$$= \alpha_{12}(-2x_2 + x_2^2) \qquad (2.40)$$

where γ_2^o is the value of the activity coefficient of component 2 at infinite dilution in component one.

Considering a ternary system under isobaric, isothermal conditions the molal value of any extensive parameter can be expressed in the form
$$dG = \bar{G}_1\, dX_1 + \bar{G}_2 dX_2 + \bar{G}_3 dX_3 \qquad (2.41)$$

where the $\bar{G}$'s are the corresponding partial molal quantities and the X's are atom fractions. Taking component 1 as the solvent equation (2.41) can be written in terms of the independent variables X_2 and X_3

$$dG = (\bar{G}_2 - \bar{G}_1)dX_2 + (\bar{G}_3 - \bar{G}_1)dX_3 \tag{2.42}$$

As dG is exact, it follows that

$$\frac{\partial(\bar{G}_2 - \bar{G}_1)}{\partial X_3} = \frac{\partial(\bar{G}_3 - \bar{G}_1)}{\partial X_2} \tag{2.43}$$

From the Gibbs-Duhem equation:

$$(1 - X_2 - X_3)d\bar{G}_1 + X_2 d\bar{G}_2 + X_3 d\bar{G}_3 = 0 \tag{2.44}$$

and thus:

$$(1 - X_3)\frac{\partial G_2}{\partial X_3} + X_3\frac{\partial G_3}{X_3} = X_2\frac{\partial G_2}{\partial X_2} + (1 - X_2)\frac{\partial G_3}{\partial X_2} \tag{2.45}$$

If G is the excess free energy, F^E, this expression becomes, in terms of activity coefficients

$$(1 - X_3)\frac{\partial \ln \gamma_2}{\partial X_3} + X_3\frac{\partial \ln \gamma_3}{\partial X_3} = X_2\frac{\partial \ln \gamma_2}{\partial X_2} + (1 - X_2)\frac{\partial \ln \gamma_3}{\partial X_2} \tag{2.46}$$

Darken required a formalism which satisfied equation (2.46), reduced to the binary formalism when X_2 or $X_3 = 0$ and was such that Raoult's law was approached by the solvent as a limiting condition at infinite dilution. He made use of the general thermodynamic relation

$$F^E = X_1 F_1^E + X_2 F_2^E = 2.303\ RT\ (X_1 \operatorname{Log} \gamma_1 + X_2 \log \gamma_2) \tag{2.47}$$

and the two binary equations (2.37) and (2.39) to obtain the following expression for the excess energy of the system

$$F^E = 2.303\ RT \left[X_2 \log \gamma_2^{\circ} - \alpha_{12} X_2^2 \right] \qquad (2.48)$$

Equation (2.48) can be regarded as the basic equation for a binary system since equations (2.37) and (2.39) can both be derived from it by means of the general thermodynamic relation for a binary solution.

$$RT\ \ln \gamma_i = F_i^E = F^E + (1-x_i)\,dF^E/dX_i \qquad (2.49)$$

A Quadratic equation for ternary solutions corresponding to equation (2.48) is

$$\frac{F^E}{2.303RT} = X_2 \log \gamma_2^{\circ} + X_3 \log \gamma_3^{\circ} - \alpha_{12} X_2^2 - \alpha_{13} X_3^2$$

$$- (\alpha_{12} + \alpha_{13} - \alpha_{23}) X_2 X_3 \qquad (2.50)$$

The equation was expressed in this form because the expression on the right reduces to $\alpha_{12} X_1 X_2 + \alpha_{13} X_1 X_3 + \alpha_{23} X_2 X_3$

if $\quad \mathrm{Log}\,\gamma_3^{\circ} = \alpha_{13} \quad$ and $\quad \mathrm{Log}\,\gamma_2^{\circ} = \alpha_{12}$

Using equation (2.50) Darken obtained expressions for the activity coefficients by means of the general thermodynamic relations corresponding to equation (2.49) which for the ternary solution were

$$2.303\ RT\ \log \gamma_1 = F_1^E = F^E + (1-X_1)\left(\frac{\partial F^E}{\partial X_1}\right)_{X_2/X_3}$$

$$2.303\ RT\ \log \gamma_2 = F_2^E = F^E + (1-X_2)\left(\frac{\partial F^E}{\partial X_2}\right)_{X_1/X_3} \qquad (2.51)$$

$$2.303\ RT\ \log \gamma_3 = F_3^E = F^E + (1-X_3)\left(\frac{\partial F^E}{\partial X_3}\right)_{X_1/X_2}$$

and equations for the activity coefficients

$$\mathrm{Log}\ \gamma_1 = \alpha_{12}X_2^2 + \alpha_{13}X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23})X_2X_3$$

$$\mathrm{Log}\ (\gamma_2/\gamma_2^o) = -2\alpha_{12}X_2 + (\alpha_{23} - \alpha_{12} - \alpha_{13})X_3 + \alpha_{12}X_2^2$$

$$+ \alpha_{13}X_3^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23})X_2X_3 \qquad (2.52)$$

$$\mathrm{Log}\ (\gamma_3/\gamma_3^o) = -2\alpha_{13}X_3 + (\alpha_{23} - \alpha_{12} - \alpha_{13})X_2 + \alpha_{12}X_2^2$$

$$+ \alpha_{13}X_2^2 + (\alpha_{12} + \alpha_{13} - \alpha_{23})X_2X_3$$

These relationships reduce to the desired relations for the binaries when X_2 or X_3 is set equal to zero and since they are derived from a common free-energy expression Eq. (2.50), they also satisfy the condition of thermodynamic consistency.

In order to test these relationships Darken expressed equation (2.52) in a form suitable for use when component 2 is held at constant activity. Under these conditions an expression for the binary may be written

$$\mathrm{Log}\ \gamma_2^*/\gamma_2^o = \alpha_{12}X_2^*(-2 + X_2^*) \qquad (2.53)$$

where the asterisk denotes the quantity which is maintained at a fixed activity.

For ternary solutions

$$\begin{aligned} \text{Log}\ \gamma'_2/\gamma^o_2 &= \alpha_{12} X'_2 (-2 + X'_2) + \alpha_{13} X_3^2 \\ &+ (\alpha_{23} - \alpha_{12} - \alpha_{13}) X_3 (1-X'_2) \end{aligned} \qquad (2.54)$$

Where the prime denotes the quantity which is at fixed activity in the ternary solution.

Since under these conditions $a_2^* = \gamma_2^* x_2^*$ is constant then

$$\text{Log}(\gamma'_2/\gamma^*_2) = \text{Log}\left(\frac{X^*_2}{X'_2}\right) \qquad (2.55)$$

combining Eq. (2.45), (2.53) and (2.54) it follows that:

$$\begin{aligned} \text{Log}(X_2^*/X'_1) + \alpha_{12}\left[X'_2(2-X'_2) - X_2^*(2-X_2^*)\right] - \alpha_{13}X_3^2 \\ = (\alpha_{23} - \alpha_{12} - \alpha_{13})\ X_3\ (1-X'_2) \end{aligned} \qquad (2.56)$$

thus α_{23} may be evaluated from solubility data when α_{12} and α_{13}, which are characteristic of the binary solutions, are known.

2.3 Thermodynamic interactions and physical models of solutions.

A number of attempts have been made to predict solution behaviour using physical models of solutions. Expressions for the excess free-energy derived from these models may be used to calculate interaction effects.

2.3.1 Regular solution. In 1927 Hildebrand (12) introduced the concept of the regular solution in which the entropy of mixing is ideal while the enthalpy of mixing is finite. It may be shown that for such solutions the activity coefficients are directly related to the partial molal heats of mixing.

e.g. $$RT \ln \gamma_i = \Delta H_i^M \qquad (2.57)$$

Many solutions behave approximately in this manner but solutions which are strictly regular appear to be almost as rare as those which are ideal (15).

Hildebrand and Scott (13) later showed that the activity coefficient of component i in a regular ternary solution could be represented by:

$$\mathrm{Ln}\ \gamma_i = \frac{\Delta H_i^M}{RT} = \frac{V_i}{RT}(\delta_i - \bar{\delta})^2$$

$$\bar{\delta} = \phi_k \delta_k + \phi_i \delta_i + \phi_j \delta_j \qquad (2.58)$$

ϕ is the volume fraction

V is the molar volume

δ is the solubility parameter which is defined as the square root of the energy of vapourization per cubic centimetre and represents the "cohesive energy density" of an element.

Interaction parameters may be obtained by differentiating with respect to mole fraction of i or j.

i.e. $$\varepsilon_i^j = \left(\frac{\delta \ln \gamma_i}{\delta X_j}\right)_{X_i = X_j = 0} = \frac{-2}{RT}\left(\frac{V_i V_j}{V_k}\right)(\delta_k - \delta_i)^2$$

$$(2.59)$$

and
$$\varepsilon_i^i = \left(\frac{\partial \ln X_i}{\partial X_i} \right)_{X_i = X_j = 0} = -\frac{2}{RT} \frac{V_i^2}{V_k} (\delta_i - \delta_k)^2 \tag{2.60}$$

These expressions predict a linear relation with the reciprocal of the absolute temperature.

It is found however (14) that even for ternary systems for which corresponding binaries are regular the above relations only predict the sign of the interaction parameter correctly in 50% of the cases examined. Thus the regular solution does not appear to be very useful for predicting interaction effects in metallic systems. According to Richardson (15) the main source of error in this model is probably the assumption that interaction energies between atom pairs are independent of the composition of the solution.

2.3.2 Sub-regular solutions. Hardy (16) proposed that the excess free energy be taken as a function of concentration; he termed this the "sub regular" model and derived the following expression for the excess free energy:

$$F^E = X_i X_j \left[A^o_{ij} + (X_i - X_j) A'_{ij} \right] = X_i X_j \left[A^o_{ij} + (1-2X_j) A'_{ij} \right] \tag{2.61}$$

A plot of F^E/RT versus X_i should thus be linear with a finite slope.

This treatment was extended to ternary systems by Yokokawa et al. (17) who derived the following expression for the excess free energy.

$$F^E = X_j X_i A^o_{ij} - X_i X_k A^o_{ik} + X_k X_j A^o_{kj} + X_j X_i \frac{X_j - X_i}{X_j + X_i} A'_{ij} + X_i X_k \frac{X_i - X_k}{X_i + X_k} A'_{ik} + X_k X_i \frac{X_k - X_i}{X_k + X_i} A'_{jk} \qquad (2.62)$$

where the A's are constants characteristic of the appropriate binary system and defined from the assumption that the heat of solution of a binary solid solution is given by

$$\Delta H = (A^o_{ij}\, x + A'_{ij}\, y)xy$$

A relation may also be derived for the excess chemical potential of constituent i which may then be differentiated with respect to the mole fraction of component j to obtain an expression for the interaction parameter ε_i^j in terms of the constants of the sub-regular model (14):

$$\varepsilon_i^j = \frac{1}{RT} \left\{ (A^o_{ij} - A^o_{ik} - A^o_{jk}) + (A'_{ij} + A'_{ik} - A'_{jk}) \right\} \qquad (2.63)$$

It is assumed here that the interactions A^o and A' are not affected by additional solutes and/or solvents.

While this model appears to predict the sign of the interaction parameter rather better than that of regular solution, the actual magnitude of the parameter is only in very approximate agreement with experimental values (14). The model is limited in that the binary behaviour must be known experimentally and the solution must conform to the expression for a sub-regular solution.

2.3.3 <u>The quasi-chemical model</u>. This model was developed by Guggenheim (18) and allows for the fact that the distribution of atoms or molecules cannot be perfectly random if there is a heat of mixing.

The basic assumptions of this model are:

i) The motion of an atom is confined to its oscillation about an equilibrium position.

ii) Only the configurational partition function is considered to contribute to the thermodynamic excess properties. Effects due to changes in vibrational frequency of solute atoms due to changes in environment of the atom are neglected. So the main source of excess entropy is configurational and hence its sign is always negative. Another source of excess entropy which is neglected is the change in bond energy with temperature. This effect is generally considered negligible for the temperature ranges encountered in practice.

iii) Only pairwise interactions occur i.e. only the influence of nearest neighbours is considered.

iv) Solutions are considered to be dilute hence the number of nearest neighbours to any atom is assumed to be equal to the coordination number of Z of the pure solvent.

Using this model Alcock and Richardson (19) derived the following expression:

$$\left(\frac{\partial \Delta H_i}{\partial X_j}\right)_{X_j \to 0} = (\Delta H_{i(j)} - \Delta H_{i(k)} - \Delta H_{j(k)}) \qquad (2.64)$$

At low concentrations of j it was assumed that $\Delta S_{i(jk)} = \Delta S_{i(k)}$

so that

$$RT\left(\frac{\partial \ln \gamma_i}{\partial X_j}\right)_{X_j\to o} = \Delta H_{i(j)} - \Delta H_{i(k)} - \Delta H_{j(k)} \qquad (2.65)$$

Alcock and Richardson then made the following assumptions;

a) $\Delta S_{i(j)} = \Delta S_{i(k)}$ at $X_i \to 0$

b) $\gamma_{i(j)}$ and $\gamma_{i(k)}$ are taken relative to the same standard state for i.

c) $\Delta S_{j(k)}$ is Raoultian.

Under these conditions equation (2.65) becomes

$$\left(\frac{\partial \ln \gamma_i}{\partial X_j}\right)_{X_j\to o} = \varepsilon_i^j = \ln \gamma_{i(j)} - \ln \gamma_{i(k)} - \ln \gamma_{j(k)} \qquad (2.66)$$

Later Alcock and Richardson (20) using a more rigorous quasi-chemical approach took into account the possible effect due to clustering and obtained the expression:

$$\text{Ln } \gamma_{i(jk)} = \ln \frac{\gamma_{i(j)}}{\gamma_{(j+k)}} - Z \ln(KX_j + X_k)$$

where

$$K = \left[\frac{\gamma_{i(k)}\,\gamma_{j(j+k)}}{\gamma_{i(j)}\,\gamma_{k(j+k)}}\right]^{1/Z} \qquad (2.67)$$

and Z is the coordination number of pure solvent. This expression was differentiated to obtain an expression for the interaction paramter:

$$\left(\frac{\partial \ln \gamma_i}{\partial \ln X_j}\right)_{X_1 \text{ or } X_k\to o} = \varepsilon_i^j = -\frac{Z(K-1)}{X_k+KX_j}, \qquad (2.68)$$

which reduces to

$$\mathcal{E}_i^j = - Z(K - 1) \qquad (2.69)$$

when the solutes are present at infinite dilution.

Wada and Saito (21) used the zeroth approximation of Guggenheim's quasi-chemical method for regular solutions and assumed the coordination number in a liquid metal solution to be between 10 and 12. Dilute solutes were then assumed to be placed substitutionally in this very nearly close-packed lattice, statistical thermodynamics applied, and the following expression for the interaction parameter derived:

$$\mathcal{E}_i^j = \frac{1}{RT} (W_{ij} - W_{jk} - W_{ik}) \qquad (2.70)$$

where the W's are interchange energies between the components indicated by the subscripts.

This expression is identical in form to that obtained by Alcock and Richardson based on a random solution model.

However Wada and Saito determined their interchange energies independently by using an expression proposed by Mott (22) for the excess free energy of mixing in binary solutions and an expression for the excess free energy of mixing in dilute solution.

$$F_i^E = W_{ij} \phi_i \phi_j \qquad (2.71)$$

The expression for the interchange energy then becomes

$$W_{ij} = V^M (\delta_i - \delta_j)^2 - 23{,}060 \, \overline{n} \, (\underline{\overline{X}}_i - \underline{\overline{X}}_j) \qquad (2.72)$$

where V^M = molar volume; X = electronegativity; $\bar{n}$ = number of ij bonds; δ = solubility parameters.

Except for $\bar{n}$, these parameters are known for most elements. Wada and Saito (21) suggested that the smaller value of the valency of the two components may be employed as the value of $\bar{n}$ and V^M should be taken as the arithmetic average of the atomic volumes of the two components in the solid state.

Lupis and Elliott (23) have recently used the quasi-chemical model in order to predict first and second order free energy interaction coefficients in multi-component solutions.

They derive the following series expression for the excess free energy of the dilute (1-i-j) solution.

$$\begin{aligned}\frac{F^E}{RT} = {} & \frac{Z}{2} X_i \ln(1-\lambda_{1i}) + \frac{Z}{2} X_j \ln(1+\lambda_{1j}) \\ & -\frac{Z}{2}\lambda_{1i} X_i^2 - \frac{Z}{2}\lambda_{1j} X_j^2 - Z\mu_{ij} X_i X_j \\ & +\frac{Z}{2}\lambda_{1i}^2 X_i^3 + \frac{Z}{2}\lambda_{1j}^2 X_j^3 + Z\mu_{ij}(\lambda_{1i} + \tfrac{1}{2}\mu_{ij})X_i^2 X_j \\ & + Z\mu_{ij}(\lambda_{1j} + \tfrac{1}{2}\mu_{ij})X_i X_j^2 + 0(X^4) \qquad (2.73)\end{aligned}$$

Where

$$\lambda_{ij} = \exp(2 \; W_{ij}) - 1$$

$$W_{ij} = u_{ij} - \frac{u_{ii} + u_{jj}}{2}$$

u is the bond energy of the appropriate pair.

$$\beta = 1/KT$$

$$= \exp\left[\beta\left(W_{1i} + W_{1j} - W_{ij}\right)\right] - 1$$

$$= \left\{\frac{(1 + \lambda_{1i})(1 + \lambda_{ij})}{(1 + \lambda_{ij})}\right\}^{\frac{1}{2}} - 1$$

The terms in the expansion correspond to equivalent terms in the Taylor expansion for G^E/RT. Thus expressions for the various interaction coefficients may be obtained by direct comparison. Lupis and Elliott (23) also express these coefficients in terms of lower order interaction coefficients.

e.g. $\varepsilon_i^j = -z\mu_{ij}$ in terms of quasi-chemical coefficients

$$\text{or } \varepsilon_i^{j} = z\left\{1 - \left[\frac{(1 - {}^{i}_{i}/z)(1 - {}^{j}_{j}/z)}{(1 - {}^{i}_{i}/z)_{i-j\ \text{binary}}}\right]\right\}$$

the thermodynamic equivalent of the quasi-chemical expression.

Similar expressions were also derived for the second order interaction parameters.

$$\text{i.e.}\quad \rho_i^j = z\mu_{ij}\lambda_{\substack{1i\\2}} + \frac{z}{2}(\mu_{ij})^2 + \frac{z}{2}\lambda_{ij}$$

$$\text{or}\quad \rho_i^j = \frac{\left[\varepsilon_i^j\right]^2}{2z} + \frac{\varepsilon_j^j}{z}\left(\varepsilon_i^j - \frac{z}{2}\right)$$

The agreement between the observed and calculated values for the various coefficients appears to be reasonably good in the systems compared by Lupis and Elliott (23). The agreement was poorest for solute elements having small radii, which one would expect since the model assumes that the atoms of the solute are placed "substitutionally" on the pseudo lattice rather than "interstitially".

The two assumptions of the quasi-chemical model which are most open to criticism are firstly the assumption of pair wise interactions or of the non-dependence of the bonding energies on the concentration of the solutes and secondly the neglect of the vibrational contributions to the excess properties. The first difficulty can be largely avoided by adopting the reference state of infinite dilution of the corresponding solute in the solvent. One consequence of the second assumption is that the only excess entropies taken into account are configurational and hence, are negative contrary to the experimental evidence that positive excess entropies are frequently observed.

2.3.4 The quasi-regular solution model. In a subsequent paper Lupis and Elliott (24) attempted to eliminate some of the weaknesses of the quasi-chemical model and at the same time develop a solution model that would predict enthalpy and entropy interaction coefficients for liquid metal solutions. This model was based to a large extent on the cell model of the liquid state (25). In the liquid state far below the critical temperature, some short range order would be expected to exist. The field acting on each atom will fluctuate rapidly but this fluctuating field can be replaced by an average field of spherical symmetry. In this model the partition function is described in terms of probabilities associated with different configurations in the nearest neighbour well about a central atom. The configuration depends mostly on the number of atoms present of any particular kind.

The regular solution assumes complete randomness of the different atoms and that the only source of entropy of mixing is configurational. Lupis and Elliott call the simplest form of this model the quasi-regular solution model. This retains the assumption of complete randomness and hence S^E conf. = 0. However other contributions to the total excess entropy are not neglected and they obtain the following expression for the excess free energy:

$$F^E = ZX_A X_B W_{AB}(1 - \frac{T}{\tau})$$

where Z is the average coordination number.

X_A, X_B are mole fractions of components A and B respectively

$$W_{AB} = u_{AB} - \frac{u_{AA} + u_{BB}}{2}$$

u_{AB} is bond energy of atoms A and B

τ is a "characteristic temperature" of the solution.

CHAPTER 3

LITERATURE REVIEW

3.1. Solubility of nitrogen in liquid iron.

Metallurgists became interested in a thermodynamic approach to metallic solutions following the development of Gibbs's phase theory in 1887 and the discovery of Raoult's Law in 1888. Investigation into the solubilities of gases in metals and alloys was stimulated by the extensive work of Sieverts and Krumbhaar (26) around 1910, who discovered the relationship between solubility and gas pressure, now known as Sieverts' Law.

No accurate determinations of the solubility of nitrogen in liquid iron or liquid iron alloys were recorded until Chipman and Murphy (30) measured its solubility in liquid iron in 1935. Prior to this date, a number of approximate results had been obtained. In 1911, Andrew (27) melted iron under nitrogen at 200 atmospheres pressure and succeeded in dissolving 0.3 wt. pct. nitrogen. Strauss (28), in 1914, introduced between 0.03 and 0.04 wt. pct. nitrogen into steel by the action of ammonia and nitrogen on the liquid metal. Sawyer (29), in 1923, using nitrogen pressures up to three atmospheres, found that his results and Andrew's could be expressed by the equation:

$$\text{Wt. Pct. Nitrogen} = 0.02\sqrt{P}$$

where P was the pressure in atmospheres. However, previous to Chipman and Murphy's determination, investigators had never established that equilibrium had in fact been attained between the gas phase and the liquid metal.

The method used by Chipman and Murphy (30) consisted in heating a charge of iron in a closed induction furnace and equilibrating the melt with a nitrogen atmosphere at temperatures between 1540°C and 1760°C. The melt was then cooled in the furnace and the resulting ingot was analysed using the vacuum fusion method. The absorption of nitrogen by the melt was followed by adding small amounts of nitrogen through gas burettes to maintain the pressure over the melt at one atmosphere. Absorption was judged to be complete when it was no longer necessary to add more gas to maintain the pressure. The cooling process was also followed using the gas burettes and by this means any gas evolved on solidification could be monitored and added as a correction factor to the percentage of nitrogen in the ingot. Using this method, the solubility of nitrogen in liquid iron was found to be 0.040 wt. pct. at 1600°C and a value was calculated for the temperature coefficient of solubility of 1.5×10^{-5} wt. pct. per °C.

Independently, Sieverts and Zapf (31) in Germany determined the solubility of nitrogen in liquid iron using what has become known as the Sieverts' method. With this method (which is described in more detail in Chapter 4), the absorption of nitrogen was measured directly at constant temperature and pressure with gas burettes. The value of 0.031 wt. pct. obtained by Sieverts and Zapf for the solubility of nitrogen in liquid iron at 1540°C was markedly lower than that obtained by Chipman and Murphy.

Following these investigations there was an increased demand for further information concerning the effect of gaseous elements dissolved in steel, particularly as the irregular behaviour of well-known steels was frequently attributed to the presence of dissolved gases. Hence, in the ensuing years a large number of investigations into the solubility of nitrogen and other gases in liquid iron and its alloys were performed. Two methods were widely used; the sampled bath technique and an improved Sieverts' technique. Paradoxically, the Europeans appeared to prefer the sampling technique while the Americans preferred the Sieverts' technique. In 1941, Kootz (35) established the important fact that the dissolution of nitrogen in pure liquid iron obeyed Sieverts' Law. Thus, the dissolution of nitrogen in liquid iron could be represented by the reaction

$$\tfrac{1}{2}N_2 \longrightarrow \underline{N}$$

where the $\underline{N}$ denotes nitrogen dissolved in liquid iron.

Interest in these types of investigation received an added stimulus when Wagner (5) and Chipman (4) around 1950 advanced solution thermodynamics to the stage where the effects of alloying elements on the solubility of other solutes could be predicted through atomic interaction effects (Chapter 2). In order to make effective use of these concepts more accurate data were required.

In 1957, Kashyap and Parlee (41) repeated the work of Kootz and confirmed that Sieverts' Law is obeyed by nitrogen dissolving in liquid iron, up to one atmosphere pressure. These workers also determined the solubility of nitrogen in Fe - Ni, Fe - Mo, Fe - V and Fe - Mo - V alloys and were able to test the validity of Wagner and Chipman's approximation formulae for the prediction of nitrogen solubilities in these alloys. Good agreement was found between experimentally determined nitrogen solubilities in the ternary alloys, and calculated values obtained from the relevant binary data.

By 1960, Elliott and co-workers (46, 47) had made an extensive study of the solubility of nitrogen in a wide variety of liquid iron alloys. In the course of this work, two separate investigations were conducted concerning the solubility of nitrogen in pure iron. Humbert and Elliott (46) determined the solubility of nitrogen at one atmosphere pressure in pure liquid iron at 1600°C, to be 0.0438 wt. pct. They also determined the solubility over the temperature range 1540°C to 1700°C and found the temperature coefficient of solubility at 1600°C to be 7.7×10^{-6} wt. pct. per °C, which was approximately half the value previously reported for this coefficient. Their results yielded the following values for the heat and free energy of solution of nitrogen in liquid iron:

$$\Delta H^{\circ} = 1200 \pm 400 \text{ cals/g. atom}$$

$$\Delta F^{\circ} = 1200 + 5.56\ T \pm 200 \text{ cals/g. atom}$$

Pehlke and Elliott (47) in their investigations, again using the Sieverts' method, found that the dissolution of nitrogen in pure liquid iron obeyed Sieverts' Law to a very high degree of precision up to one atmosphere pressure of nitrogen. This confirmed the results of all previous investigations, except those of Kasamatu and Matoba (40), who found a departure from Sieverts' Law at all concentrations. Pehlke and Elliott found the solubility of nitrogen in pure liquid iron to be 0.0451 ± 0.0006 wt. pct. at 1600°C. The temperature coefficient of solubility was found to be 8×10^{-6} wt. pct. per °C at 1600°C. The heat and free energy of solution were reported as:

$$\Delta H^{\circ} = 860 \pm 400 \text{ cal/g. atom}$$

$$\Delta F^{\circ} = 860 + 5.71\ T \pm 100 \text{ cal/g. atom}$$

These data are in good agreement with those of Humbert and Elliott (46), but it is worth noting, that while highly consistent data were obtained from any one experiment, the consistency of the data from one experiment to another is, by comparison, rather poor. This inconsistency results in a relatively large error in the average value for the heat of solution, in spite of the fact that the root mean square error on all experiments performed at 1600°C was only 0.0006 wt. pct. N. (Fig. 2).

A more recent investigation of nitrogen solubility in pure liquid iron is that by Turnock and Pehlke (51) in 1966. Using the Sieverts' technique, they obtained results which agreed well with those of Elliott and co-workers (46, 47). The solubility of nitrogen in pure liquid iron at 1600°C has also been measured by a number of other investigators who were primarily interested in determining its solubility in liquid iron alloys.

A summary of the results available in the literature for the dissolution of nitrogen in pure liquid iron is shown in Table 1 and some of the more recent values for solubilities determined as a function of temperature are plotted in Fig. 3. It will be noted that, while there are discrepancies between the results of the various workers, the data from the last three investigations mentioned, (46, 47, 51), are in good agreement.

3.2 Solubility of nitrogen in liquid iron-carbon alloys.

If prediction formulae are to be useful for steelmaking purposes, a precise knowledge of the interaction effects between nitrogen and carbon in liquid iron is required. Unfortunately, this system has proved difficult to deal with using the Sieverts' method, probably because of the difficulties associated with the gaseous reaction product which can form when iron carbon alloys are held in a refractory crucible.

Since this technique requires the melt to be held in a closed reaction vessel, and the nitrogen absorption to be measured directly using gas burettes, any gaseous products formed during an experiment will give low values for the solubility of nitrogen. For this reason, it is considered that the most reliable data to be found in the literature for this particular system are those obtained by the sampled bath technique.

The first reported study of the solubility of nitrogen in liquid iron carbon alloys was made by Eklund (32) in 1939. Using the sampled bath method, he found that carbon markedly decreased the solubility of nitrogen in liquid iron. Solubilities were measured at 1550°C in the range 0 to 4 wt. pct. C. From his various data, Eklund selected only the highest values for nitrogen solubility as a basis for drawing his solubility curve. (Fig. 4). More recently, Chipman (52) has shown that when all of Eklund's results are taken into consideration a value of +0.13 is obtained for the first order free energy interaction parameter, e_N^C.

Kootz (35) obtained data for the solubility of nitrogen in liquid iron carbon alloys at 1600°C. Again the sampled bath technique was used. From the results of this work, Pehlke and Elliott (47) have calculated a value of 0.13 for e_N^C.

Saito (37, 38) has used both the Sieverts' and sampled bath techniques for determining nitrogen solubilities in this system. The two solubility curves obtained at 1600°C had approximately the same slope, but the Sieverts' method gave considerably lower solubility values, probably for the reason mentioned previously. The value for the interaction parameter e_N^C obtained from this work was 0.135.

Using the sampled bath technique, Maekawa and Nakagawa (44) found that the logarithm of the activity coefficient, f_N^C, could be represented as a linear function of the carbon content, in the range 0 - 4 wt. pct. C., and in the temperature range 1550° to 1700°C, by the equation:

$$\mathrm{Log}\ f_N^C = 0.135\ (\%C) \qquad \text{i.e.} \quad e_N^C = 0.135$$

Again, using the sampled bath technique, Schenck et al.(42) have determined nitrogen solubilities in liquid iron carbon alloys in the temperature range 1550° to 1650°C, at one atmosphere pressure and in the range 0 to 5 wt. pct. C. They found that their results could be represented by a first order free energy interaction parameter, $e_N^C = 0.125$. Solubilities were measured at various partial pressures of nitrogen (1, 0.52, 0.32, 0.16 atmospheres) at 1600°C and it was found that on a plot of $(\%\underline{N})$ alloy$/\sqrt{P_{N_2}}$ versus carbon content, all the data could be represented satisfactorily by the same line. This indicated that nitrogen obeys Sieverts' Law in all liquid iron carbon alloys up to 5 wt. pct. carbon at 1600°C.

A recent investigation of the solubility of nitrogen in liquid iron carbon alloys was reported by Pehlke and

Elliott (47). These workers found that the Sieverts' technique was unsuitable for this system, and their data were obtained using the sampled bath method. For a given concentration of carbon, their results for the solubility of nitrogen were lower, and thus the value for e_N^C (0.25) was higher than those obtained in previous investigations. Again it was found that Sieverts' Law was obeyed throughout the carbon concentration range investigated (0 - 5 wt. pct.).

The solubility relationships obtained in the above investigations are shown in Fig. 4, and it is evident that a lack of agreement exists between the various data. It has been noted already that of the two techniques employed for nitrogen solubility studies, the most reliable data for iron carbon alloys has been obtained using the sampled bath method. However, evidence obtained during the present investigation (Chapter 5) indicates that the quench rates achieved in the sampled bath technique may not always be adequate to retain all the nitrogen in the metal during solidification.

3.3 Solubility of nitrogen in liquid iron-aluminium alloys.

Eklund (32) has studied the solubility of nitrogen in liquid iron-aluminium alloys (0 to 3 wt. pct. aluminium) at 1550°C using the sampled bath technique. The few data collected were somewhat scattered, but did indicate that aluminium tends to increase the solubility of nitrogen in liquid iron. From this work, Pehlke and Elliott (47) have calculated a value for e_N^{Al} of -0.0103.

Maekawa and Nakagawa (44) investigated this system in the range 0.5 to 8.5 wt. pct. Al, at 1700°C, using the sampled bath technique. At lower temperatures difficulties were experienced due to the formation of aluminium nitride, and satisfactory results were not obtained. However, at 1700°C it was found that the nitrogen content of the melt decreased sharply with increasing aluminium content (Fig. 5). Using the results from this investigation and their data for nitrogen solubility in pure iron, they obtained a relationship for log f_N^{Al} in terms of aluminium concentration, which could be represented by the equation:

$$(\text{Log } f_N^{Al})_{1700^\circ C} = 0.009\ (\%Al)^2 + 0.008\ (Al)$$

valid for alloys with aluminium contents less than 8 wt. pct.

Pehlke and Elliott (47), using the Sieverts' method, determined the solubility of nitrogen in liquid iron-aluminium alloys at 1600°C and one atmosphere pressure in the range 0 to 0.5 wt. pct. Al; above this concentration they noted that a film of "what appeared to be aluminium nitride" formed on the surface. It was found that aluminium slightly decreased the solubility of nitrogen, and a value of 0.0025 was proposed for e_N^{Al} at 1600°C. (Fig. 6).

The only other work reported in the literature for this system is that of Evans and Pehlke (53) using the Sieverts' method. These workers measured the equilibrium nitrogen solubility in liquid Fe - Al alloys as a function of nitrogen gas pressure. Measurements were made for alloys containing up to 3.85 wt. pct. Al in the temperature range 1600° to 1750°C and 0.01 to 0.85 atmospheres of nitrogen.

They determined the solubility product by admitting nitrogen in small increments until a deviation from Sieverts' Law in the form of a "pressure halt" was observed. X-ray powder patterns and wet chemical analyses were used to identify the nitride phase precipitated. These values were subsequently checked by equilibrating liquid iron in an aluminium nitride crucible under a known partial pressure of nitrogen. When equilibrium had been attained, the crucible was quenched and the resulting ingot was analysed for aluminium and nitrogen.

Fig. 7 shows the results plotted by Evans and Pehlke (53). A pressure of 20.25 cm Hg (0.267 atm.) was selected by them for tabulation of the solubility data, since it represents a pressure below that required for the precipitation of AlN in most of their experiments. Aluminium-nitrogen interaction parameters obtained by these investigators and others mentioned previously are presented in Table 2. It will be noted that the data of Evans and Pehlke (53), like those of Eklund (32), indicate that aluminium increases the solubility of nitrogen in liquid iron; whereas, the data of Elliott and Pehlke (47) and Maekawa and Nakagawa (44) indicate that aluminium decreases the solubility of nitrogen in liquid iron.

CHAPTER 4

EXPERIMENTAL TECHNIQUES USED IN PREVIOUS INVESTIGATIONS

In the past, two methods have been widely used to determine nitrogen solubilities. The Sieverts' technique, in which the amount of nitrogen required to saturate a given mass of liquid metal at a particular temperature or pressure is measured volumetrically, and the sampled bath technique, in which the melt is equilibrated with a nitrogen atmosphere, and samples drawn from the melt are quenched and analysed.

4.1 The Sieverts' technique. A diagram of a typical apparatus is shown in Fig. 8. The apparatus consists of a reaction vessel, a gas burette, a manometer and gas train. The design of the reaction vessel is critical, as the volume of gas above the melt must be kept to a minimum to obtain accurate results. A crucible, usually alumina, containing the melt is located inside a second crucible, which acts as a radiation shield. These crucibles rest on insulators, which are in turn supported by a water-cooled pedestal. The reaction vessel is completely surrounded by a water-jacket, except for a narrow neck just above the melt through which the gas enters. Temperatures are generally measured by viewing the surface of the melt with an optical pyrometer.

The pressure within the reaction vessel is measured with a mercury manometer. If the capillary of this manometer is too large, unnecessary error may be introduced during the hot volume calibration of the apparatus. If it is too small, the pressure measurements may contain errors due to surface tension effects. A suitable capillary diameter has been found to be approximately 1 mm.

The gas burettes generally have a capacity of 100 ml. and may be read to an accuracy of ± 0.05 ml. They are enclosed in isothermal water-jackets and mercury is generally employed as the pumping and measuring fluid.

The melt is heated by means of an induction coil surrounding the reaction vessel. At the start of each experiment, the charge is heated to about 1500°C for approximately thirty minutes under a reduced pressure of about 10 microns Hg in order to degas the apparatus. An inert gas with physical characteristics very similar to those of the experimental gas is then introduced into the reaction vessel, and the charge is brought to the desired temperature. The bulb is evacuated, and the hot volume is measured at different pressures with the inert gas. The reaction vessel is again evacuated to approximately 10 microns. At this stage metal may evaporate from the melt and deposit on the cooler portions of the reaction chamber and this may cause significant error in determining nitrogen solubilities; the melt should therefore be held under vacuum for as short a time as possible, commensurate with proper evacuation; this time is usually on the order of ten minutes. Following this preliminary procedure, the volume of nitrogen required to saturate the melt at a given temperature and pressure is measured. The melt is judged to be saturated when the pressure remains constant with temperature without further addition of gas. The time required to reach equilibrium is generally about 2 to 3 hours. After an experiment a further check is made of the hot volume calibration.

4.2 Disadvantages.

4.2.1 Hot volume calibration. The term "hot volume" refers to the volume of gas in the space between the surface of the melt and the gas burette, when the melt is held at the temperature at which the solubility is to be measured. The determination of this volume is carried out under identical conditions to those prevailing during an experiment except that an inert gas is used. This gas should have similar thermal properties to those of the gas under investigation. For example, in the determination of nitrogen solubilities argon is used to measure the hot volume. The temperature profile through argon will not, however, be identical to that through nitrogen, hence for a given melt temperature, the hot volumes for the two gases will not be exactly the same. Another factor which tends to make this calibration imprecise is that the hot volume is continually changing with time during a particular run, due to evaporation from the melt. These errors are in addition to the error involved in measuring the actual volume of gas flowing from the burette. Gas volumes can usually be read to an accuracy of ±0.05 ml. but the fluctuation of the water temperature in the jacket of the burette is generally about ±0.5C° and this will increase the total error in the measurement of gas volumes to approximately ±0.25 ml. (46). As the experimental technique involves the subtraction of two volume readings (i.e. the nitrogen volume - the inert hot volume) this error is increased to about ±0.5 ml. For a melt containing 50 gm. of pure iron the volume of nitrogen actually dissolved in the melt would be about 20 ml. at 1600°C and one atmosphere pressure. Hence the uncertainty in the actual measurement of the nitrogen solubility is about ±2.5 pct. In the presence of alloying elements which decrease the solubility of nitrogen in liquid iron these errors could be much greater.

4.2.2 *Crucible attack*. Uncertainty in the determination of gas solubilities may be introduced by reaction between the melt and the crucible material. The solubility of nitrogen in the melt will be influenced by the presence of other elements taken into solution from the walls of the crucibles. Furthermore, if the melt reacts with the crucible material to form a gaseous reaction product, the measured solubility will be less than the true value.

4.2.3 *Initial nitrogen content of the melt*. The charged material will in general contain a small amount of nitrogen. This must be determined by a separate analysis and taken into account in the final result. This effect will in general be small and will probably amount to no more than $\pm 0.0002\%$N in the final result.

4.2.4 Gas adsorption on metal films. During a prolonged experiment evaporation of the melt will give rise to the formation of metallic films on the cooler portions of the reaction chamber. These freshly deposited highly active films will adsorb nitrogen from the gas phase. This effect will produce anomalously high values for the nitrogen solubility in the melt.

4.3 The Sampled-Bath technique.

In this method the melt is held in a refractory crucible, usually alumina, and heated in an atmosphere of nitrogen. Sometimes the gas is bubbled through the melt in order to obtain a more rapid approach to equilibrium. The temperature may be measured by an optical pyrometer or a thermocouple, however the former is preferable since there is less risk of contamination. At frequent intervals during an experiment, samples are drawn from the melt with either silica or copper tubes approximately 2 to 5 m.m. I.D. and immediately quenched in water. The nitrogen content of these samples is then determined using either the Kjeldahl technique or the vacuum-fusion method. A comparison of these two analytical techniques is given in section 5.10.

4.4 Disadvantages.

The main disadvantages of the sampled bath method is the possibility that some nitrogen may be lost or gained during the quenching operation (45).

Again, a possible source of error is contamination of the melt by the crucible material, but in general this effect will be small. Large errors due to crucible-melt reactions which produce gaseous products are eliminated in this technique as these products are continuously swept away in the gas stream.

CHAPTER 5

EXPERIMENTAL PROCEDURE

5.1 The Levitation technique (54).

Conducting material when placed in a coil of proper geometry through which a high frequency alternating current is flowing, may be made to levitate. This effect is due to the interaction of electro-magnetic fields due to the current in the coil and the induced currents in the specimen. The eddy currents will also heat the specimen to temperatures which will depend on:

a) Geometry of the coil.

b) Power into the coil, and the ratio of voltage to current in the coil.

c) The nature of the specimen. i.e. density, thermal and electrical conductivity.

d) Size of specimen.

e) The atmosphere in which the specimen is located.

A conductor placed in an electromagnetic field will move to the weakest part of the field. Hence, for levitation the field strength must decrease vertically to provide a lifting force and radially towards the field axis to provide a restoring force towards the centre of the coil.

The levitation coil assembly used in the present work was of the form shown in Fig. 9. The coil was wound from 1/8 inch copper tubing enclosed in fibre-glass sleeving. This sleeve material prevented shorting between the various turns of the coil during operation. The bottom coil, consisting of four turns, was wound on a conical former having a half angle of 30°. The two reverse turns placed co-axially above the main levitating coil gave the specimen greater stability. Cooling water was passed through the windings to prevent over-heating of the coil.

The induction unit used in the present work was a 450 kc/s, 10 kw Toccotron generator and the high frequency current was delivered to the levitation coil through a 7.5: 1 step-down transformer. By using the transformer it was much easier to obtain temperatures in the range 1400° to 1600°C.

5.2 Advantages of levitation melting.

5.2.1 Noncontamination of the melt.

In the past there have been a number of physico-chemical studies in which the reaction between the melt and the crucible material has presented problems. Difficulties of this nature are avoided with levitation melting since there is no physical contact between the melt and any supporting material.

5.2.2 Efficient stirring of the melt.

The high frequency current induced in the specimen produces very efficient stirring. This results in a rapid attainment of equilibrium, particularly since a relatively large metallic surface is exposed to the gas phase. It also ensures good mixing of alloying elements throughout the bulk of the specimen.

5.2.3 Temperature range of the investigation may be increased. The temperature range in which a gas/liquid metal system can be studied is often extended to much higher temperatures than those which most crucible materials are able to withstand. Also, in many cases lower temperatures may be attained using this technique since the absence of a crucible decreases the chance of heterogeneous nucleation in a supercooled melt. The degree of undercooling will however depend upon the conductivity of the gaseous atmosphere and the chemical nature of the reaction.

A further advantage of this technique is that hot volume calibrations and complex glassware involving gas burettes are not required.

5.3 Disadvantages of levitation melting.

The main disadvantages of the technique are due to difficulties in temperature control (section 5.6) and the relatively severe vaporization of volatile elements from the melt due to the large surface to volume ratio of the droplet, and the rapid stirring induced by the high frequency current.

It is frequently found that when sufficient power is provided for levitation, the energy transferred to the droplet produces excessively high temperatures. The coil design used in the present work was selected because of all the types investigated it gave the greatest degree of lift with the minimum degree of heating (55, 56).

5.4 Quenching procedure.

When this project was initiated, the levitated metal was dropped into a copper mould held in the reaction tube approximately one inch below the coil. The results of these preliminary experiments on the solubility of nitrogen in pure iron are shown in Fig. 10. It was clear from the random nature of the results and the spread in the data, (approx. ±0.002 wt. pct. N compared with an expected uncertainty of ±0.0003 wt. pct. due mainly to error in the chemical analysis) that nitrogen was being lost from the specimen during quenching.

The quenching method finally adopted was a modification of a technique developed by Pietrokowsky (57). The quenching effect is obtained by allowing the levitated droplet to fall between two copper blocks which then come together rapidly, squeezing the droplet between them.

A diagram and photographs of the apparatus are shown in Figs. 11, 12, 13 and 14. The reaction tube (a) is held by an O-ring and clamp (b) in the mild steel cylinder (c). When the specimen is to be quenched the pendulum (d) is released. At a point along the path of the pendulum, contact between a slide (g) (fixed to the pendulum) and the brass slide rod (h) is broken. This breaks a relay circuit, (Fig. 14) which in turn trips a relay in the generator, cutting the power to the levitation coil. The liquid metal droplet then falls freely down the Vycor tube and between the two copper blocks (i). At the same instant, the base of the pendulum hits the piston (m) and the droplet is squeezed between the two copper blocks (i) to give a thin disc approximately 0.005 inches thick and two inches in diameter.

To reduce the effect of gas exhausting up the reaction tube as the copper blocks come together, two solenoid valves are placed in the system. When contact is broken between (g) and (h), the solenoid valve (j) is closed and at the same time, the solenoid valve (k) is opened. The gas trapped between the two blocks and the normal gas flow now escape through the valve (k) and thus hindrance to the free fall of the droplet by an upward flowing gas stream is eliminated.

Assuming the quenched disc of metal (Fig. 15) was liquid with this shape just before solidification, it is estimated that the quench rate at the solidification temperature was approximately 10^6 c^o/sec. (Appendix C). In order to check that this quench rate was sufficient to retain the equilibrium melt concentration of nitrogen in the iron at room temperature secondary experiments were made in which the copper blocks were faced with iron, which has a thermal conductivity approximately one order of magnitude less than that of copper. This arrangement gave a quench rate approximately 1/10th that obtained with the copper blocks. Using both the copper and iron quenching systems, the values obtained for nitrogen solubility were in agreement within the limits of experimental error. It was concluded therefore that the quench obtained with the copper blocks was sufficiently rapid to retain all the nitrogen in solution during solidification. The reproducibility of the data obtained using the copper blocks also confirms this conclusion.

5.5 Attainment of Equilibrium.

A series of preliminary experiments were performed in order to determine the optimum time required, at temperature, for the specimen to reach equilibrium with the nitrogen atmosphere. Specimens were held under identical conditions for 2, 4, 8 and 16 mins. but no significant difference in the nitrogen content of the specimens could be detected. (Table 3). During an actual experiment, melts were equilibrated with the gas phase for four minutes and then quenched.

5.6 Temperature measurement and control.

The temperature of a specimen was measured by means of a Milletron two colour pyrometer. The specimen was viewed through an optical flat arrangement as shown in Fig. 11. The pyrometer was calibrated by viewing the surface of pure liquid iron contained in an alumina crucible and held under a nitrogen atmosphere. The pyrometer readings were compared with those obtained from a standard Pt/Pt-13% Rh thermocouple immersed in the melt. The optical arrangement used during calibration was the same as that shown in Fig. 11.

Several calibration experiments were performed using a carbon saturated iron melt contained in a graphite crucible.

These experiments established that carbon dissolved in the melt had no effect on the temperature, as indicated by the pyrometer.

Calibration experiments were made over the temperature range 1350°C to 1700°C. The suitability of the calibration data for the solubility experiments was confirmed by observing the melting point of pure iron droplets under levitation conditions. This latter procedure was used to check the pyrometer calibration each time it was used.

The temperature of the droplet was coarsely controlled by adjusting the flow rate of nitrogen over the specimen and finely controlled by adjusting the level of power in the coil. The latter adjustment had the effect of varying the height of the specimen in the coil and hence, the transfer of energy to the specimen. By these means, a specimen could be held to within ±5C° of the desired value. Allowing for an error of ±5C° in the calibration of the pyrometer, it is considered that the reported temperatures are accurate to within ±10C°.

5.7 The Gas-train.

The gases were passed over magnesium perchlorate and a proprietry material (Indicarb) to absorb any moisture or carbon dioxide respectively which might be present. The gas was then passed through the quench unit, over the specimen in the Vycor tube, through solenoid valve (j), thence through a bubbler to exhaust. The exhaust tube just touched the surface of the oil in the bubbler, in order to minimize the back pressure in the system. For the same reason all tubing had an internal diameter equal to that of the reaction chamber (15 mm). All specimens were equilibrated in a nitrogen atmosphere at atmospheric pressure.

5.8 Materials used.

The specimens for the various experiments were prepared from the following materials; (the analytical data are reported in ppm.):

Armco Iron having an analysis:

C	Mn	S	P	O
120	170	250	50	750

were levitated and deoxidized in a hydrogen atmosphere at 1600°C for four minutes before use. By this treatment, the oxygen content was reduced to less than 10 ppm. AUC graphite with the following analysis was obtained from Union Carbide:

S	Fe	Ca	Si
40	50	160	14

Total ash as oxide = 300 ppm

Aluminium was obtained from a high purity aluminium ingot which had the following composition:

Cu	Fe	Mg	Others
150	40	10	10

A prepurified grade of nitrogen with the following analysis was obtained from Matheson of Canada Ltd.:

O	H_2O	CO_2	Argon
5	11	5	20

5.9 Experimental Procedure.

5.9.1 Pure Iron. Pieces of Armco iron approximately 1 gm in weight were cut from 1/4" rod. The rubber stopper "o" (Fig.11) was removed and a pyrex glass rod placed in the reaction tube. The Armco iron was dropped onto the rod from "p", the current into the coil was increased to the maximum value, the rod removed, and the specimen levitated in the coil. The system was flushed with nitrogen and the specimen then deoxidized in hydrogen at 1600°C for four minutes. After deoxidation, pure nitrogen was passed over the melt, which was then held at the required temperature for a further four minutes to ensure attainment of equilibrium. The specimen was quenched between the copper blocks and analysed for nitrogen using the standard Kjeldahl steam distillation technique (5.10).

5.9.2 Iron-carbon alloys. Each alloy was prepared in situ as follows. A hole was drilled in a one gram sample of Armco iron and graphite placed in the hole which was then closed by squeezing in a vice. The specimens were equilibrated in nitrogen, quenched and cut into two halves. One half was analysed for nitrogen and the other half for carbon using the Leco combustion technique.

5.9.3 Iron-aluminium alloys. Nitrides may form in these alloys at 1600°C and one atmosphere pressure of nitrogen, when the aluminium concentration exceeds about 1 wt. pct. Alloys having the following compositions 0.9, 0.8, 0.63, 0.52, 0.47, 0.43, and 0.2 wt. pct. Al, were prepared by melting a weighed amount of Armco iron in an alumina crucible and passing hydrogen over the melt for about 30 minutes in order to deoxidize the iron. The melt was then held under argon and a weighed quantity of aluminium added. After about 10 minutes a suction sample was withdrawn from the melt by means of a quartz tube, quenched in water, and weighed. More aluminium was added to the melt and the same procedure followed until the required number of alloys was obtained.

The alloys were ground in order to remove any surface oxide which might be present and samples approximately one gm in weight cut from each rod. After equilibration in nitrogen, the samples were quenched, cut in half and one piece retained for nitrogen analysis, the other for aluminium.

5.10 Nitrogen analysis. Specimens were analysed for nitrogen using the Kjeldahl steam-distillation technique (58). The full procedure is presented in Appendix A.

The only other technique generally available for the determination of nitrogen in metals is the vacuum-fusion method. An exhaustive study (58) has been made of the methods for determining nitrogen in steel in which the chemical method and the vacuum-fusion method were compared. The results obtained from a number of laboratories indicated that the confidence limits for the chemical method were in general closer than those for the vacuum-fusion method. This was true both for the agreement between different laboratories and within a single laboratory.

In the present study preliminary checks on the accuracy of the chemical method were made by determining the nitrogen content of various quantities of standard aluminium ammonium sulphate solutions. From these results it was found that the analyses were accurate to ±3 ppm at a nitrogen level equivalent to 450 ppm in an iron sample.

A further check was made to determine whether there was any segregation or variation of the quantity of nitrogen in the metal at the thinner periphery region of the quenched disc. All checks showed that there was no such radial variation in nitrogen content.

5.11 Carbon analysis.

Samples were analysed for carbon using the standard Leco combustion method. This method has been described in detail elsewhere (59).

The accuracy of the analytical procedure was checked using standard samples from the National Bureau of Standards, and it is considered that the reported carbon analyses are accurate to at least ±0.05 wt. pct. C.

5.12 Aluminium analysis.

The samples were analysed for aluminium by a colorimetric method using "Chromazurol S" as the colouring agent. This method was obtained through the courtesy of The Steel Company of Canada and is described in Appendix A. It is estimated that the aluminium contents measured using this procedure are accurate to ±0.02 wt. pct. Al.

CHAPTER 6

PRESENTATION OF RESULTS

6.1 The solubility of nitrogen in liquid iron.

Data for the solubility of nitrogen in liquid iron at temperatures in the range 1530° to 1780°C are shown in Table 4 and Fig. 17. The error bars on this plot represent the effect of errors of ±0.0003% in the nitrogen analysis. A least squares fit to the data yields the following equation for the effect of temperature on the solubility of nitrogen in liquid iron, when the nitrogen pressure in the gas phase is one atmosphere:

$$\text{Log}\ [\text{Wt\%N}] = -\frac{285}{T}\ (\pm 110) - 1.21\ (\pm 0.01) \qquad (6.1)$$

When the solution of nitrogen in liquid iron is described by the reaction

$$\tfrac{1}{2}N_2\ (\text{gas}) = \underline{N}\ (\text{in liquid iron}) \qquad (6.2)$$

the equilibrium constant K is given by:

$$K = [a_N] \ / \ (P_{N_2})^{\frac{1}{2}}$$

$$= (\text{Wt\%N}) \,.\, f_N \ / \ (P_{N_2})^{\frac{1}{2}} \qquad (6.3)$$

where the reference state for the activity coefficient f_N is taken as the infinitely dilute solution of nitrogen in liquid iron. It has been established by previous investigators (35, 41, 47) that nitrogen dissolved in liquid iron obeys Henry's law, and thus the activity coefficient of nitrogen in binary iron nitrogen solutions can be taken as unity.

Thus:

$$\text{Log } K = \log (\text{wt.\%N}) - \tfrac{1}{2} \log P_{N_2} \qquad (6.4)$$

Since the solubility data in this study are all referred to one atmosphere pressure of nitrogen, the effect of temperature on the equilibrium constant is given by:

$$\text{Log } K = -\frac{285}{T} (\pm 110) - 1.21 (\pm 0.01) \qquad (6.5)$$

The standard free energy change for the reaction is:

$$\Delta F^{o} = 1300 (\pm 500) + 5.53 (\pm 0.03)\, T \qquad (6.6)$$

and the heat of solution is:

$$\Delta H^{o} = 1300 (\pm 500) \text{ cals/gm atom} \qquad (6.7)$$

The results of the present study are compared with those of previous investigators in Fig. 18 and Table 1 and it is evident that the data for the solubility and heat of solution of nitrogen in liquid iron, as determined by the levitation technique, are in good agreement with the data obtained by Elliott and co-workers (46, 47), and Turnock and Pehlke (51) using the Sieverts' method.

6.2 The solubility of nitrogen in liquid iron-carbon alloys.

The effect of carbon on the solubility of nitrogen in liquid iron at 1450°, 1550°, 1660° and 1750°C is shown in Table 5 and Figs. 19, 20, 21, 22 and 23. At 1450°C solubility data were obtained for carbon concentrations between 1.5 and 5 wt. pct. The intercept value for the solubility of nitrogen in pure liquid iron at this temperature was obtained by extrapolation of the data shown in Fig. 17. Consequently, the hypothetical carbon-nitrogen solubility relationship at 1450°C for carbon concentrations below about 1.5 wt. pct. is represented in Fig. 19 by a broken line. At the other temperatures, data were obtained for carbon concentrations between pure iron and the solubility limit of carbon in liquid iron.

The results of the present study have been used to compute solubilities at 1600°C, and these are compared with those of previous investigators in Fig. 24. While there is marked disagreement between the various published data, the results of the present investigation are in good agreement with the work of Schenck et al. (42).

At one atmosphere pressure of nitrogen, and a constant temperature, the activity of nitrogen in the melt is the same for both pure iron and iron-carbon alloys and thus:

$$\left[\mathrm{Wt\%N}\right]_{Fe} = \left[\mathrm{Wt\%N}\right]_{Fe-C} \cdot f_N \qquad (6.8)$$

Activity coefficients of nitrogen in the ternary alloys were calculated from equation (6.8) and the logarithm of the activity coefficient is plotted against carbon concentration in Fig. 25. (See Table 5).

Fig. 26 shows the effect of temperature on the solubility of nitrogen in liquid iron-carbon alloys for different carbon levels. The equations for these lines yield values for the heat of solution (ΔH_N^{alloy}) and the entropy of solutions (ΔS_N^{alloy}) of nitrogen in the various alloys.

In Fig. 27 these heats and entropies of solution are plotted against carbon concentration and it is found that the relationships obtained can be represented by parabolic equations of the form:

$$y = a + bx + cx^2 \qquad (6.9)$$

The coefficient "a" represents the enthalpy or entropy of solution of nitrogen in pure liquid iron, as given in equation (6.6). The coefficients b and c were determined by least squares analysis. This treatment yields the following equations:

$$\Delta H_N^{alloy} = 1300 + 1646\ (\%C) + 504\ (\%C)^2 \qquad (6.10)$$

$$\Delta S_N^{alloy} = -5.53 + 0.409\ (\%C) + 0.233\ (\%C)^2 \qquad (6.11)$$

Combining equations (6.10) and (6.11), an expression is obtained for the effect of temperature and carbon concentration on the free energy of solution of nitrogen in liquid iron:

$$\begin{aligned}\Delta F_N^{alloy} &= 1300 + 1646\ (\%C) + 504\ (\%C)^2 \\ &\quad - \left\{ -5.53 + 0.409\ (\%C) + 0.233\ (\%C)^2 \right\} T \qquad (6.12)\end{aligned}$$

From equation (6.6), the free energy of solution of nitrogen in pure liquid iron is given by

$$\Delta F^o = 1300 + 5.53\ T \qquad (6.6)$$

The excess free energy of solution $\mathcal{F}_N^E$ is defined as

$$\mathcal{F}_N^E = \Delta F_N^{alloy} - \Delta F^o = RT \ln f_n \qquad (6.13)$$

Combining equations (6.6) and (6.13):

$$\mathcal{F}_N^E = 1646\ (\%C) + 504\ (\%C)^2 - \left\{ 0.409(\%C) + 0.233(\%C)^2 \right\} T \qquad (6.14)$$

and thus:

$$\text{Log } f_N = \frac{1}{4.575T}\left\{1646\ (\%C) + 504\ (\%C)^2\right\} - \frac{1}{4.575}\left\{0.409\ (\%C) + 0.233\ (\%C)^2\right\} \quad \text{----(6.15)}$$

Since $$\text{Log}\left[\text{Wt. }\%N\right]_{Fe-C} = \text{Log}\left[\text{Wt}\%N\right]_{Fe} - \text{Log } f_N \quad \text{----(6.16)}$$

combining equation (6.1), (6.15), and (6.16) yields an expression for the solubility of nitrogen in liquid iron-carbon alloys which is valid for 1 atm. pressure of nitrogen and for temperatures between 1450°C and 1750°C:

$$\text{i.e. Log}\left[\text{Wt.}\%N\right] = -\left[\frac{285}{T} + 1.21 + \frac{(\%C)}{4.575}\left\{\frac{1646}{T} - 0.409\right\} + \frac{(\%C)^2}{4.575}\left\{\frac{504}{T} - 0.233\right\}\right] \quad \text{----(6.17)}$$

Equation (6.17) yields nitrogen solubility values which agree with the experimental values to within ±0.001 wt. pct. N. For carbon levels below 1 wt. pct. the term involving $(\%C)^2$ may be neglected without introducing appreciable error.

As stated previously in Chapter 2, Wagner (5) has shown that the activity coefficient of a solute in a multicomponent alloy may be expressed in the form of a Taylor series. In this case, where the third and higher order terms are neglected the activity coefficient of nitrogen in liquid iron-carbon solutions is given by:

$$\text{Log } f_N = \frac{\partial \text{ Log } f_N}{\partial[\%N]} \cdot \%N + \frac{\partial \text{ Log } f_N}{\partial[\%C]} \cdot [\%C]$$

$$+ \frac{1}{2} \frac{\partial^2 \mathrm{Log}\, f_N}{\partial [\%C]^2} \cdot [\%C]^2 + \frac{1}{2} \frac{\partial^2 \mathrm{Log}\, f_N}{\partial [\%N]^2} \cdot [\%N]^2$$

$$+ \frac{\partial^2 \log f_N}{\partial [\%C] \partial [\%N]} \cdot [\%C] \cdot [\%N] \qquad \text{-----}(6.18)$$

Since nitrogen dissolved in liquid iron obeys Henry's law, the first and fourth terms in the above expression are zero.

In the present study, measurements were made at one atmosphere pressure of nitrogen and the cross interaction contribution of the fifth term cannot be determined. Deviations from linearity of the curves shown in Fig. 25 are therefore ascribed solely to the second order carbon effect. Equation (6.18) can now be written

$$\mathrm{Log}\, f_N = \frac{\partial \mathrm{Log}\, f_N}{\partial [\%C]} \cdot [\%C] + \frac{1}{2} \frac{\partial^2 \log f_N}{\partial [\%C]^2} \cdot [\%C]^2 \qquad \text{----}(6.19)$$

Using the convention of Lupis and Elliott (6) $\partial \mathrm{Log}\, f_N / \partial [\%C]$ is defined as the first order interaction parameter e_N^C, and $\frac{1}{2} \partial^2 \log f_N / \partial [\%C]^2$ is defined as the second order interaction parameter r_N^C. Equation (6.19) then becomes:

$$\mathrm{Log}\, f_N = e_N^C\, (\%C) + r_N^C\, (\%C)^2 \qquad (6.20)$$

A diagramatic representation of this equation is shown in Fig. 28.

The excess enthalpy of solution, $\mathcal{H}_N^E$ is defined as

$$\mathcal{H}_N^E = \Delta H_N^{alloy} - \Delta H^o \qquad (6.21)$$

As stated previously, $\mathcal{H}_N^E$ may be expressed in the form of a Taylor series in a similar manner to $\mathcal{F}_N^E / RT$.

i.e.

$$\mathcal{H}_N^E = \frac{\partial \mathcal{H}_N^E}{\partial (\%C)} \cdot (\%C) + \tfrac{1}{2} \frac{\partial^2 \mathcal{H}_N^E}{\partial (\%C)^2} \cdot (\%C)^2 \qquad (6.22)$$

Enthalpy interaction parameters defined in terms of the above first and second order derivatives are

$$h_N^C = \frac{\partial \mathcal{H}_N^E}{\partial (\%C)} \quad \text{and} \quad l_N^C = \tfrac{1}{2} \frac{\partial^2 \mathcal{H}_N^E}{\partial (\%C)^2} \qquad (6.23)$$

Using equations (6.21) and (6.22), equation (6.23) can now be written in the form:

$$\Delta H_N^{alloy} = \Delta H^o + h_N^C (\%C) + l_N^C (\%C)^2 \qquad (6.24)$$

Similarly, the entropy of solution of nitrogen in these alloys may be expressed in the form

$$\Delta S_N^{alloy} = \Delta S^o + s_N^C (\%C) + p_N^C (\%C)^2 \qquad (6.25)$$

where s_N^C and p_N^C are first and second order entropy parameters respectively and are defined in terms of the excess entropy of solution $\mathcal{S}_N^E$:

i.e.

$$s_N^C = \frac{\partial \mathcal{S}_N^E}{\partial [\%C]} \quad \text{and} \quad p_N^C = \tfrac{1}{2} \frac{\partial^2 \mathcal{S}_N^E}{\partial [\%C]^2} \qquad (6.26)$$

Comparison of equations (6.10) and (6.11) with equations (6.24) and (6.25) yields the following values for the first and second order enthalpy and entropy paramenters

$$h_N^C = 1646 \qquad l_N^C = 504$$

$$s_N^C = 0.409 \qquad p_N^C = 0.233$$

The excess properties are related by the equation:

$$\mathcal{F}_N^E = \mathcal{H}_N^E - T\mathcal{S}_N^E = RT \ln f_N \qquad (6.27)$$

Using this relation it was shown in Chapter 2 that the various first and second order interaction parameters are related in the following way:

$$e_N^C = \frac{1}{4.575}\left[\frac{h_N^C}{T} - s_N^C\right] \qquad (6.28)$$

$$r_N^C = \frac{1}{4.575}\left[\frac{l_N^C}{T} - p_N^C\right] \qquad (6.29)$$

Substituting the values for the parameters in the bracketed terms:

$$e_N^C = \frac{360}{T} - 0.089 \quad \text{and} \quad r_N^C = \frac{110}{T} - 0.051 \qquad (6.30)$$

e_N^C and r_N^C are plotted against the reciprocal of the absolute temperature in Fig. 29.

At 1600°C, $e_N^C = 0.103$ and $r_N^C = 0.007$. Values obtained in previous investigations for e_N^C at 1600°C are listed in Table 6. Values for the various interaction parameters obtained in the present sutdy are listed in Table 7.

Turkdogen (60) has suggested that if the logarithm of the activity coefficient γ_N^C (where the reference state is the infinitely dilute solution of nitrogen in liquid iron) were plotted against mole fraction of carbon, a linear relationship might be obtained and if so the data could then be expressed in terms of first order parameters alone. The data obtained at 1550°C are plotted on a mole fraction scale in Fig. 30. In Fig. 31, Log γ_N^C is plotted as a function of X_C but the curve through the points was drawn using the parameters e_N^C and r_N^C determined on the wt. pct. scale and converted to the mole fraction scale using the relationship derived by Lupis and Elliott. It will be seen that the data in Fig. 31 follow a non-linear relationship and that the derived curve is in good agreement with the experimental points even up to 0.20 mole fraction carbon where the second order effects become more significant.

In Table 7, values are given for the various parameters on the mole fraction scale. These have all been calculated from the corresponding parameter on the wt. pct. scale using the conversion relationships of Lupis and Elliott (6) which were presented in Chapter 2.

6.3 The solubility of nitrogen in liquid iron-aluminium alloys.

Experimental results for the effect of aluminium on the solubility of nitrogen in liquid iron at 1550°, 1650° and 1750°C up to approximately the concentration of aluminium for which AlN becomes stable are presented in Table 13 and Figs.

32, 33. From these data it can be seen that aluminium decreases the solubility of nitrogen in liquid iron and that the effect of aluminium decreases with increasing temperature. These results do not agree with those of Pehlke and Evans (53) (Fig. 7) or with those of Eklund (32), but are in fair agreement with those of Pehlke and Elliott (47) (Fig.6).

When the AlN phase becomes stable the total nitrogen content of the sample (i.e. nitrogen dissolved in the metal together with nitrogen combined with aluminium in the form of AlN) increases rapidly and hence the aluminium content corresponding to the critical concentrations for aluminium nitride formation can be estimated from the breaks in the nitrogen solubility curve. These breaks occur between 0.6 and 0.7 wt. pct. at 1550°C and between 0.75 and 0.85 wt. pct. at 1650° and 1750°C.

Figure 33 shows the effect of aluminium on the logarithm of the activity coefficient of nitrogen dissolved in liquid iron. It will be seen that there is a spread in the data for each of the temperatures investigated. This is largely attributable to the fact that $f_N^{Al} = \frac{[\%N]\ \text{Pure Fe}}{[\%N]\ \text{alloy}}$ is close to unity and hence a small error in the denominator gives rise to a large error in f_N^{Al} which is magnified when the logarithm of the coefficient is taken. The lines as drawn are based on a least squares analysis of the data.

The logarithm of the activity coefficient of nitrogen in iron aluminium alloys may be represented in terms of free energy interaction parameters. However, in this case the accuracy of the data does not warrant the use of second or higher order parameters and thus the relationship between Log f_N^{Al} and aluminium content are adequately represented by first order equations. The slope of these lines yield values for the first order free energy interaction parameter e_N^{Al}. The values of this parameter for the various temperatures at which solubilities were determined are given in Table 14.

These values of e_N^{Al} are plotted against the reciprocal of the absolute temperature in Fig. 34. The equation of the line is given by:

$$e_N^{Al} = \frac{590}{T} - 0.28 \qquad (6.31)$$

Comparing the above equation with the relation:

$$e_N^{Al} = \frac{1}{4.575} \left[\frac{h_N^{Al}}{T} - s_N^{Al} \right] \qquad (6.32)$$

the following values for the enthalpy and entropy interaction parameters are obtained:

$$h_N^{Al} = 2700 \qquad (6.33)$$

$$s_N^{Al} = 1.28 \qquad (6.34)$$

Combining these data with equation (6.6) for the free energy of solution of nitrogen in liquid iron expressions are obtained for the effect of aluminium on the enthalpy and entropy of solution of nitrogen in liquid iron:

$$\Delta H_N^{alloy} = 1300 + 2700\ (\%Al) \qquad (6.35)$$

$$\Delta S_N^{alloy} = -5.53 + 1.28\ (\%Al) \qquad (6.36)$$

These quantities are plotted as a function of aluminium concentration in Fig. 35. From equations (6.35) and (6.36) the effect of aluminium on the free energy of solution of nitrogen in liquid iron is given by:

$$\Delta F_N^{alloy} = 1300 + 2700\ (\%Al) - T\left\{-5.53 + 1.28(\%Al)\right\} \qquad (6.37)$$

Since:

$$\text{Log } f_N = e_N^{Al}\ \left[\ \%Al\ \right] \qquad (6.38)$$

equation (6.38) may be rewritten in the form:

$$\text{Log } f_N = \frac{\%Al}{4.575} \cdot \left\{ \cdot \frac{2700}{T} - 1.28 \right\} \quad (6.39)$$

Combining equations (6.1) and (6.39) and using the relationship:

$$\text{Log } \left[\text{Wt.}\%N\right]_{Fe-Al} = \text{Log } \left[\text{Wt.}\%N\right]_{Fe} - \text{Log } f_N \qquad (6.40)$$

an expression is obtained for the solubility of nitrogen in iron-aluminium alloys in terms of temperature and aluminium concentration. This expression is valid for temperatures in the range 1550° to 1750°C and for aluminium concentrations ranging from zero to the solubility limit corresponding to the formation of aluminium nitride:

$$\text{Log } \left[\text{Wt.}\%N\right]_{Fe-Al} = -\left[\frac{285}{T} + 1.21 + \frac{\%Al}{4.575}\left\{\frac{2700}{T} - 1.28\right\}\right] \qquad (6.41)$$

CHAPTER 7

DISCUSSION

Corrigan and Chipman (61) have derived an empirical equation to predict the solubility of nitrogen in liquid iron alloys. On comparing the first order enthalpy interaction parameters and first order free energy interaction parameters of a number of Fe-N-X alloys at about 1600°C, they found that h^j_N was approximately directly proportional to e^j_N. This empirical relationship (shown in Fig. 36) was represented by the equation

$$h^j_N \text{ (cal)} = 15{,}000\ e^j_N\ (1873^\circ\text{K}) \qquad (7.1)$$

Since the excess properties are related by the equation:

$$\mathcal{S}^E_N = (\mathcal{H}^E_N - \mathcal{F}^E_N)/T \qquad (7.2)$$

$$\text{i.e.} \quad \frac{\partial \mathcal{S}}{\partial \%j} = s^j_N = \frac{1}{T}\left[\frac{\partial \mathcal{H}^E_N}{\partial \%j} - \frac{\partial \mathcal{F}^E_N}{\partial \%j}\right] \qquad (7.3)$$

On substituting equation (7.1) in (7.3) the relation

$$s^j_N = 3.44\ e^j_N\ (1873^\circ\text{K}) \qquad (7.4)$$

is obtained. Hence an equation representing the interaction coefficient at any temperature

$$2.3RTe^j_N = 15{,}000\ e^j_N(1873^\circ\text{K}) - 3.44Te^j_N(1873^\circ\text{K}) \qquad (7.5)$$

and an equation for the activity coefficient of nitrogen in any liquid iron solution.

$$\text{Log } f_{N(T)} = \left[\frac{3280}{T} - 0.75\right] \sum_j e^{j}_{N(1873)} \left[\%j\right] \qquad (7.6)$$

Equation (7.6) was then combined with the data of Pehlke and Elliott (47) for the solubility of nitrogen in pure liquid iron to give an equation which predicted the solubility of nitrogen at any temperature in any liquid iron alloy whose solubility could be expressed in terms of first order interaction parameters.

$$\text{Log}(\%N) = -\frac{188}{T} - 1.25 - \left[3280/T - 0.75\right] \sum_j e^{j}_{N(1873)} \left[\%j\right] \qquad (7.7)$$

It is interesting to note that the data available in the literature (42, 47, 62) for h_N^C and e_N^C are inconsistent with equation (7.7) However, the present work generates values for h_N^C and e_N^C which agree very well with equation (7.7) and thus the equation presented by Chipman and Corrigan (61) for predicting nitrogen solubilities in these alloys agrees well with the experimental data obtained in the present work up to approximately 2 pct. C. For alloys containing more than 2 pct. C second order effects become increasingly important and under these conditions equation (6.17) will yield more accurate values.

Results obtained from the work on the iron-aluminium system did not confirm this relationship. However, since these results could only be obtained at low concentrations of aluminium and aluminium has only a small effect on the solubility of nitrogen, the accuracy of the parameters obtained for this system will be somewhat less than those obtained for the iron-carbon system.

Lupis and Elliott (24) have recently derived an expression for the relationship between h_N^j and e_N^j on the basis of the "central atoms" theory of liquid metal solutions. They showed that as a first approximation the excess free energy varies linearly with temperature.

$$\text{i.e.} \quad F^E = \alpha(\tau - T) \qquad (7.8)$$

where τ was termed the "characteristic temperature" of the solution or the temperature at which the system would become ideal if the results at temperature T were extrapolated. From this relationship and the fact that

$$F^E = H^E - TS^E \qquad (7.9)$$

$$\text{then } H^E = \tau S^E \qquad (7.10)$$

$$\text{and } F^E = H^E \left(1 - \frac{T}{\tau}\right) \qquad (7.11)$$

Differentiating with respect to composition they obtained

$$RT\,\varepsilon_i^j = \eta_i^j - T\sigma_i^j = \eta_i^j - \eta_i^j \frac{T}{\tau} \qquad (7.12)$$

$$\text{i.e.} \quad \eta_i^j = \tau\sigma_i^j \qquad (7.13)$$

Lupis and Elliott (24) suggest that τ may be considered to take values in the range 3,000° ± 1,000°K for metallic solutions. It is interesting to note that the τ values obtained from the present work using relation (7.13) above, fall in this range. For the Fe - Al - N system $\tau = 2{,}800°K$ and for the Fe - C - N system $\tau = 4{,}000°K$.

Darken (63) has pointed out that if $\sigma_i^j \neq 0$ Chipman and Corrigan's results imply that ε_i^j changes sign at some point as T increases. However it is evident that equation (7.12) can only be valid for a limited range of temperatures, since at the temperature τ, at which the system becomes ideal σ_i^j and η_i^j must also become zero. (i.e. $F_i^E = H_i^E = S_i^E = 0$). Both σ_i^j and η_i^j are functions of temperature and their absolute values should decrease when the temperature increases. The consideration that F^E is proportional to $(\tau - T)$ is a first approximation which is only valid for a limited temperature range (64).

It was mentioned previously (Chapter 2) that Darken (9, 10) derived a relation between activity coefficients of solutes which he used as a condition for thermodynamic consistency (Eq. 2.46).

$$(1 - X_3)\frac{\partial \ln \gamma_2}{\partial X_3} + X_3\frac{\partial \ln \gamma_3}{\partial X_3} = X_2\frac{\partial \ln \gamma_2}{\partial X_2} + (1 - X_2)\frac{\partial \ln \gamma_3}{\partial X_2} \qquad (7.14)$$

He then used this relation to test the ε formalism by setting

$$\ln \gamma_2/\gamma_2^o = \varepsilon_{22}X_2 + \varepsilon_{23}X_3 \qquad (7.15)$$

$$\ln \gamma_3/\gamma_3^o = \varepsilon_{32}X_2 + \varepsilon_{33}X_3 \qquad (7.16)$$

and substituting in equation (7.14) to obtain

$$(1 - X_3)\varepsilon_{23} + X_3\varepsilon_{33} = X_2\varepsilon_{22} + (1 - X_2)\varepsilon_{32} \qquad (7.17)$$

If $X_2 = X_3 = 0$ in equation (7.17), then the Wagner reciprocal relationship is obtained. However, Darken (10) points out that equation (7.17) cannot be generally valid for finite solutions and can, in fact, only be valid in the special case where

$$\varepsilon_{22} = \varepsilon_{23} = \varepsilon_{32} = \varepsilon_{33}$$

Darken maintains that this is a serious thermodynamic inconsistency of the ε formalism at finite concentrations which, of course, always have to be used in practice to determine these parameters. He states that under unfavourable conditions activity coefficients computed on this basis may be in error by at least a factor of two for compositions in range 10 to 20 at. pct. solute.

Lupis (65) objects to Darken's formalism because the degree of the polynomial for the activity coefficient is not deduced from an analysis of the experimental data but is decided *a priori* to be quadratic. Consequently, Darken assumes higher order interactions are zero and hence if expressions for $\ln \gamma_2$ or $\ln \gamma_3$ containing terms in ε only are used at concentrations where second order terms are not negligible thermodynamic inconsistencies could be introduced.

In the light of this discussion, it is of interest to express the results obtained from the present investigation in terms of Darken's formalism. As shown in Section 2.2, the basic equation for ternary metallic solutions was of the form

$$\mathrm{Log}(X^*/X') + \alpha_{12}\left[X_2'(2 - X_2') - X_2^*(2 - X_2^*)\right] - \alpha_{13}X_3^2 = (\alpha_{23} - \alpha_{12} - \alpha_{13})X_3(1 - X_2') \qquad (7.18)$$

Since in the present investigation the nitrogen was held at constant activity, (all solutions were exposed to one atm. partial pressure of nitrogen) this equation in terms of carbon and nitrogen may be written

$$\mathrm{Log}\ (X_N^*/X_N') + \alpha_{FeN}\left[X_N'(2 - X_N') - X_N^*(2 - X_N^*)\right] - \alpha_{FeC}X_C^2 = (\alpha_{NC} - \alpha_{FeN} - \alpha_{FeC})\ X_C(1 - X_N') \qquad (7.19)$$

Sieverts' law is obeyed for liquid iron-nitrogen alloys up to 1 atm. pressure of nitrogen. i.e. Nitrogen obeys Henry's law under these conditions. It follows that iron obeys Raoult's law under the same conditions. Hence α_{FeN} is zero for all values of nitrogen solubility under consideration. Equation (7.19) can now be written:

$$\mathrm{Log}(X_N^*/X_N') - \alpha_{FeC}X_C^2 = (\alpha_{NC} - \alpha_{FeC})X_C(1-X_N') \qquad (7.20)$$

α_{FeC} has been determined previously to be -2.38 (9). A plot of Log $(X_N^*/X_N') + 2.38X_C^2$ vs $X_C(1-X_N')$ using the data from the present investigation is shown in Fig. 37. This should give a straight line through the origin with a slope of $(\alpha_{NC} + 2.38)$. It is evident that the curve deviates quite markedly from linearity especially at high solute concentrations. The slope at lower concentrations is 3.0 giving a value for α_{NC} of 0.62. It is clear, however, equation (7.20) does not adequately represent the data for carbon concentrations higher than about 8 mole. pct. It seems likely that further terms are required to represent the data at these concentrations. To do this, however, would depreciate to some extent the value of the formalism.

The quasi-chemical model of Lupis and Elliott (23) may be tested using the relationship between the first and second order free energy interaction parameters derived from the model and using values obtained for these parameters from the present investigation for the Fe-C-N system.

From the model

$$\rho_N^C = \frac{\left[\varepsilon_N^C\right]^2}{2Z} + \frac{\varepsilon_C^C}{Z}\left(\varepsilon_N^C - \frac{Z}{2}\right) \qquad (7.21)$$

Substituting Z = 10, then at 1600°C, $\varepsilon_C^C = 11.7$ (42) and $\varepsilon_N^C = 5.86$ (from the present investigation) and a value for $\rho_N^C = 2.7$ is obtained. This value is considerably lower than the experimental value of $\rho_N^C = 11.69$.

If the above relationship is used to calculate an average coordination number from the experimental values of ε_N^C and ρ_N^C, a value of Z = 7 is obtained. For a system such as Fe-C-N in which the solute atoms are normally interstitial in the solid state, one would expect that the number of nearest neighbours to the solute atom would be considerably less than the number around the much larger solvent atoms. On this basis a value of seven does not seem unreasonable for the average coordination number for the system.

For certain liquid metal solutions which may tend to be interstitial in nature the mole fraction as a concentration unit loses much of its fundamental significance. Since interstitial solutions appear to be rather less complex than substitutional ones a more fundamental concentration unit might simplify the representation of activity data for this type of solution. With this in mind Chipman (67) has recently proposed a new method for representing the activities of interstitial and non-metallic solutes in dilute metallic solutions. The concentration unit proposed is the lattice ratio which is the ratio of the number of solute atoms of the given species to the number of vacant interstitial sites remaining in the "lattice". For a solution of carbon and nitrogen in iron the concentration of nitrogen is given by $Z_N = n_N/(n_{Fe} - n_C - n_N)$. An activity coefficient ψ_i is defined such that $\psi_i = a_i/Z_i$ and the reference state for ψ_i is taken as the infinitely dilute solution i.e. $\psi_i = 1$ when $Z_i \rightarrow 0$.

For a solution of nitrogen in pure iron $\psi_N = 1$ since Henry's law is obeyed

i.e. $$[a_N]_{Fe} = [Z_N]_{Fe} \qquad (7.22)$$

When nitrogen dissolves in iron-carbon alloys

$$\begin{aligned}\psi_N &= [a_N]_{FeC} / [Z_N]_{FeC} \\ &= [a_N]_{Fe} / [Z_N]_{FeC} \\ &= [Z_N]_{Fe} / [Z_N]_{FeC} \qquad (7.23)\end{aligned}$$

In an analogous manner to the Henrian and Raoultian activity coefficients:

$$\psi_N = \psi_N^N \cdot \psi_N^C \tag{7.24}$$

Since nitrogen obeys Henry's law in pure iron

$$\mathrm{Ln}\ \psi_N^N = 0$$

$$\therefore\ \mathrm{Ln}\,\psi_N = \mathrm{Ln}\,\psi_N^C = \theta_N^C Z_C \tag{7.25}$$

where $\theta_N^C = \dfrac{\partial \ln \psi_N^C}{\partial Z_C}$

Chipman has found that for all the data available for these types of solutions θ_i^j is independent of Z_j to high solute concentrations. This treatment was tested using the data obtained during the present investigation for the solubility of nitrogen in iron-carbon alloys (See Figs. 38, 39, 40, 41). It will be seen that the plots of Log.ψ_N vs Z_C for the various temperatures investigated may all be represented by straight lines and the slopes of these lines yield values for θ_N^C at 1450°, 1550°, 1650°, and 1750°C of 2.49 , 1.87, 1.46, and 1.33 respectively.

Also since

$$\mathrm{Ln}\,\psi_N = \mathrm{Ln}\left[Z_N\right]_{Fe} - \mathrm{Ln}\left[Z_N\right]_{FeC}$$

or

$$\mathrm{Ln}\left[Z_N\right]_{Fe} - \mathrm{Ln}\left[Z_N\right]_{FeC} = \theta_N^C\left[Z_C\right]$$

$$\mathrm{Ln}\left[Z_N\right]_{FeC} = -\theta_N^C\left[Z_C\right] + \mathrm{Ln}\left[Z_N\right]_{Fe}$$

i.e.

$$\mathrm{Log}\left[Z_N\right]_{FeC} = -\frac{\theta_N^C}{2.303}\left[Z_C\right] + \mathrm{Log}\left[Z_N\right]_{Fe} \tag{7.26}$$

Thus an alternate method of obtaining values for θ_N^C is to plot Log $[Z_N]_{FeC}$ vs Z_C and this is shown in Fig. 42 where the intercept values represent the solubility of nitrogen in pure iron.

The advantage of this approach is that the solubility data can be adequately represented by first order coefficients alone.

In common with many of the models so far proposed for liquid metal solutions, the quasi-chemical model derived by Lupis and Elliott (23) assumes a substitutional lattice model. One would not expect such a model to adequately represent an interstitial solution even though this term may lose some of its significance when applied to the liquid state.

It would be useful therefore to obtain a model for interstitial solutions based on an interstitial lattice model. With this in mind a simple interstitial model has been developed (Appendix B) which is an extension of the work by Kirkaldy and Purdy (69) on ternary austenite solutions and Burylev (68) on the solutions of non-metals in liquid iron. This model is based on the following assumptions:

(i) The solvent atoms are arranged on a face-centred cubic lattice.

(ii) The available interstitial sites are the octahedral holes in the f c c lattice. These holes form another f c c lattice with the same number of sites as the solvent lattice.

(iii) The interstitial sites are the only sites available to the solute atoms.

(iv) The entropy changes of the solution are due solely to configurational entropy changes.

(v) The energy of the lattice is assumed to consist of interaction energies of all nearest neighbour pairs in the lattice including interstitial pairs on adjacent octahedral sites, although these are not strictly nearest neighbour pairs.

On the basis of this model the following expressions are obtained for the first and second order free energy interaction parameters

$$\varepsilon_B^C = \left(\frac{12Au_{BC}}{RT} - 2\right) \qquad (7.27)$$

$$\rho_B^C = 2\left(\frac{12Au_{BC}}{RT} - 2\right) \qquad (7.28)$$

where A is Avogadro's number and u_{BC} is the energy of formation of an interstitial pair.

$$\text{i.e.} \quad 2\varepsilon_B^C = \rho_B^C \qquad (7.29)$$

This relationship is in good agreement with the results of the present work for carbon and nitrogen in liquid iron. It is also in reasonable agreement with the data available for solutions for which the solute components may be considered "interstitial". Values of ρ_j^i calculated from the respective ε_j^i values using equations (7.21) and (7.29) are given in Table 15. These calculated values for e_j^i may be compared with the experimentally determined values. The agreement between the experimental values and those predicted by equation (7.21) is rather poor but the agreement between the experimental values and those predicted by equation (7.29) is very good especially when one considers the simplicity of the model upon which it is based.

If equation (7.27) is compared with the theoretical relationship $\varepsilon_N^C = \frac{1}{R}\left\{\frac{\eta_N^C}{T} - \sigma_N^C\right\}$ derived in Chapter 2. It will be seen that the proposed model predicts a value of 2 R for the first order entropy interaction parameter and a value of RT (ε_N^C + 2) for the enthalpy interaction parameter. At 1600°C, $\varepsilon_N^C = 5.86$, and thus the values predicted for σ_N^C and η_N^C are 4 and 29,000 respectively. These are in reasonable agreement with the values of 7.2 and 35,000 obtained experimentally. The prediction power of the model is less satisfactory when applied to the second order enthalpy and entropy parameters. The agreement does indicate however that an interstitial rather than substitutional model is more suitable for predicting the behaviour of solutions in which the atoms of the solute are much smaller in size than those of the solvent.

SUMMARY AND CONCLUSIONS

A technique involving levitation melting and a rapid quench apparatus has been devised to study the solubility of nitrogen in liquid iron alloys. Determinations of solubility have been made for pure liquid iron, liquid iron-carbon and iron-aluminium alloys. Previous techniques for studying the Fe-C-N and Fe-Al-N systems have produced various data which are in marked disagreement. This disagreement is due in large measure to reaction between the molten alloy and the crucible material. Using levitation melting, the possibility of errors arising from this source have been eliminated and very precise data have been obtained which allow one to calculate values for first and second order free energy enthalpy and entropy parameters.

The solubility of nitrogen in pure liquid iron in the temperature range 1500°C to 1800°C may be represented by the equation:

$$\mathrm{Log}\left[\mathrm{Wt.\ pct.\ N}\right] = -\frac{285}{T} - 1.21$$

The free energy of solution of nitrogen in liquid iron is given by

$$\Delta F^{o} = 1300 + 5.53\ T$$

The solubility of nitrogen in liquid iron-carbon alloys for the temperature range 1450°C to 1750°C and in the range of 0%C to the solubility limit of carbon in liquid iron may be represented by the equation:

$$\mathrm{Log}\left[\mathrm{Wt.\ pct.\ N}\right]_{\mathrm{Fe-C}} = -\left[\frac{285}{T} + 1.21 + \frac{\%C}{4.575}\left\{\frac{1646}{T} - 0.409\right\} + \frac{(\%C)^2}{4.575}\left\{\frac{504}{T} - 0.233\right\}\right]$$

The free energy of solution of nitrogen in liquid iron-carbon alloys is given by

$$\Delta F_N^{\mathrm{alloy}} = 1300 + 1646(\%C) + 504(\%C)^2 - \left\{-5.53 + 0.409(\%C) + 0.233(\%C)^2\right\} T$$

The solubility of nitrogen in liquid iron-aluminium alloys for the temperature range 1550°C to 1750°C and the range 0%Al to the solubility limit of aluminium nitride may be represented by the equation:

$$\mathrm{Log}\left[\mathrm{Wt.\ pct.\ N}\right]_{\mathrm{Fe-Al}} = -\left[\frac{285}{T} + 1.21 + \frac{\%\mathrm{Al}}{4.575}\left\{\frac{2700}{T} - 1.28\right\}\right]$$

The free energy of solution of nitrogen in liquid iron-aluminium alloys is given by

$$\Delta F_N^{\mathrm{alloy}} = 1300 + 2700(\%\mathrm{Al}) - T\left\{-5.53 + 1.28(\%\mathrm{Al})\right\}$$

The results of the present investigation have been interpreted in terms of the interaction parameters proposed by Wagner (5) and Lupis and Elliott (6). Both first and second order free energy interaction parameters have been used to express the logarithm of the activity coefficient of nitrogen in liquid iron-carbon alloys. The results of the present investigation for the solubility of nitrogen in liquid iron-aluminium alloy may be adequately described using first order parameters. First order free energy, enthalpy, and entropy parameters have been determined for aluminium-nitrogen interactions.

The data for iron-carbon nitrogen solutions have been used to test the quadratic formalism proposed by Darken (9, 10), the quasi-chemical model of Lupis and Elliott (23), and the formalism proposed by Chipman (67) for interstitial solutions.

An interstitial lattice model has been developed to describe the interactions between elements of small atomic size dissolved in liquid iron. Data for carbon-nitrogen interactions from the present study together with published data for a number of other ternary solutions are in good agreement with the predictions of this model.

SUGGESTIONS FOR FURTHER WORK

a) An interesting extension to this investigation would be a study of nitrogen solubilities in Fe-C alloys at various partial pressures of nitrogen. This would enable a determination of the cross-interaction coefficients.

b) Since the interactions between nitrogen and most of the more common alloying constituents of steel are now known to a high degree of precision, it would be interesting to use this information to predict the nitrogen solubility in a number of commonly used steels and compare the predicted values with solubilities obtained experimentally.

c) The kinetics of nitrogen absorption in liquid iron alloys in the presence of oxidising atmospheres and the effect oxygen has on the solubility of nitrogen under equilibrium conditions remains to be determined precisely before much of the information now known of nitrogen interactions in liquid iron alloys can be used to maximum advantage in steel-making processes.

d) It might be interesting to study carbon-nitrogen interactions in a liquid metal solvent other than iron.

REFERENCES

1. C. Bodsworth: Physical Chemistry of Iron and Steel Manufacture, Longmans, London, (1963), p. 206.
2. W. A. Peifer: J. Metals, (1965), vol. 17, p. 487.
3. R. G. Ward: An Introduction to the Physical Chemistry of Iron and Steel Making, Edward Arnold, London, (1962).
4. J. Chipman and C. W. Sherman: Trans. AIME, (1950), vol. 188, p. 334.
5. C. Wagner: Thermodynamics of Alloys, Addison Wesley, (1952), p. 51-53.
6. C. H. P. Lupis and J. F. Elliott: Acta. Met., (1966), vol. 14, p. 529.
7. J. V. Gluck and R. D. Pehlke: Trans. AIME, (1965), vol. 233, p. 233.
8. H. Schenck, M. G. Frohberg and E. Steinmetz: Arch. Eisenhuettenw., (1960), vol. 31, p. 671.
9. L. S. Darken: Trans. AIME, (1967), vol. 239, p. 80.
10. L. S. Darken: Trans. AIME, (1967), vol. 239, p. 90.
11. K. Schwerdtfeger and H. J. Engell: Arch. Eisenhuettenw., (1964), vol. 35, p. 533.
12. J. H. Hildebrand: J. Am. Chem. Soc., (1929), vol. 51, p. 66.
13. J. H. Hildebrand and R. L. Scott: The Solubility of Non-electrolytes, Third ed., Reinhold, New York, (1950).

14. J. V. Gluck: Ph.D. Thesis, University of Michigan, (1965).

15. F. D. Richardson: "The Solutions of the Metallurgist - Retrospect and Prospect," Physical Chemistry of Process Metallurgy, Interscience, New York, (1961), p. 1.

16. H. K. Hardy: Acta. Met., (1953), vol. 1, p. 202.

17. T. Yokokawa, A. Doi, and K. Niwa: J. Phys. Chem., (1961), vol. 65, p. 202.

18. E. A. Guggenheim: Mixtures, Oxford Clarendon Press, (1952).

19. C. B. Alcock and F. D. Richardson: Acta. Met., (1958), vol. 6, p. 385.

20. C. B. Alcock and F. D. Richardson: Acta. Met., (1960), vol. 8, p. 882.

21. H. Wada and T. Saito: Trans. Japan Inst. of Metals, (1961), vol. 2, p. 15.

22. B. W. Mott: Phil. Mag., (1952), Series 2, p. 259.

23. C. H. P. Lupis and J. F. Elliott: Acta. Met., (1966), vol. 14, p. 1019.

24. C. H. P. Lupis and J. F. Elliott: Acta. Met., (1967), vol. 15, p. 265.

25. H. Eyring: J. Chem. Phys., (1936), vol. 4, p. 283.

26. A. Sieverts and H. Krumbhaar: Ber. deut. chem. Ges., (1910), vol. 43, p. 893.

27. J. H. Andrew: Iron and Steel Inst., Carnegie Schol. Mem., (1911), vol. 3, p. 236.

28. B. Strauss: Stahl u. Eisen, (1914), vol. 34, p. 1814.

29. C. B. Sawyer: Trans. AIME, (1923), vol. 19, p. 798.

30. J. Chipman and D. Murphy: Trans. AIME, (1935), vol. 116, p. 179.

31. A. Sieverts and G. Zapf: A. physik. Chem., Leipzig, (1935), vol. A172, p. 314.

32. L. Eklund: Jernkontorets Ann., (1939), vol. 123, p. 545.

33. J. C. Vaughan and J. Chipman: Trans. AIME, (1940), vol. 140, p. 224.

34. R. M. Brick and J. A. Creevy: Metals Technol., AIME Tech. Pub. No. 1165, (1940).

35. T. Kootz: Arch. Eisenhuettenw., (1941), vol. 15, p. 77.

36. M. M. Karnaukhov and A. M. Morozov: Bull. acad. sci. URSS Classe sci. tech., (1947), vol. 735.

37. T. Saito: Sci. Repts. Research Inst. Tohoku Univ., Ser. A, (1949), vol. 1, p. 411.

38. T. Saito: Sci. Repts. Research Insts., Tohoku Univ. Ser. A, (1950), vol. 2, p. 909.

39. H. Wentrup and O. Reif: Arch. Eisenhuettenw., (1949), vol. 20, p. 359.

40. Y. Kasamatu and S. Matoba: Technol. Repts. Tohoku Univ., (1957), vol. 22, no. 1.

41. V. Kashyap and N. Parlee: Trans. AIME, (1958), vol. 212, p. 86.

42. H. Schenck, M. Frohberg, and H. Graf: Arch. Eisenhuettenw., (1959), vol. 30, p. 533.

43. V. P. Fedotov and A. M. Samarin: Doklady Akad. Nauk SSSR, (1958), vol. 122, p. 597.

44. S. Maekawa and Y. Nakagawa: Tetsu to Hagane, J. Iron Steel Inst., Japan, (1959), vol. 45, p. 255.

45. T. Busch and R. A. Dodd: Trans. AIME, (1960), vol. 218, p. 483.

46. J. C. Humbert and J. F. Elliott: Trans. AIME, (1960), vol. 218, p. 1076.

47. R. D. Pehlke and J. F. Elliott: Trans. AIME, (1960), vol. 218, p. 1088.

48. W. A. Fisher and A. Hoffmann: Archiv. Eisenhuettenw., (1960), vol. 31, p. 215.

49. S. Z. Beer: Trans. AIME, (1961), vol. 221, p. 2.

50. R. A. Dodd and N. A. Gokcen: Trans. AIME, (1961), vol. 221, p. 233.

51. P. H. Turnock and R. D. Pehlke: Trans. AIME, (1966), vol. 236, p. 1540.

52. J. Chipman: J.I.S.I., (1955), vol. 180, p. 97.

53. D. B. Evans and R. D. Pehlke: Trans. AIME, (1946), vol. 230, p. 1651.

54. W. A. Peifer: Journal of Metals, (1965), vol. 17, p. 487.

55. S. Y. Shiraishi and R. G. Ward: Can. Met. Quarterly, (1964), vol. 3, p. 117.

56. D. W. Gomersall, S. Y. Shiraishi, and R. G. Ward: J. Aust. Inst. of Metals, (1965), vol. 10, p. 1.

57. P. Peitrokowsky: Rev. Sci. Inst., (1963), vol. 34, p. 445.

58. "The Determination of Nitrogen in Steel," Special Report No. 62, Iron and Steel Inst., London, (1958).

59. "Methods of Chemical Analysis of Metals," ASTM, (1960).

60. Discussion (1967) AIME Annual Meeting, Los Angeles.

61. J. Chipman and D. A. Corrigan: Trans. AIME, (1965), vol. 233, p. 1249.

62. E. C. Nelson: Trans. AIME, (1963), vol. 227, p. 189.

63. L. S. Darken: Oral discussion of Ref. 61 at the AIME Pittsburg meeting of May 6, 1965.

64. C. H. P. Lupis and J. F. Elliott: Trans. AIME, (1966), vol. 236, p. 130.

65. C. H. P. Lupis - to be published.

66. A. Rist and J. Chipman: Rev. Met., (1956), vol. 53, p. 796.

67. J. Chipman - to be published.

68. B. P. Burylev: Russian Journal of Phys. Chem., (1963), vol. 37, p. 1120.

69. J. S. Kirkaldy and G. R. Purdy: Can. Journal of Phys., (1962), vol. 40, p. 202.

APPENDIX A

ANALYSIS PROCEDURES

1. Nitrogen analysis.

Each sample was weighed and transferred to a Kjeldahl flask. 20 ml of redistilled hydrochloric acid was added and the mixture heated until solvent action ceased. The solution was evaporated until salts deposited. The flask and contents were cooled, 10 ml of sulphuric acid and 2 gms of sodium sulphate added, and the solution fumed at 350°C for 60 minutes. The solution was cooled, 50 ml of ammonia free water added, and the solution boiled until all soluble salts were dissolved. This solution was cooled and transferred to the distillation flask of the apparatus shown in Fig. 14 into which 50 ml of 40% sodium hyroxide solution had previously been added. The solution was washed down the funnel with ammonia-free water. Steam from flask A was then passed through the solution in flask F carrying over with it to the condenser G any ammonia which may have been in solution flask F. The condensate was collected in a beaker containing 10 ml of boric acid solution (1%) and first change point with hydrochloric acid (N/250 approx.). Approximately 100 ml of distillate were collected, after which the condenser tip was rinsed with distilled water. The distillate was titrated back to the change point of the indicator with N/250 HCl.

1 ml of N/250 HCl solution = 0.14/2.5 mg of N

$$\text{Pct.Nitrogen} = \frac{A \times 0.00014 \times 100}{W \times 2.5}$$

where A = Vol. (ml) of N/250 HCl

and W = weight (gms) of sample taken.

The blank value for the apparatus and reagents were determined under the conditions of an actual determination. This blank value was determined each time fresh reagents were used and after every six determinations. In general the blank for the apparatus and reagents was approximately 0.2 ml of N/250 HCl, which was usually less than 10% of the volume required for the determination of nitrogen in an actual sample.

The ammonia-free water used throughout was prepared by passing distilled water through a mixed bed cation-exchange column.

The N/250 HCl was standardized using a standard N/100 sodium borate solution prepared by dissolving 1.9072 gm of freshly recrystalized sodium borate ($Na_2 B_2O_7.10H_2$) in one litre of distilled water.

2. Aluminium analysis.

The samples were analysed for aluminium by a colorimetric method using "Chromazurol S" as a colouring agent. This method was obtained through the courtesy of The Steel Company of Canada.

Reagents used:

Deionized water was used throughout.

1. Sulphuric acid: 100 ml H_2SO_4 (Sp. Gr. 1.84) diluted to 110 ml.

2. Ascorbic acid: 4 gms of this reagent were dissolved in 250 ml of water. This solution must be freshly prepared every time it is used as it deteriorates with time.

3. Acetate buffer pH 7.3: 50 gms of CH_3 COONa.$3H_2O$ crystals were dissolved in water, the solution diluted to 1 litre and the pH adjusted to 7.3.

4. Chromazurol S: 0.10 gms were dissolved in 250 ml of 50% ethanol.

5. Fused Potassium Bisulphate powder.

6. Iron Solution: 1.000 gms of Ferrovac E was dissolved in 20 ml of H_2SO_4 (prepared as above) and made up to 500 ml with water. 1 ml of this solution corresponds to 2 mg Fe.

7. Standard Aluminium Solution: 8.946 gms of Al Cl_3 .$6H_2O$ were dissolved in water and the solution diluted to one litre. This solution contained 1 mg of Al per ml. To obtain the solution used for calibration, 2 ml of the solution were pipetted into a litre flask containing 5 ml. of H_2SO_4 and diluted to 1 litre with water. This solution provides the standard working solution for calibration.

Calibration

10 ml of freshly prepared ascorbic acid, 25 ml of acetate buffer and 5 ml of Chromazurol 'S' solution were added to a series of 100 ml volumetric flasks. 10 ml of iron

solution were added to each flask except the first and 1,2, ...10 ml of aluminium solution were added to each flask except the first and second. The contents of each flask were then diluted to 100 ml with distilled water.

Procedure

A weighed sample was dissolved in 20 ml of sulphuric acid and filtered into a 500 ml volumetric flask. The residue was reserved to determine the acid insoluble aluminium content. The solution was made up to 500 ml with distilled water. A quantity of this solution was diluted ten times and a 10 ml aliquot of this diluted solution transferred to a 100 ml volumetric flask. 10 ml of freshly prepared ascorbic acid solution, 25 ml of acetate buffer and 5 ml of Chromazurol "S" solution were added to this flask and the solution made up to 100 ml with distilled water. A blank solution was made up in exactly the same manner using 10 ml of iron solution instead of 10 ml of the solution under investigation.

The light absorbance of the solution was measured at a wave length of 545 μ with the blank solution in the reference cell. The aluminium concentration was then read from the calibration graph and multiplied by a conversion factor which takes into account the weight of the original sample.

The insoluble aluminium content was measured by igniting the reserved residue in a platinum crucible at 500°C for one hour. This was cooled and 0.5 gms of potassium bisulphate added and the mixture fused carefully on a low bunsen flame. The crucible contents were cooled, dissolved in water and the solution made up to 500 ml. A 10 ml aliquot of this solution was transferred to a 100 ml volumetric flask and the same procedure followed as the acid soluble portion. In the present investigation, the insoluble component was, in general, very small ($\sim$ 0.02%Al).

APPENDIX B

AN INTERSTITIAL MODEL FOR LIQUID METAL SOLUTIONS

The model is based on the following assumptions:

(i) The solvent atoms are arranged on a face-centred cubic lattice.

(ii) The available interstitial sites are the octahedral holes in the f c c lattice. These holes form another f c c lattice with the same number of sites as the solvent lattice.

(iii) The interstitial sites are the only sites available to the solute atoms.

(iv) The entropy changes of the solution are due solely to configurational entropy changes.

(v) The energy of the lattice is assumed to consist of interaction energies of all nearest neighbour pairs in the lattice including interstitial pairs on adjacent octahedral sites, although these are not strictly nearest neighbour pairs.

This model is an extension of models developed by Kirkaldy and Purdy (69) for ternary austenite solutions and by Burylev (68) for solutions of non-metals in liquid iron.

The energy of the solution E

The total energy of the solution is given by the sum of the energies of the various bonds present

$$E = N_{AA}u_{AA} + N_{BB}u_{BB} + N_{CC}u_{CC} + N_{AB}u_{AB} + N_{AC}u_{AC} + N_{BC}u_{BC}$$

where the N's represent numbers of pairs and u's are the corresponding interaction energies based on any convenient standard state. i.e. u_{AA} is the energy of formation of a substitutional atom pair, u_{AB}, u_{AC} are the energies of formation of a substitional - interstitial atom pair for a completely isolated interstitial atom, u_{BC} is the energy of formation of an interstitial pair from atoms at isolated interstitial sites.

For dilute solutions the N's are related to the number of atoms of the three species n_A, n_B, n_C by the following relations.

$$6n_C = N_{CA}$$

$$6n_B = N_{BA}$$

$$12n_A = 2N_{AA}$$

$$\frac{6\,n_B^2}{n_A} = N_{BB}$$

$$\frac{6\,n_C^2}{n_A} = N_{CC}$$

$$\frac{12\,n_B n_C}{n_A} = N_{BC}$$

On substitution the total energy becomes

$$E = 6n_A u_{AA} + \frac{6n_B^2 u_{BB}}{n_A} + \frac{6n_C^2 u_{CC}}{n_A} + 6n_B u_{AB} + 6n_C u_{AC} + \frac{12n_B n_C u_{BC}}{n_A}$$

The entropy of the solution S_C

The total number of ways in which n_B and n_C atoms can be arranged amongst n_A interstitial sites is given by

$$W = \frac{n_A!}{n_B!\; n_C!\; (n_A - n_B - n_C)!}$$

Since the configurational entropy is given by

$$S_C = k \ln W$$

then using the Stirling approximation

$$S_C = k\Big\{ n_A \ln n_A - n_A - n_B \ln n_B + n_B - n_C \ln n_C + n_C - (n_A - n_B - n_C) \times \ln(n_A - n_B - n_C) + n_A - n_B - n_C \Big\}$$

$$S_C = k \Big\{ n_A \ln n_A - n_B \ln n_B - n_C \ln n_C - (n_A - n_B - n_C) \ln (n_A - n_B - n_C) \Big\}$$

The free energy of the solution F

In this case

$$F = E - TS$$

since terms in P and V may be neglected for a condensed system.

$$F = 6\, n_A\, u_{AA} + 6 \frac{n_B^2}{n_A} u_{BB} + 6 \frac{n_C^2}{n_A} u_{CC} + 6\, n_B\, u_{AB}$$

$$+ 6 n_C\, u_{AC} + 12 \frac{n_B n_C}{n_A} u_{BC} - kT \;\; n_A \ln n_A - n_B \ln n_B$$

$$- n_C \ln n_C - (n_A - n_B - n_C) \ln (n_A - n_B - n_C)$$

The molal free energy is given by

$$\mu_B = A\, (\partial F / \partial n_B)$$

where A is Avogadro's number.

Hence
$$\mu_B = A\left[12\,\frac{n_B}{n_A}\,u_{BB} + 6\,u_{AB} + 12\,\frac{n_C}{n_A}\,u_{BC}\right]$$

$$- AkT\left\{-\ln n_B - 1 + \ln\left(n_A - n_B - n_C\right) + 1\right\}$$

$$= A\left[12\,\frac{n_B}{n_A}\,u_{BB} + 6\,u_{AB} + 12\,\frac{n_C}{n_A}\,u_{BC}\right] + RT\ln\left(\frac{n_B}{n_A - n_B - n_C}\right)$$

In terms of atom fractions

$$\mu_B = \mu^o_B + \frac{12\,A\,x_B\,u_{BB}}{1 - x_B - x_C} + \frac{12\,A\,x_C\,u_{AC}}{1 - x_B - x_C} \qquad \text{(A)}$$

$$+ R\,T\ln\left(\frac{x_B}{1 - 2(x_B + x_C)}\right)$$

Where $\mu^o_B = 6Au_{AB}$

Using the relation

$$\mu = \mu^o_B + RT\ln a_B = \mu^o_B + RT\ln x_B + RT\ln\gamma_B$$

and substituting in equation (A) we obtain

$$F^E = RT\ln\gamma_B = \frac{12Au_{BB}x_B}{1-x_B-x_C} + \frac{12Au_{BC}x_C}{1-x_B-x_C} - RT\ln\left(1 - 2(x_B + x_C)\right)$$

For the case of a binary solution:

$$RT\ln\gamma'_B = \frac{12Au_{BB}x_B}{1 - x_B} - RT\ln\left(1 - 2x_B\right)$$

and since

$$RT\ln\gamma^C_B = RT\ln\frac{\gamma_B}{\gamma'_B}$$

$$RT\ln\gamma^C_B = \frac{12Au_{BB}x_Bx_C}{(1-x_B)(1-x_B-x_C)} + \frac{12Au_{BC}x_C}{(1 - x_B - x_C)} + R\,T\ln\frac{(1 - 2x_B)}{(1 - 2(x_B + x_C))}$$

Expanding the denominators of the first two terms and the logarithm in the third term and ignoring all terms above those to power two and all mixed terms of higher order than $x_A x_B$

$$RT \ln \frac{\gamma_B}{\gamma_B^1} = 12\,A\,u_{BB} x_B x_C + 12A\,u_{BC} \left\{ x_C + x_C x_B + x_C^2 \right\}$$

$$- 2\,RT \left\{ x_C + 2x_B x_C + x_C^2 \right\}$$

$$\text{or} \quad \ln \gamma_B^C = \left(\frac{12A\,u_{BC}}{RT} - 2 \right) x_C + \left(\frac{12A\,u_{BC}}{RT} - 2 \right) x_C^2$$

$$+ \left\{ \frac{12A}{RT} \left(u_{BB} + u_{BC} \right) - 4 \right\} x_B\, x_C$$

The first order free energy interaction parameter is defined as $\varepsilon_B^C = \left.\frac{\partial \ln \gamma_B^C}{\partial x_C}\right)_{x_A \to 1}$ and the second order free energy interaction parameter is defined as $\rho_B^C = \left.\frac{\partial^2 \ln \gamma_B^C}{\partial x_C^2}\right)_{x_A \to 1}$

Thus from this interstitial model:

$$\varepsilon_B^C = \left(\frac{12\,Au_{BC}}{RT} - 2 \right)$$

$$\rho_B^C = 2\left(\frac{12Au_{BC}}{RT} - 2 \right)$$

$$\text{and} \quad 2\,\varepsilon_B^C = \rho_B^C$$

APPENDIX C

AN ESTIMATE OF THE COOLING RATE DURING SOLIDIFICATION OF A QUENCHED SAMPLE

A typical sample weighed 1 gm which after quenching had the form of a disc approximately 0.005 in. thick and 2 ins. in diameter.

Assuming:

1) The liquid sample had this shape immediately prior to solidification
2) The copper blocks are perfect heat sinks
3) That the disc cools uniformly

then we can equate the loss in heat in 1 sec. at 1900°K from the sample to the flow of heat from the sample in this time as follows

$$m \times s \times \Delta T = \frac{K\,A\,1500}{t/2}$$

m = mass of sample = 1 gm

s = specific heat of sample $\approx$ 0.15 cals/gm

Δ T = temperature drop of sample in 1 sec.

K = thermal conductivity of sample $\approx$ 0.075 cals/sec cm/°K

A = area of one side of disc

t = thickness of disc.

Hence $$\Delta T \approx \frac{0.075 \times 22 \times (2.54)^2 \times 1500}{7 \times 0.15 \times 0.0063}$$

$$\Delta T \approx 10^6 \ C^o$$

i.e. cooling rate during solidification is of the order of 10^6 C°/sec.

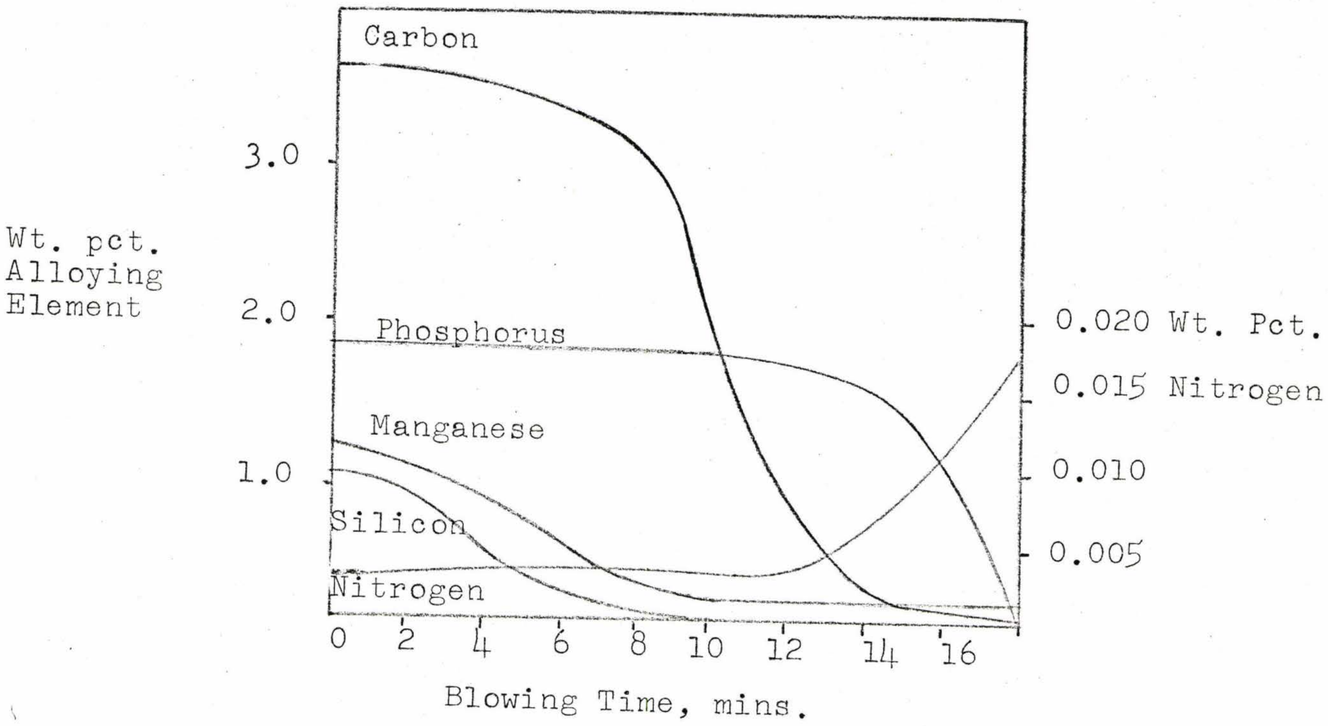


Fig. 1. Change of metal composition with time in the basic Bessemer Converter process. (1)

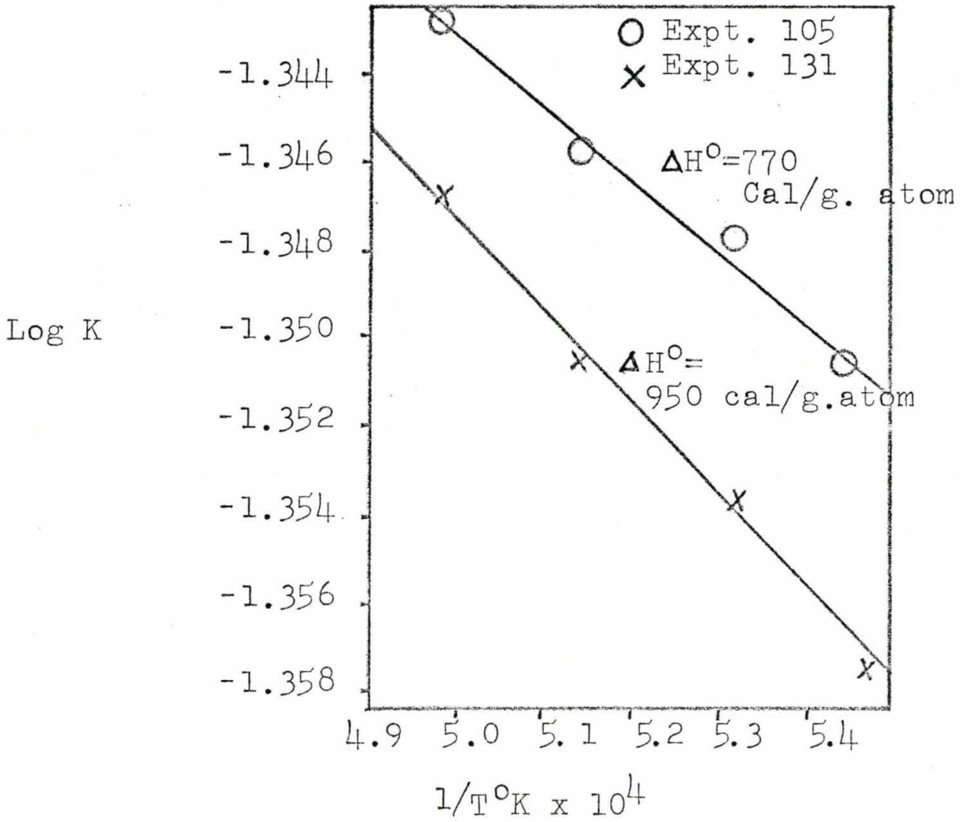


Fig. 2. Variation of Log K with temperature for the solubility of nitrogen in pure iron. (after Pehlke and Elliott (47))

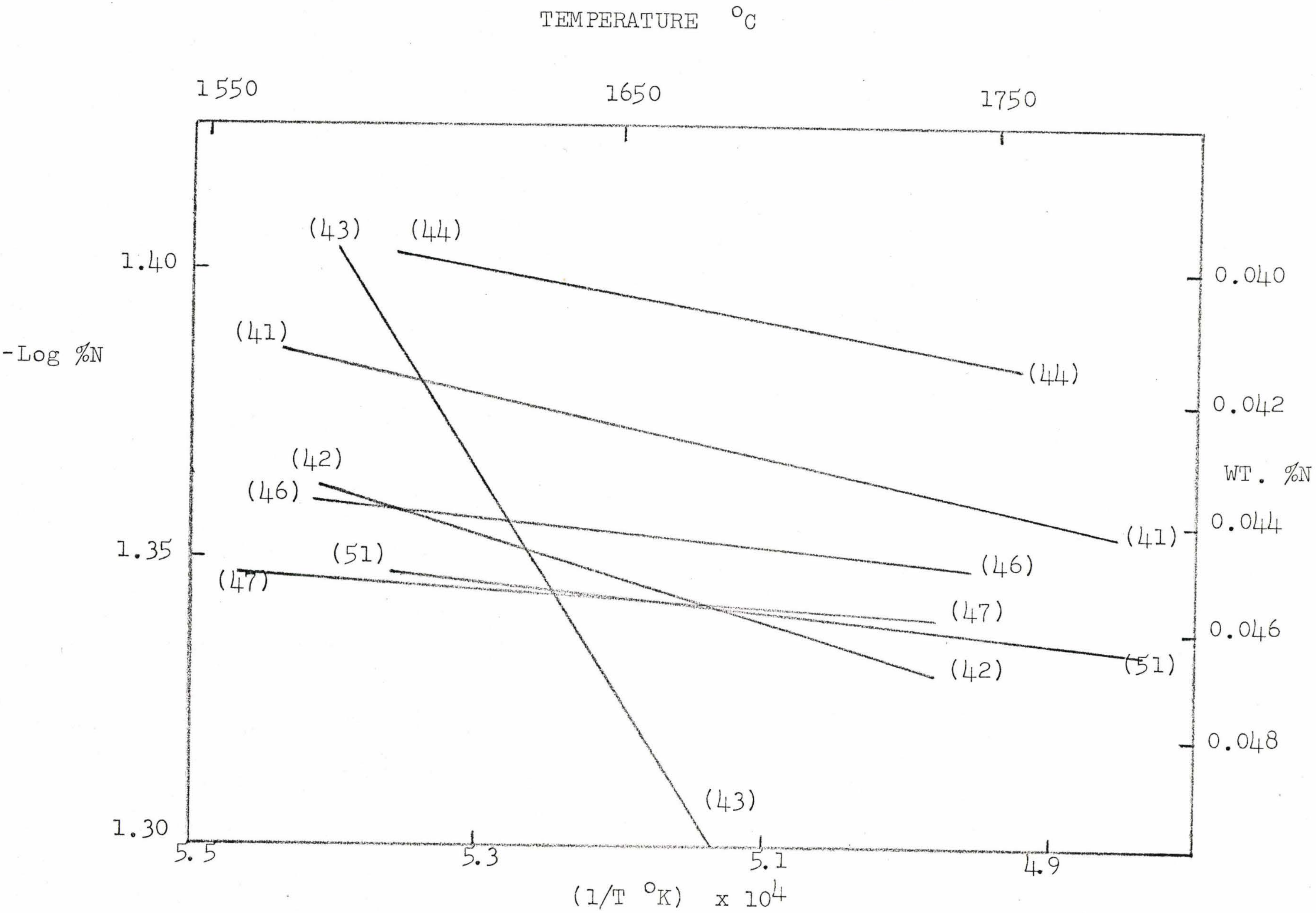


Fig. 3. Some recent investigations of the solubility of nitrogen in pure iron.

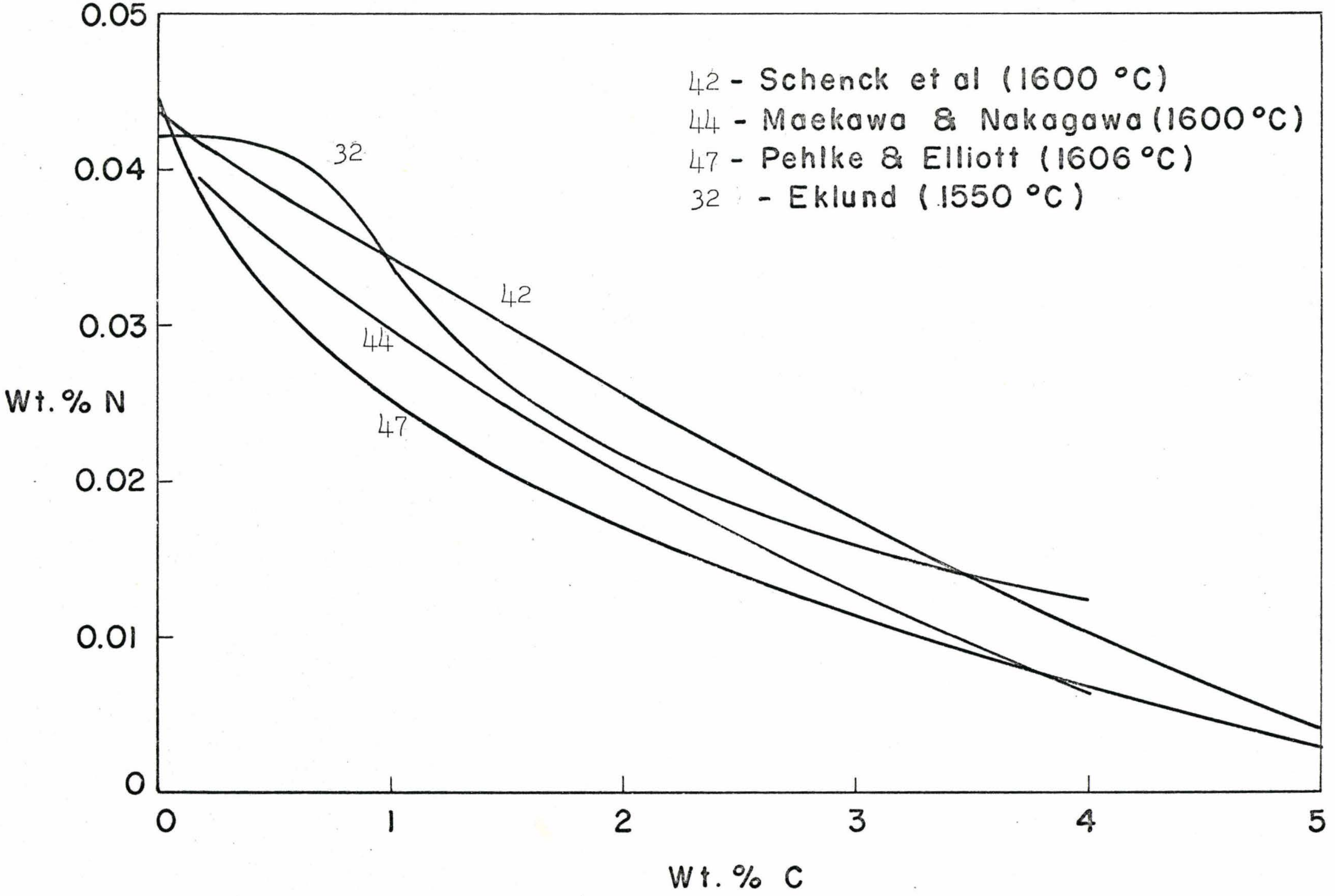


Fig. 4. Solubility of nitrogen in iron carbon alloys found by previous investigators.

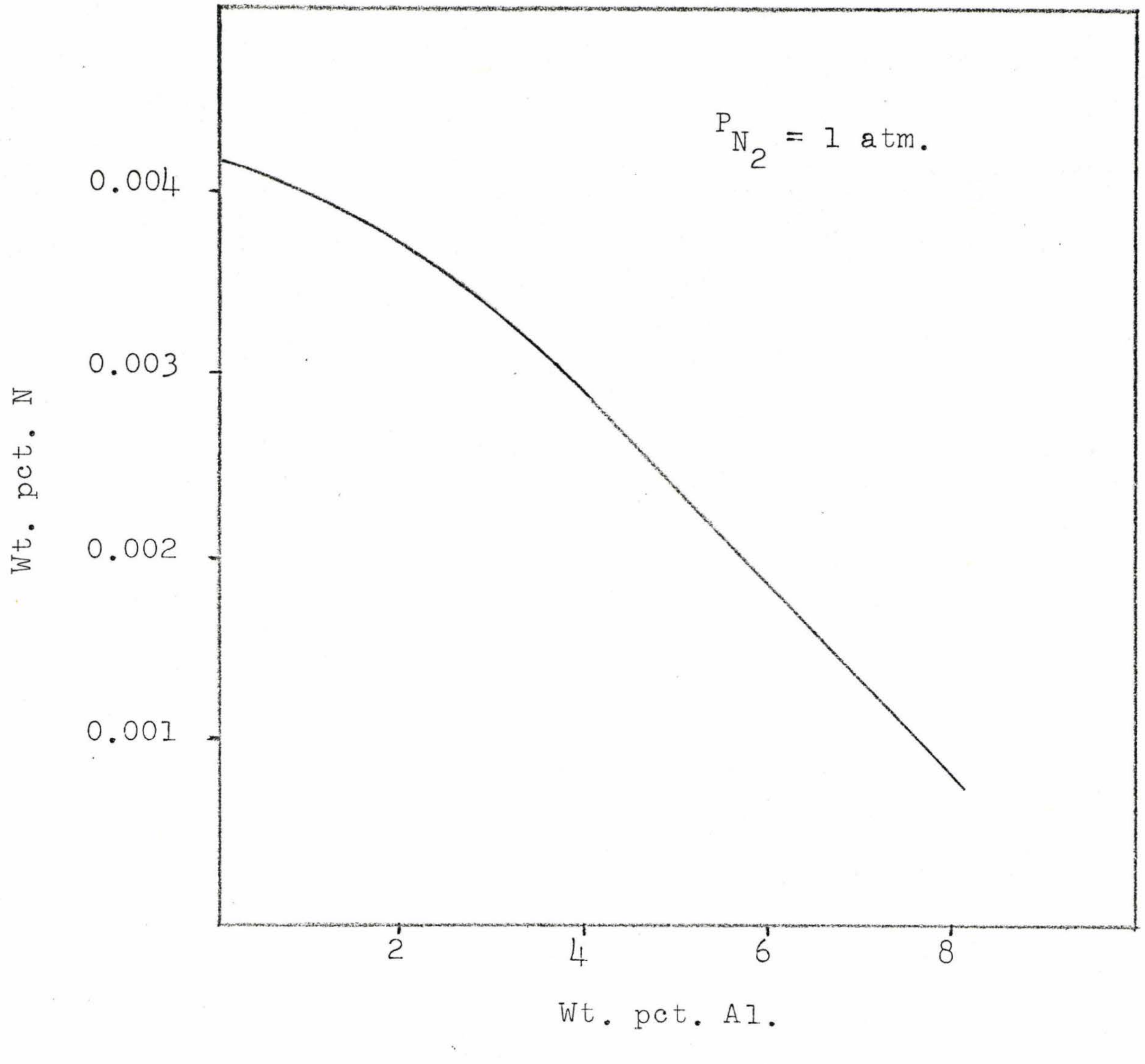


Fig. 5. Solubility of nitrogen in liquid Fe-Al alloys at 1700°C. (after Maekawa and Nakagawa (44))

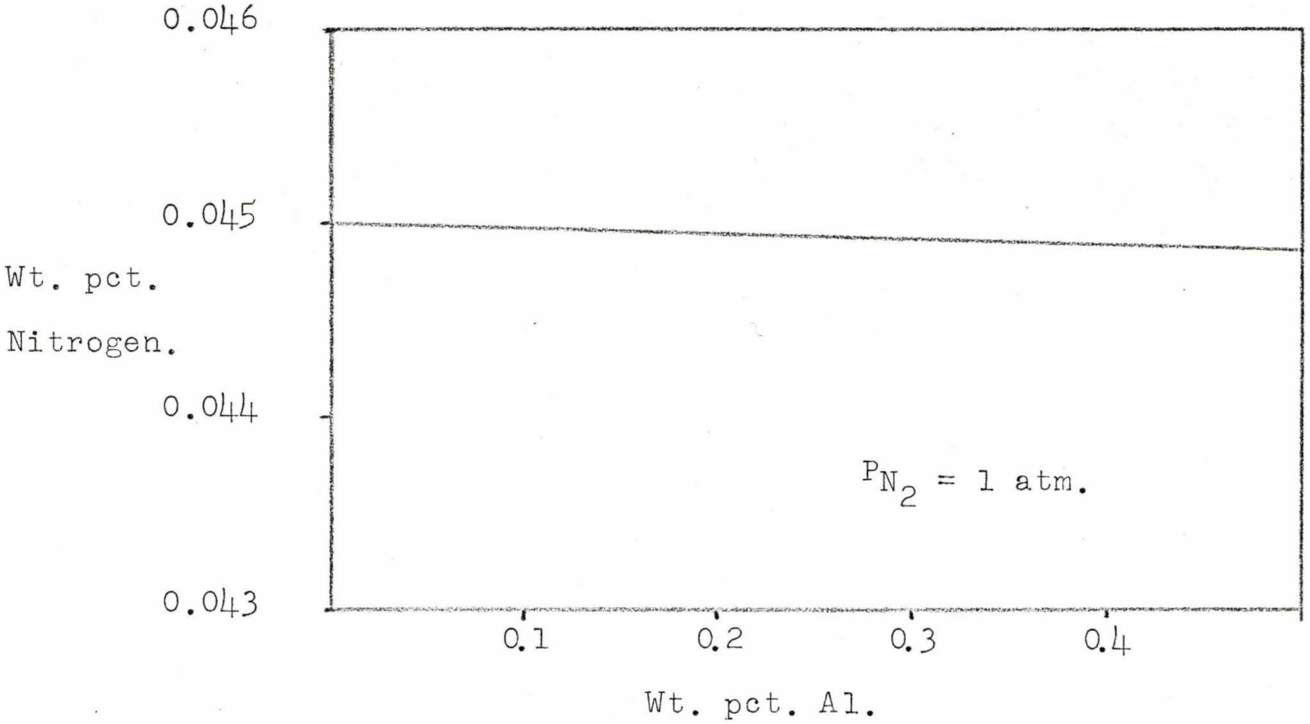


Fig. 6. Solubility of nitrogen in liquid Fe-Al alloys at 1606°C. (after Pehlke and Elliott (47))

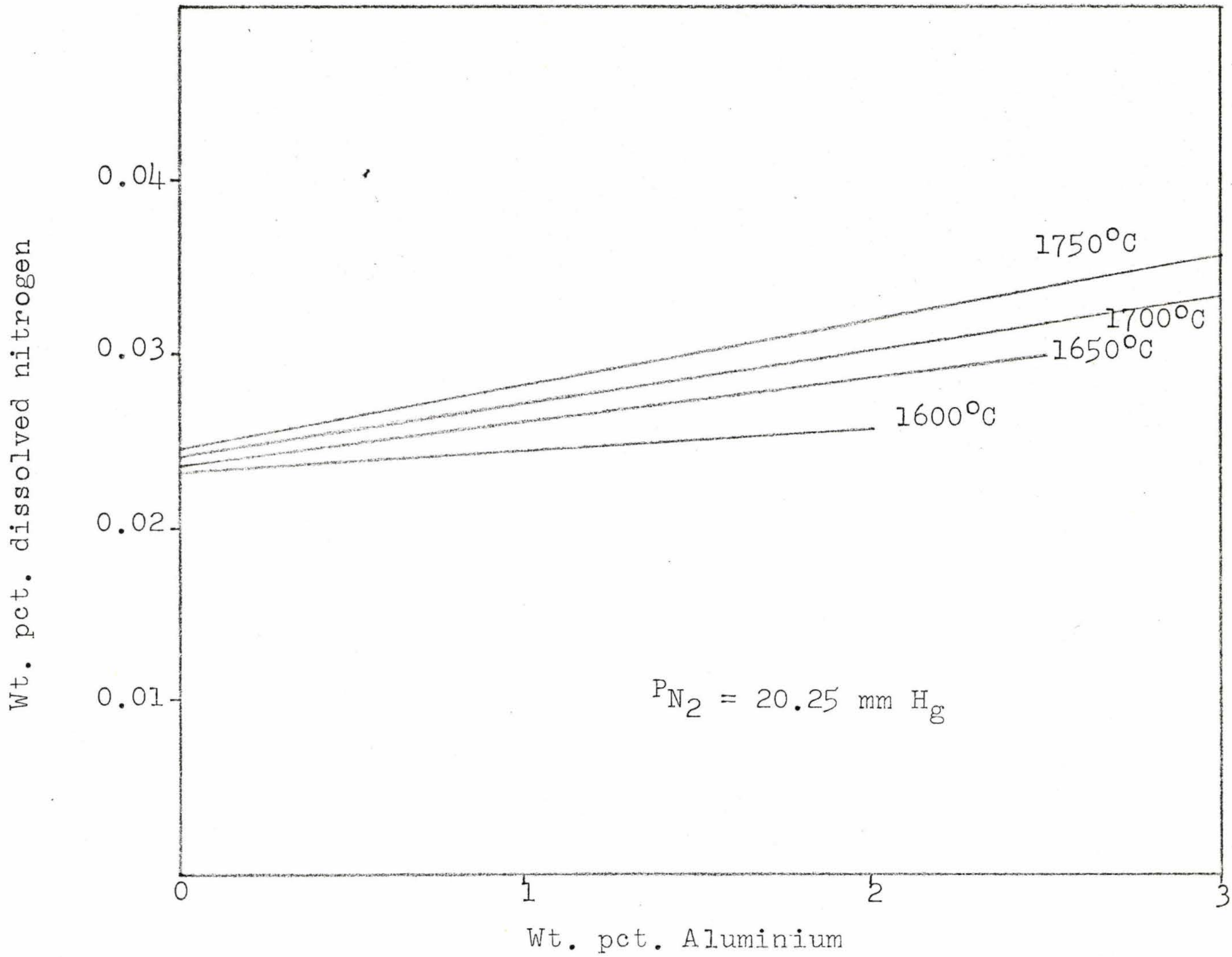
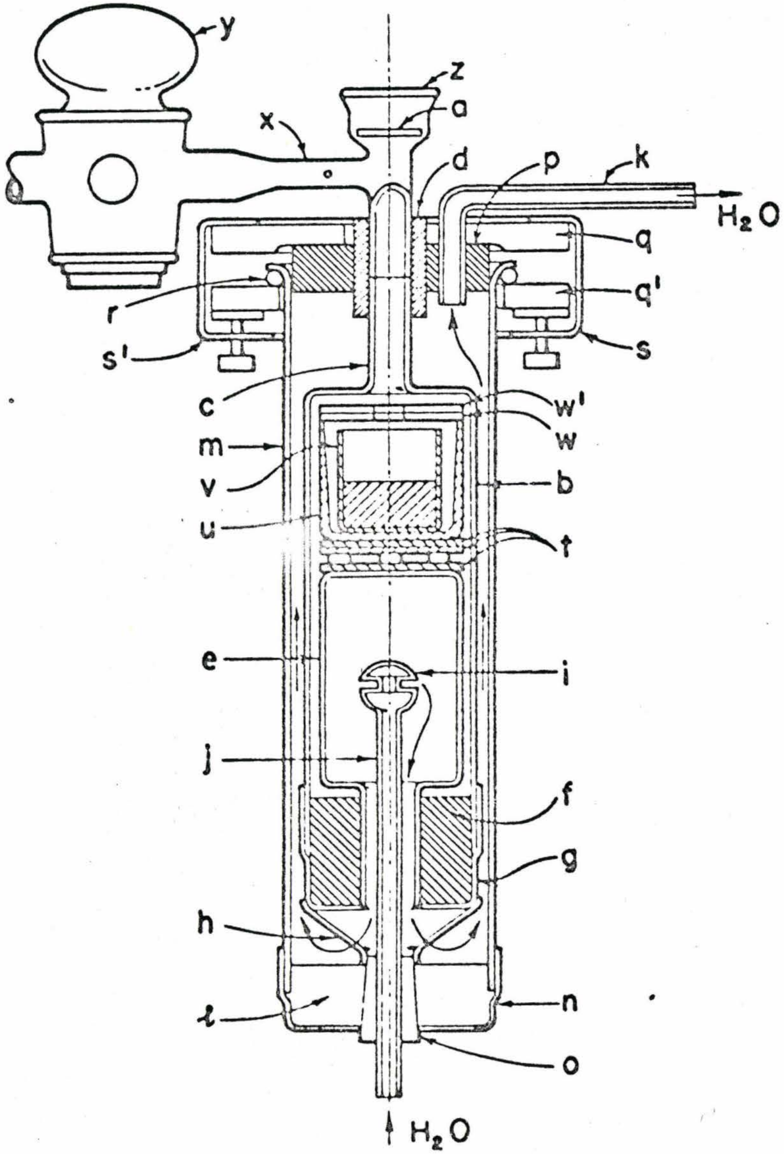


Fig. 7. Solubility of nitrogen in liquid Fe-Al alloys (after Evans and Pehlke (53))



nomenclature

a	shield
b	main body
c	connecting tubing
d	high-vacuum tubing
e	bottom bulb
f	rubber stopper
g	rubber sleeve
h	hard plastic pusher
i	water inlet openings
j	water inlet
k	water outlet
l	rubber stopper
m	water jacket
n	rubber sleeve
o	small rubber stopper
p	rubber stopper
q, q'	plexiglass pieces
r	rubber ring
s, s'	clamps
t	insulating disks
u	radiation shield crucible
v	crucible
w, w'	radiation shield
x	place where additions are stored
y	stop-cock
z	quartz window

Fig. 8. Reaction Chamber of Sieverts' apparatus

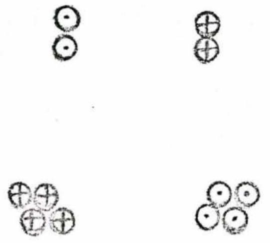


Fig. 9. Schematic diagram showing the configuration of the levitation coil used.

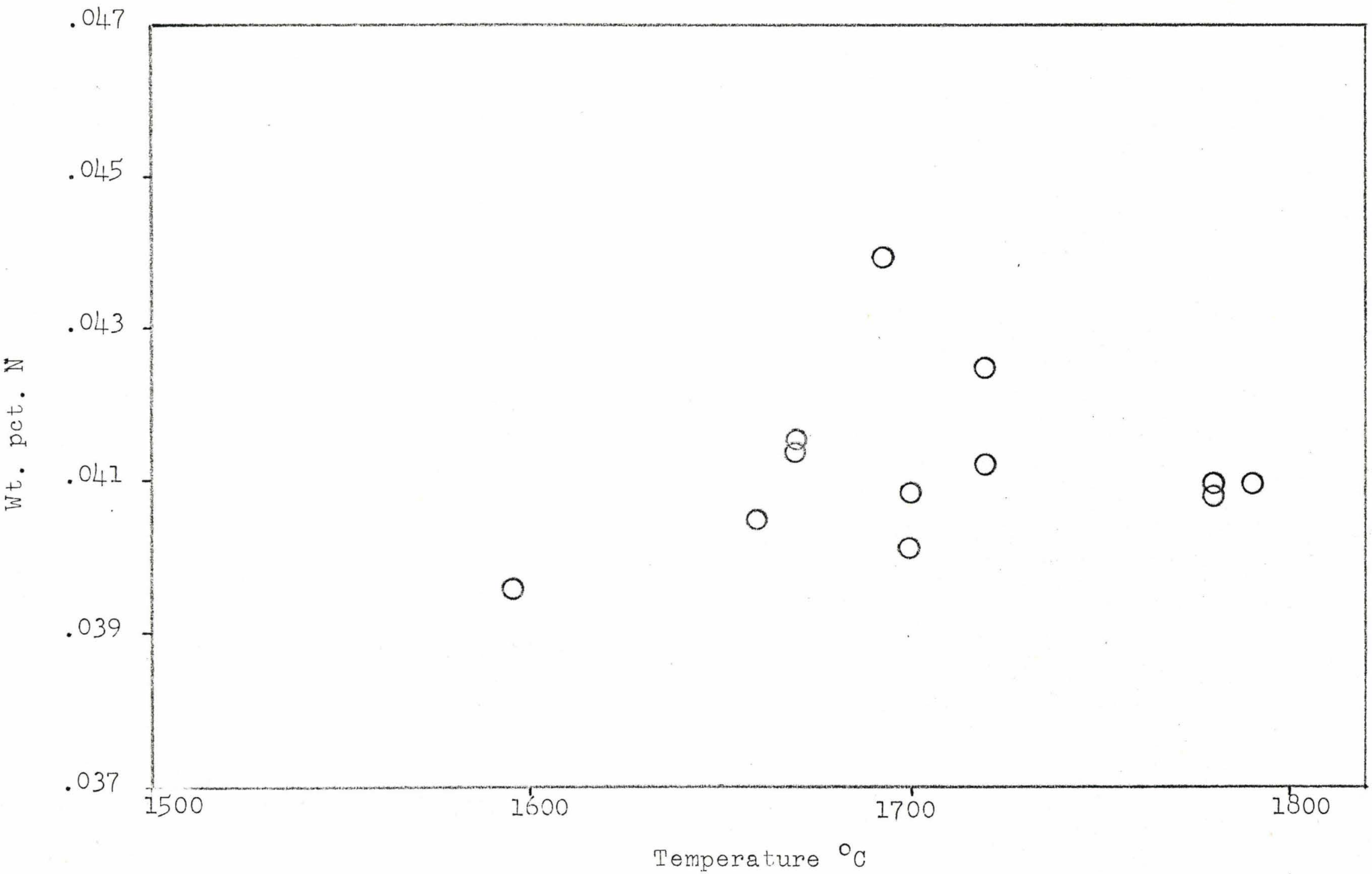


Fig. 10. Nitrogen content of samples quenched into a copper mould.

a) 15mm. Vycor Tube
b) O-ring and clamp
c) Mild steel cylinder
d) Pendulum
g) Sliding brass contact
h) Brass slide-rod
i) Copper blocks
j,k) Solenoid valves
l) Levitation coil
m) Steel piston
n) 12 lb. lead hammer
O,p) Rubber stoppers
r) Gas inlet

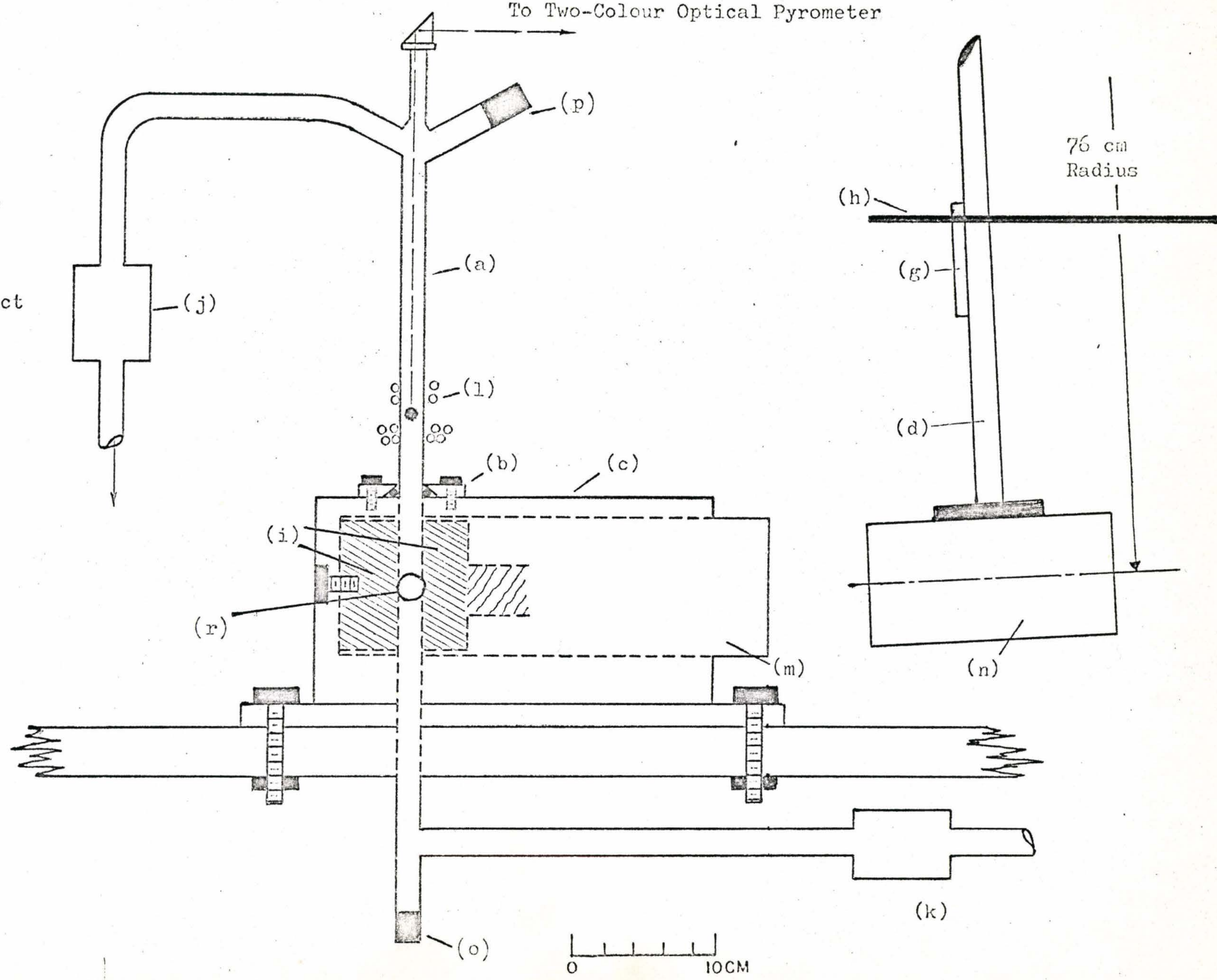


Fig 11. SCHEMATIC DIAGRAM OF QUENCH APPARATUS

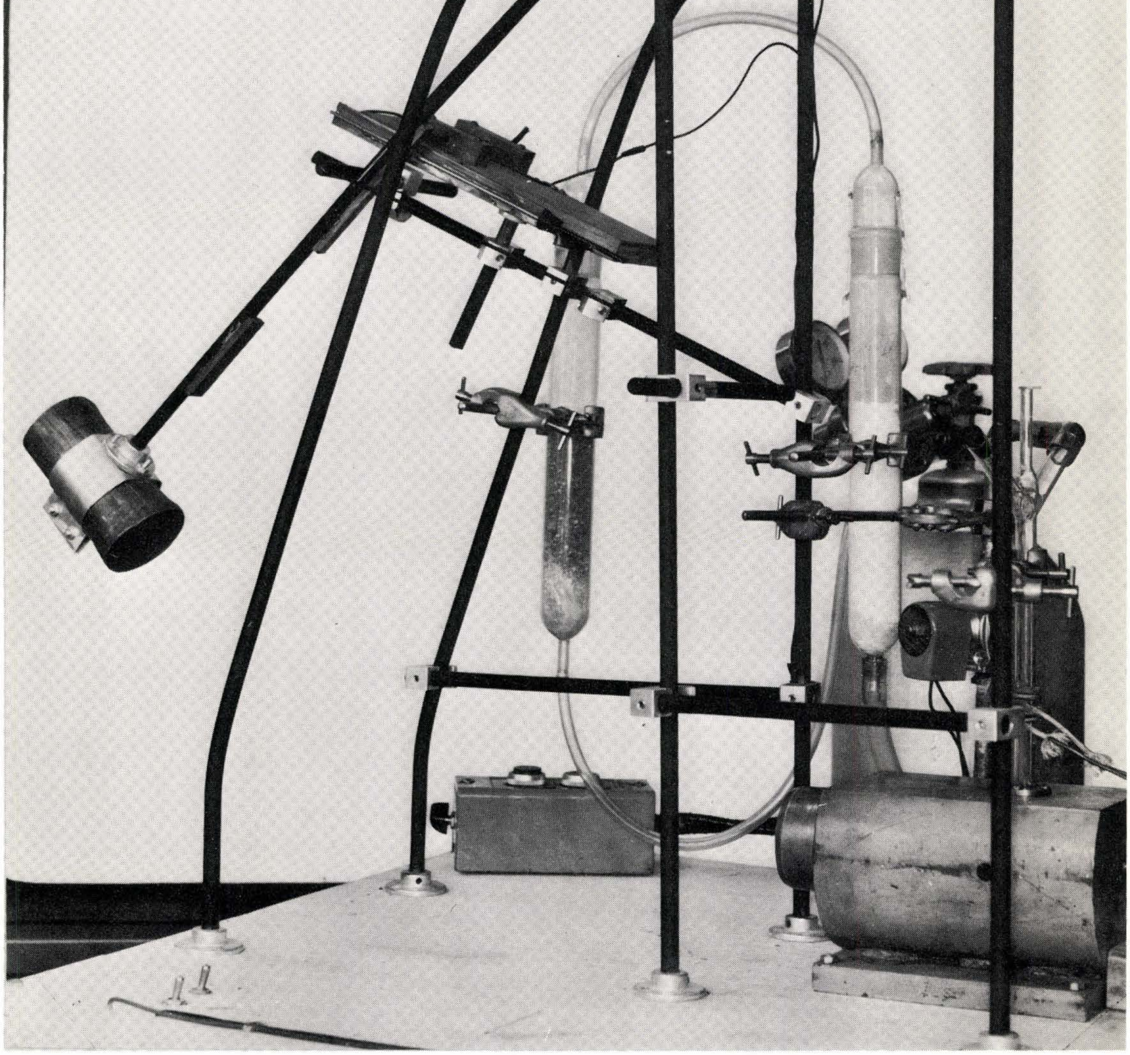


FIGURE 12 THE QUENCH APPARATUS

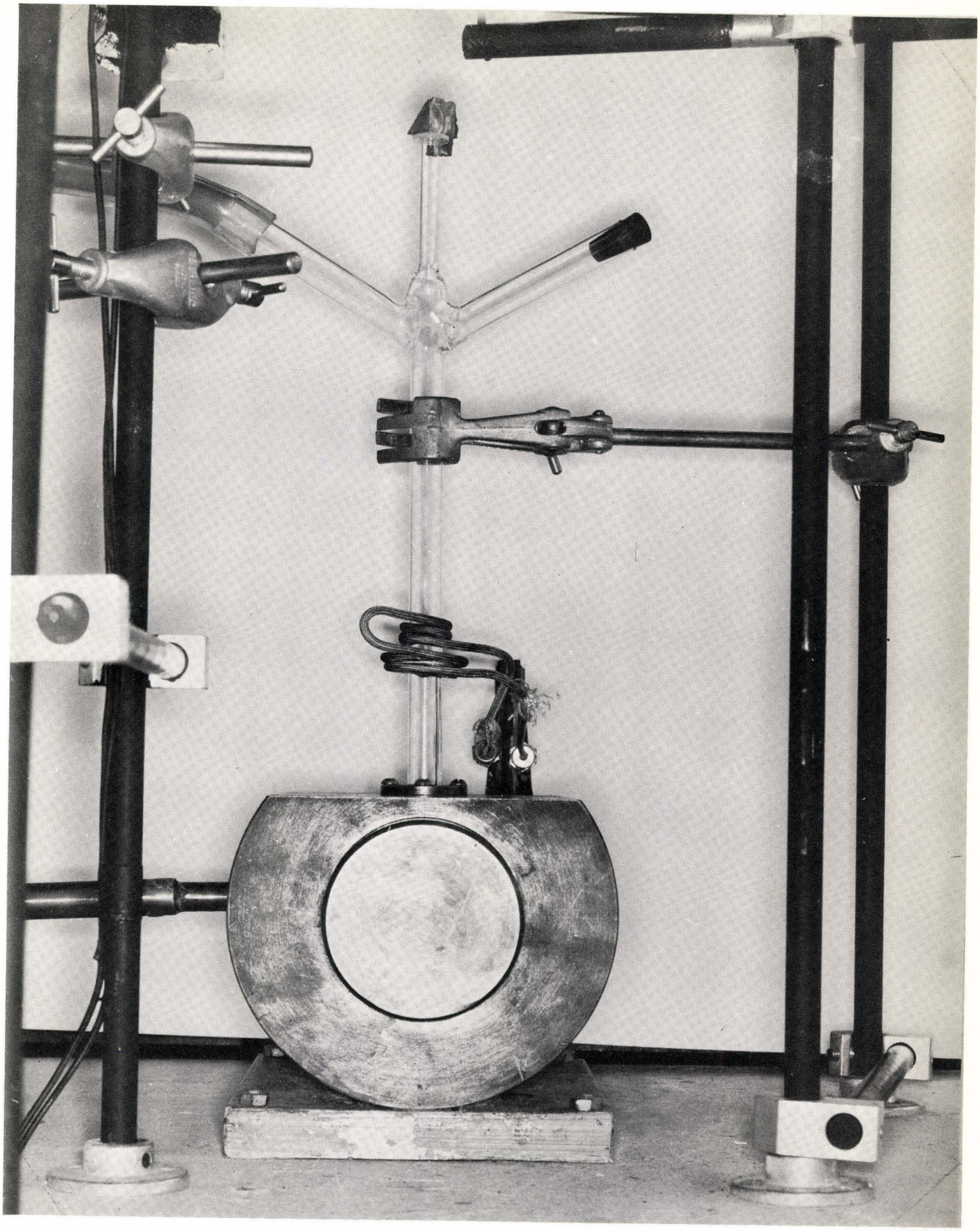


FIGURE 13 CLOSE UP OF QUENCH APPARATUS

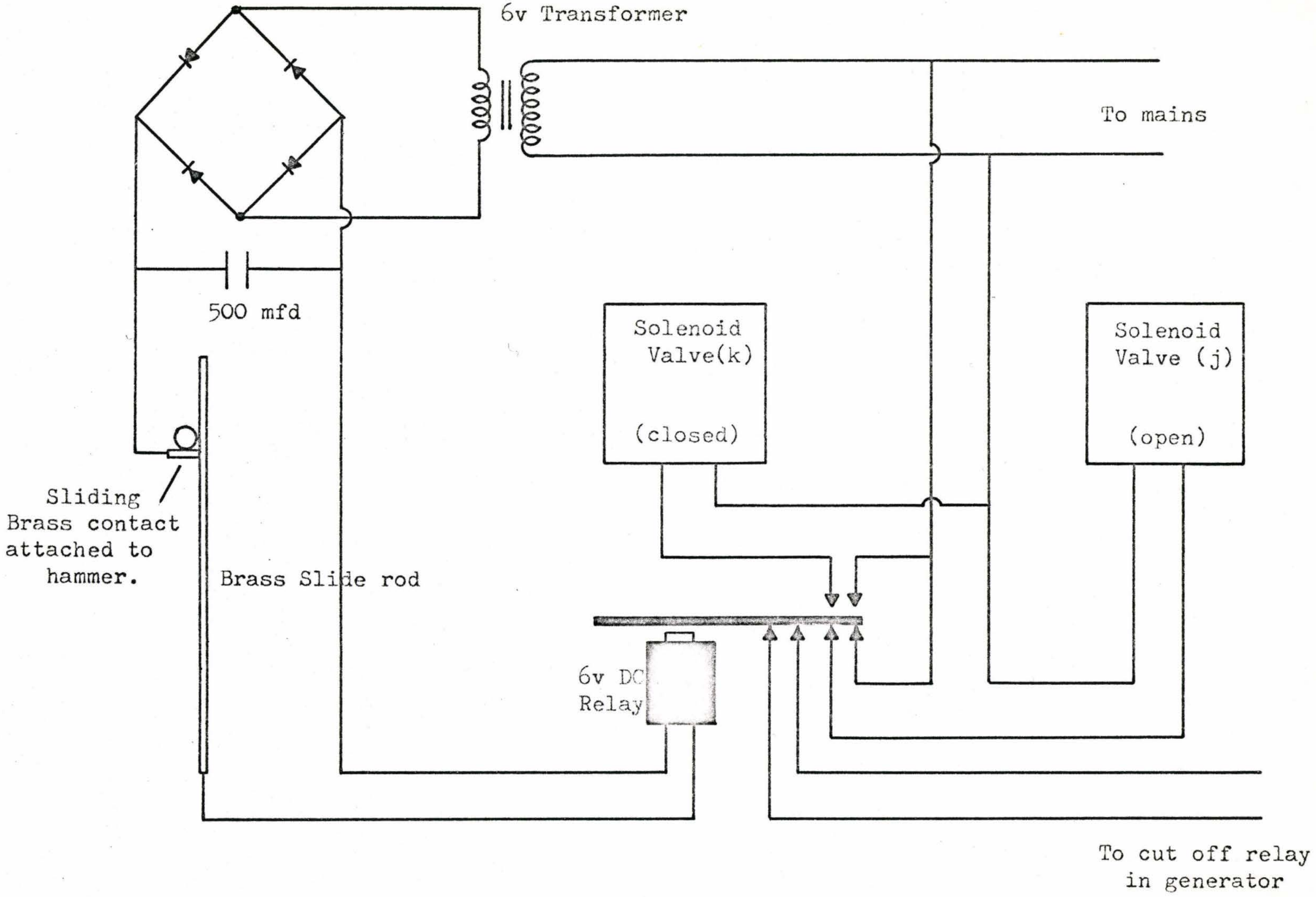


Fig. 14. **CIRCUIT DIAGRAM FOR QUENCH APPARATUS**

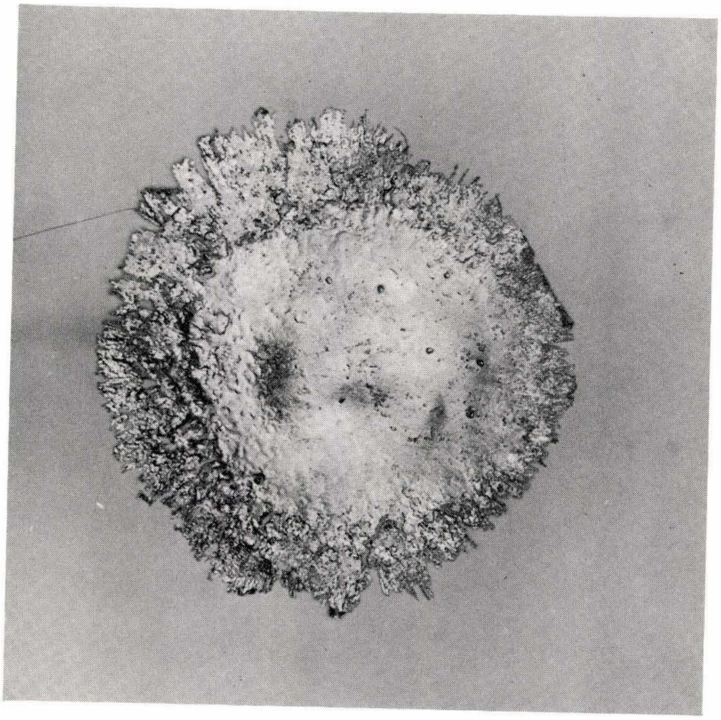


FIGURE 15 TYPICAL QUENCHED SAMPLE

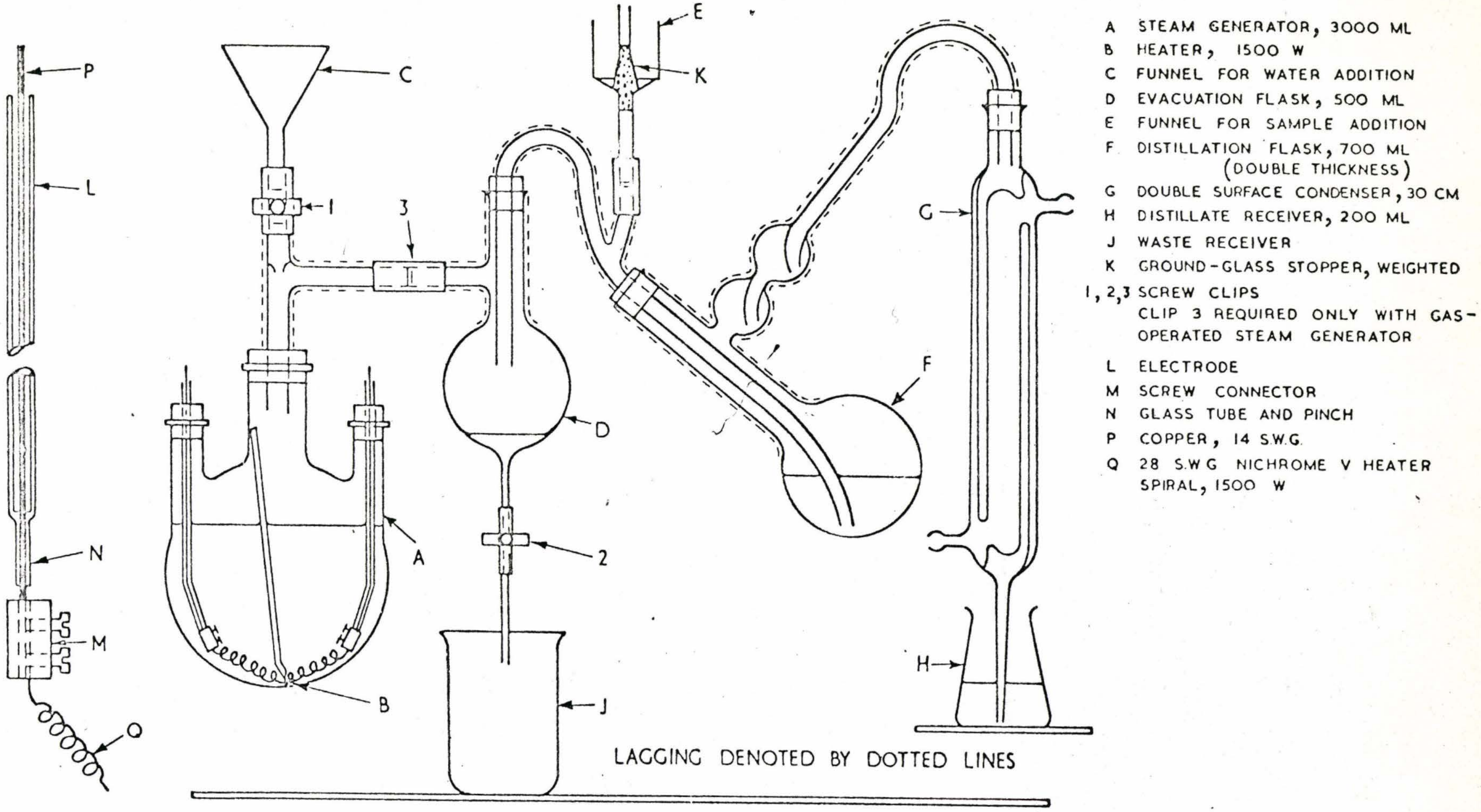


Fig 16

The steam distillation apparatus.

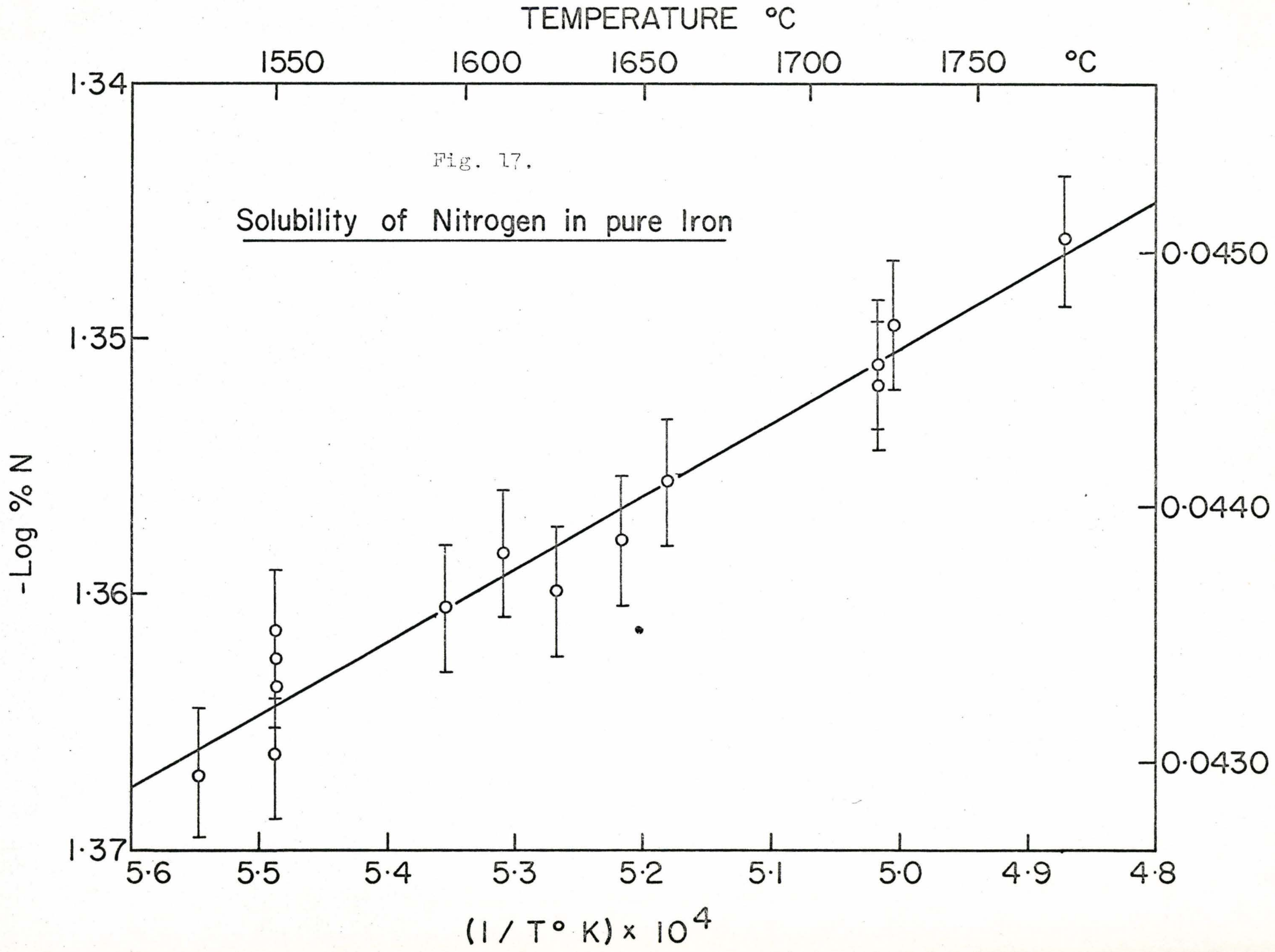


Fig. 17.

Solubility of Nitrogen in pure Iron

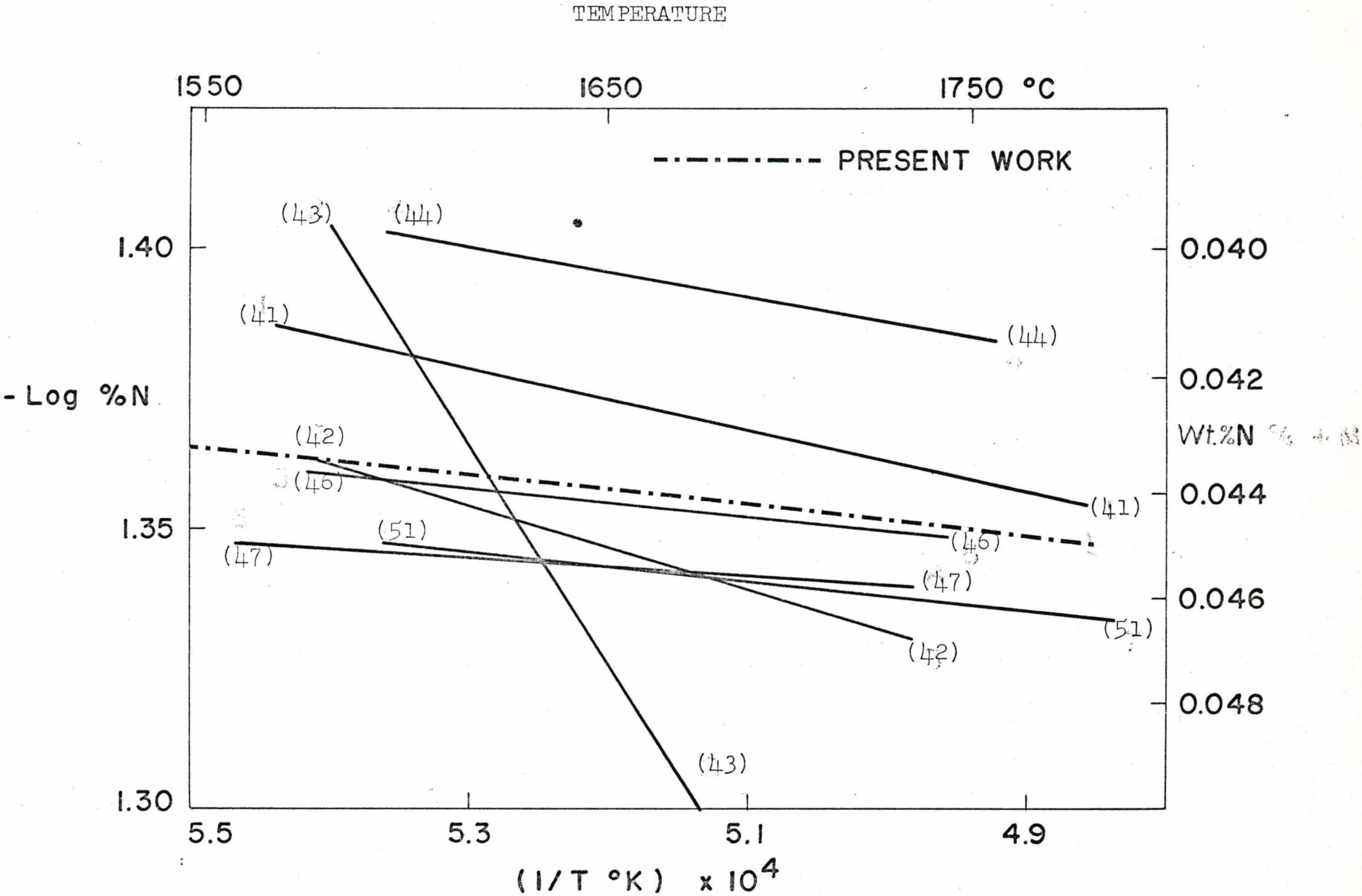


Fig. 18. Comparison of present results with previous investigations.

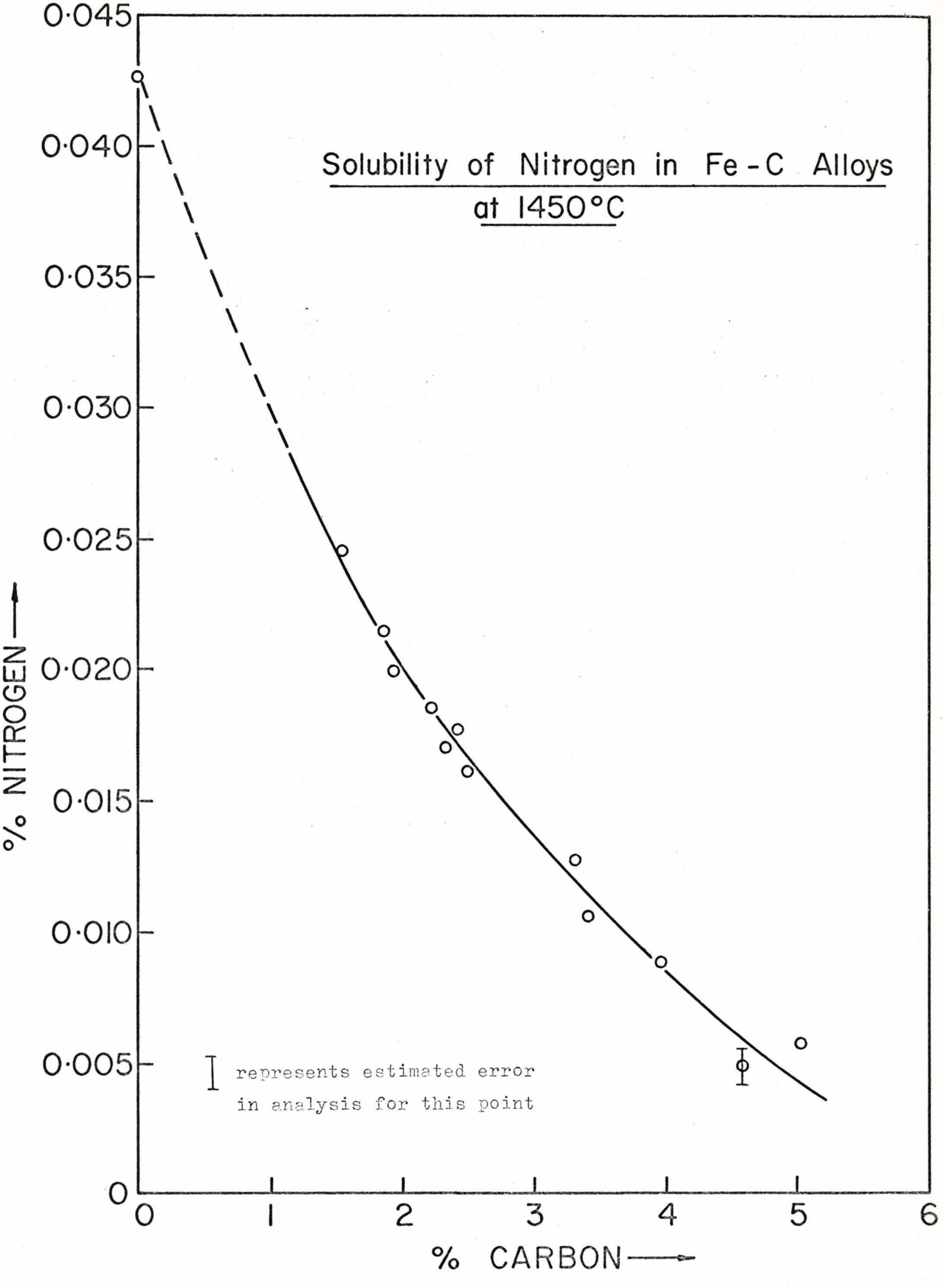

Solubility of Nitrogen in Fe - C Alloys at 1450°C
0·045
0·040
0·035
0·030
0·025
0·020
0·015
0·010
0·005
0
% NITROGEN
0
1
2
3
4
5
6
% CARBON
represents estimated error in analysis for this point

Fig. 19

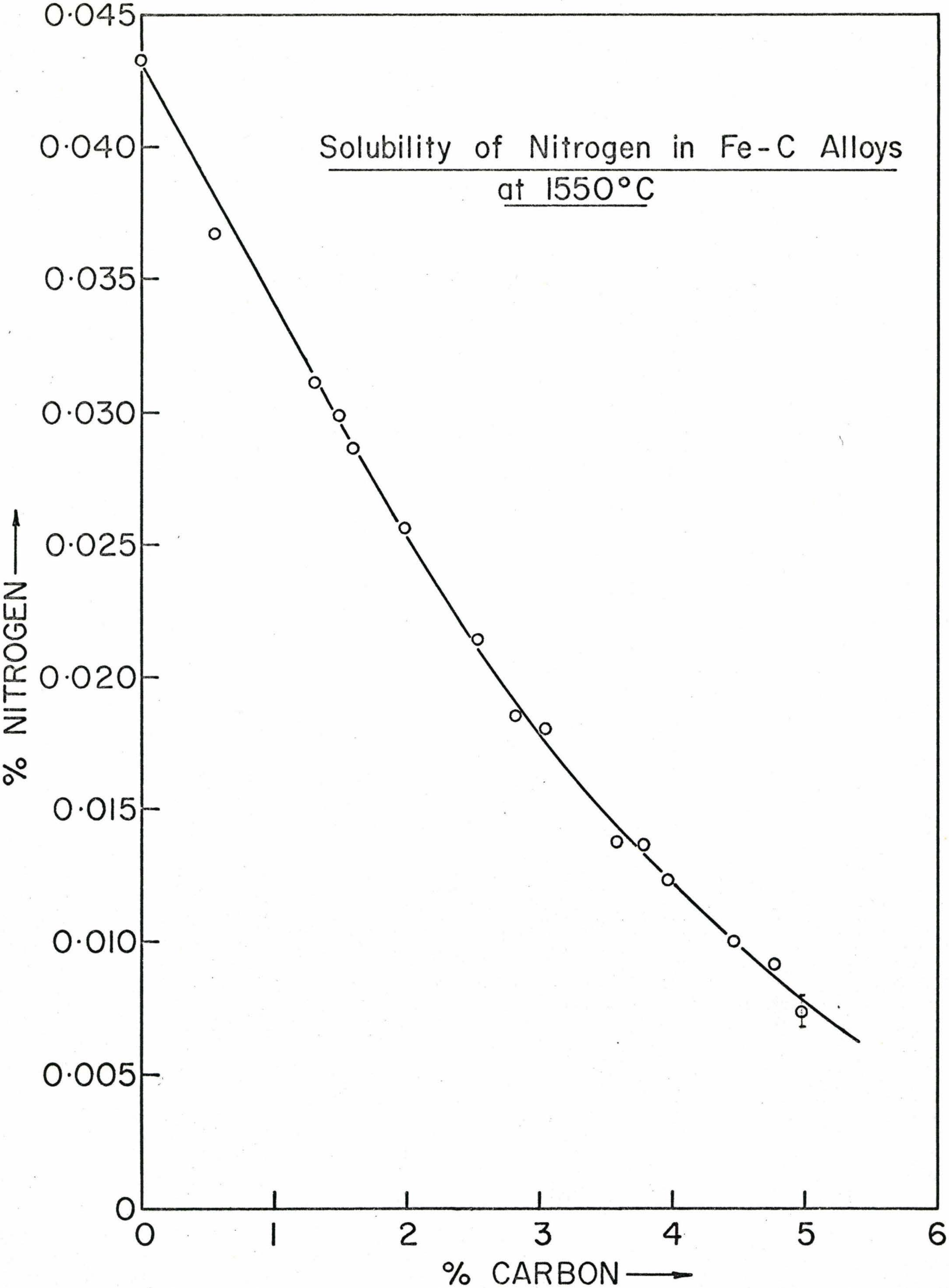

Solubility of Nitrogen in Fe-C Alloys
at 1550°C
% NITROGEN
0·045
0·040
0·035
0·030
0·025
0·020
0·015
0·010
0·005
0
% CARBON
0
1
2
3
4
5
6

Fig. 20

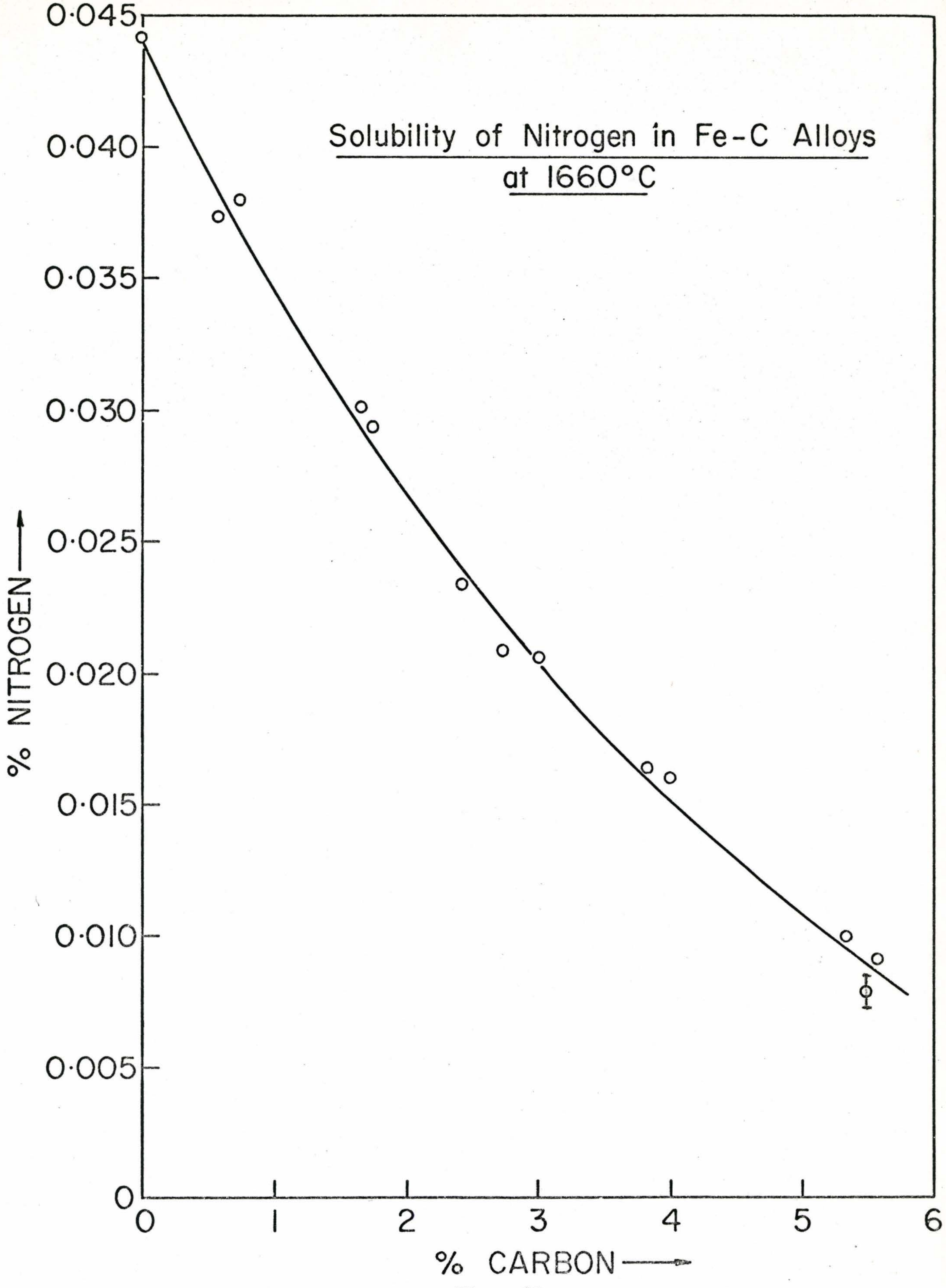

Solubility of Nitrogen in Fe-C Alloys
at 1660°C
0·045
0·040
0·035
0·030
0·025
0·020
0·015
0·010
0·005
0
% NITROGEN
0
1
2
3
4
5
6
% CARBON

Fig. 21

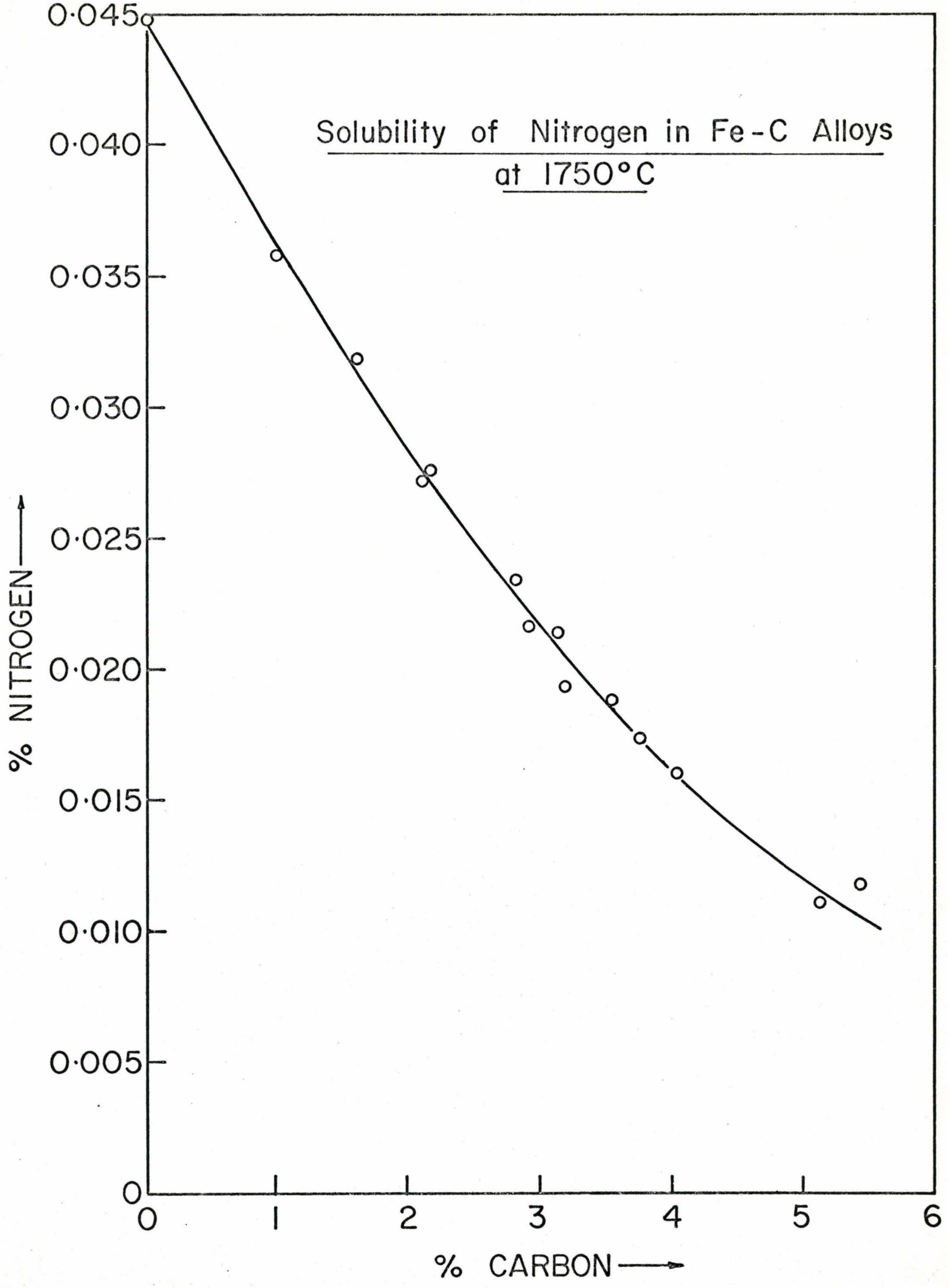

Solubility of Nitrogen in Fe-C Alloys at 1750°C
0·045
0·040
0·035
0·030
0·025
0·020
0·015
0·010
0·005
0
% NITROGEN
0
1
2
3
4
5
6
% CARBON

Fig. 22

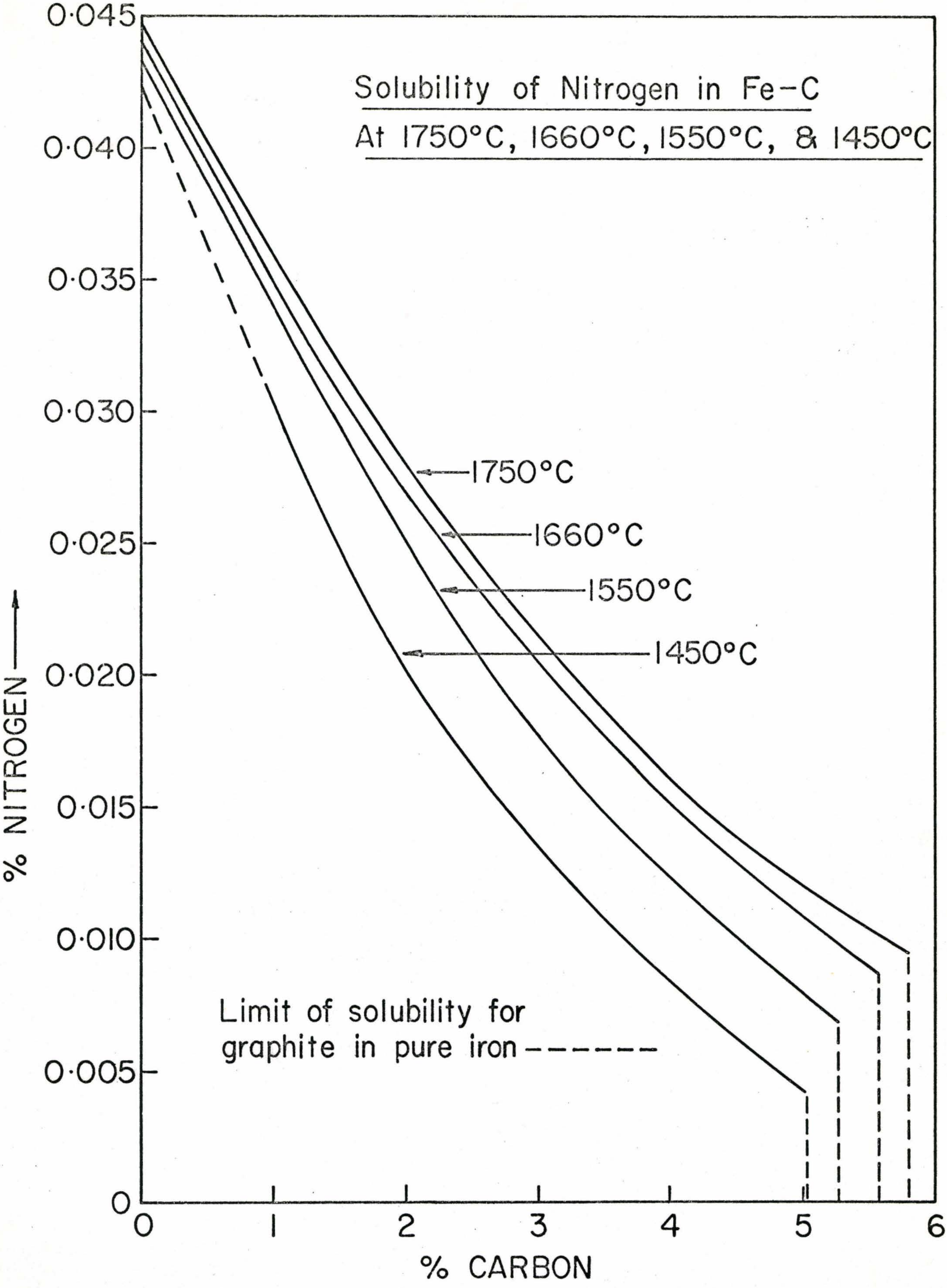

Solubility of Nitrogen in Fe-C
At 1750°C, 1660°C, 1550°C, & 1450°C
1750°C
1660°C
1550°C
1450°C
Limit of solubility for graphite in pure iron
% NITROGEN
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0
% CARBON
0
1
2
3
4
5
6

Fig. 23

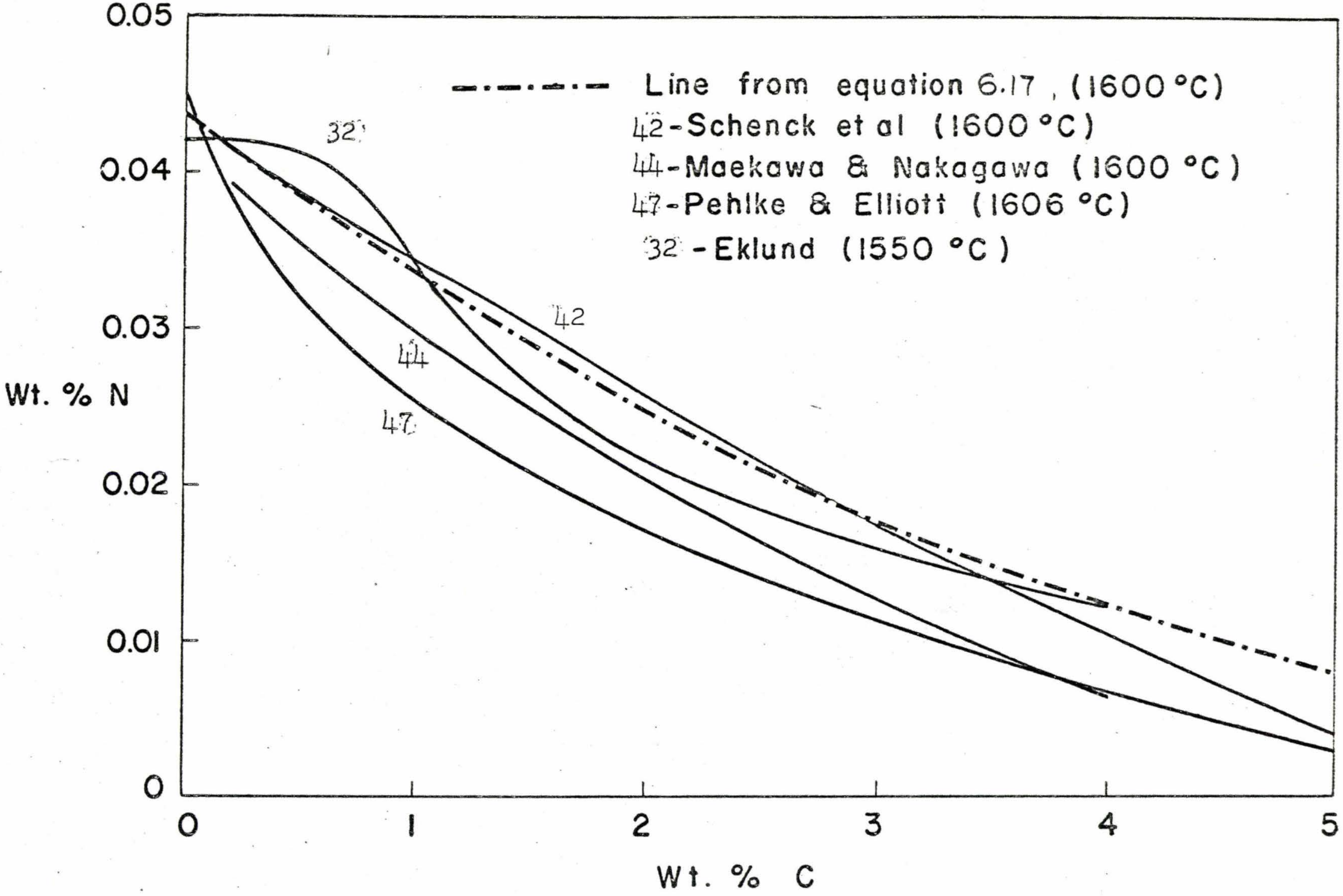


Fig. 24. Comparison of present results for Fe-C alloys with those of previous investigations.

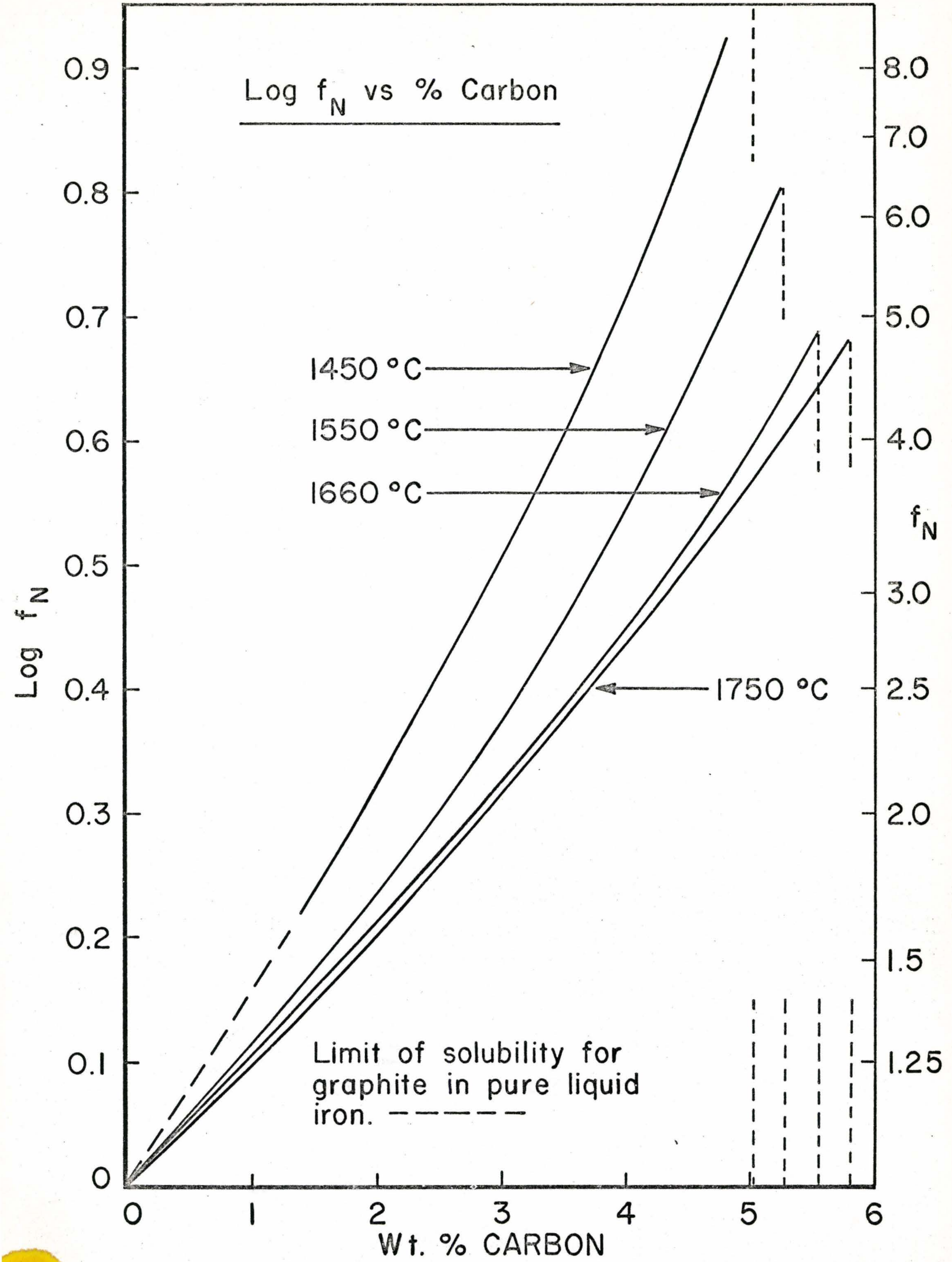

Log f_N vs % Carbon
1450 °C
1550 °C
1660 °C
1750 °C
Limit of solubility for graphite in pure liquid iron. ------
Log f_N
f_N
Wt. % CARBON
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.25
1.5
2.0
2.5
3.0
4.0
5.0
6.0
7.0
8.0
0
1
2
3
4
5
6

Fig. 25

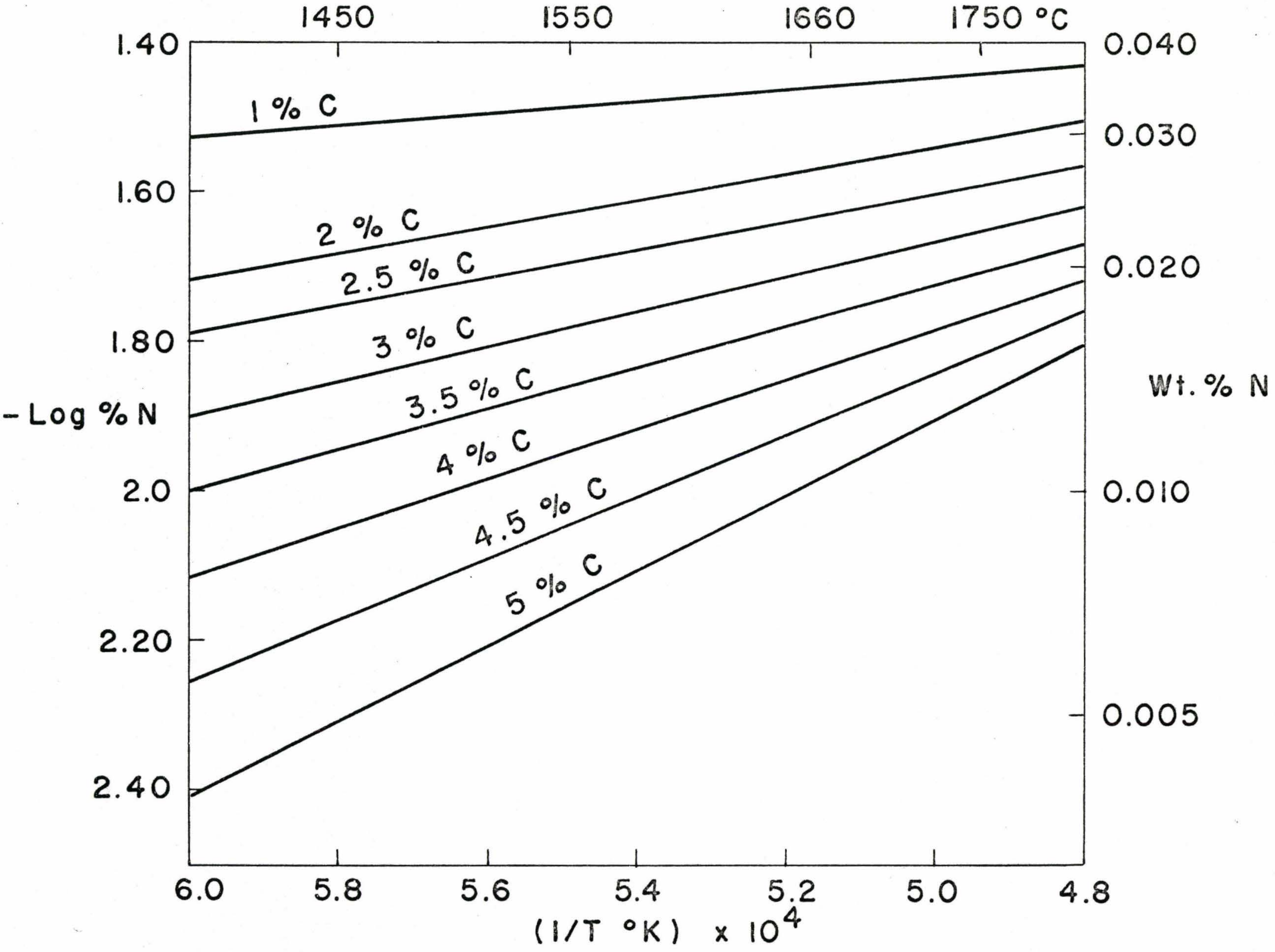

1450
1550
1660
1750 °C
1.40
1.60
1.80
2.0
2.20
2.40
-Log % N
0.040
0.030
0.020
0.010
0.005
Wt. % N
1 % C
2 % C
2.5 % C
3 % C
3.5 % C
4 % C
4.5 % C
5 % C
6.0
5.8
5.6
5.4
5.2
5.0
4.8
(1/T °K) x 10⁴

Fig. 26

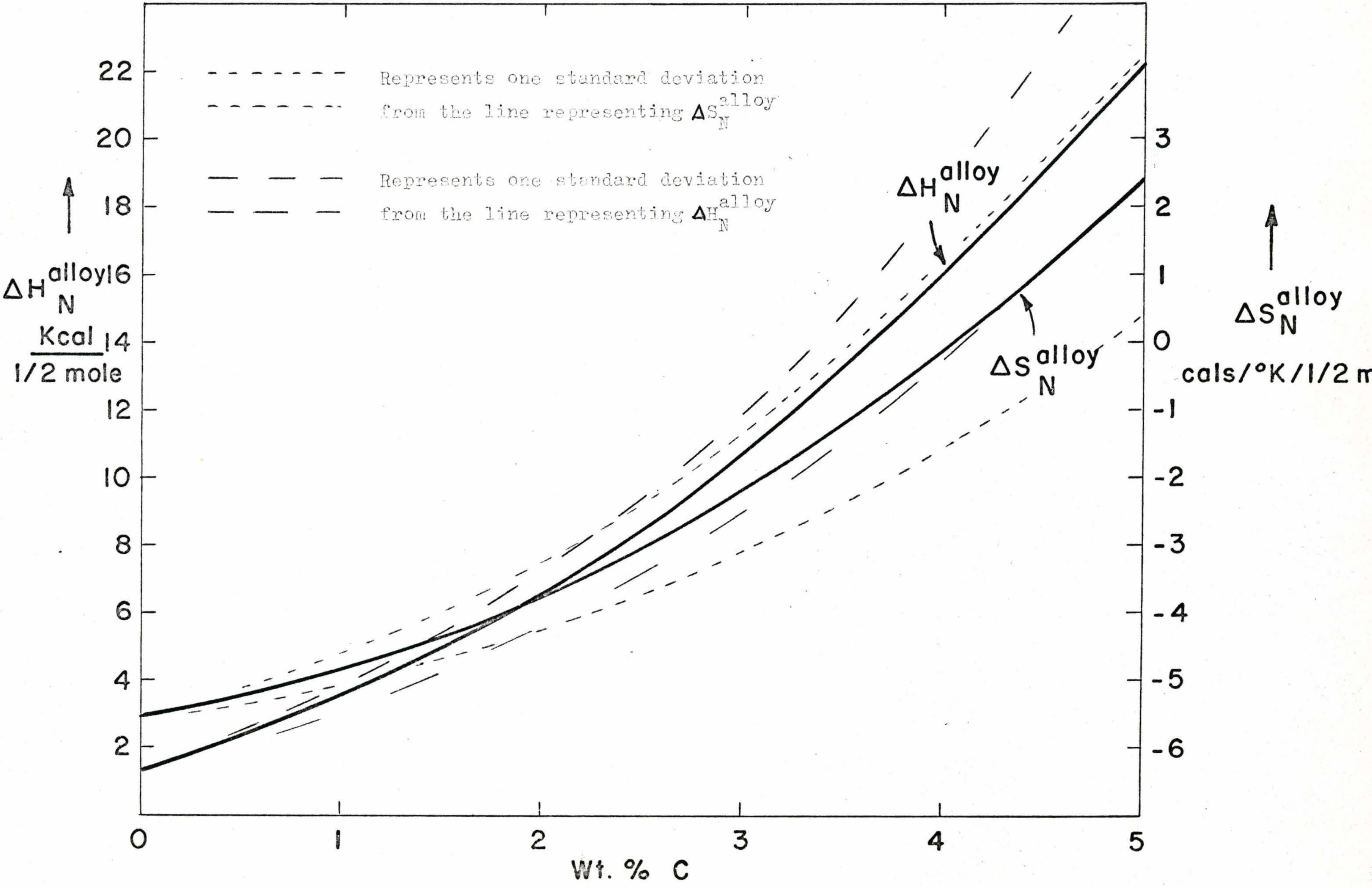

Represents one standard deviation from the line representing ΔS_N^{alloy}
Represents one standard deviation from the line representing ΔH_N^{alloy}
ΔH_N^{alloy}
ΔS_N^{alloy}
ΔH_N^{alloy} Kcal / 1/2 mole
ΔS_N^{alloy} cals/°K/1/2 m
22
20
18
16
14
12
10
8
6
4
2
3
2
1
0
-1
-2
-3
-4
-5
-6
0
1
2
3
4
5
Wt. % C

Fig. 27

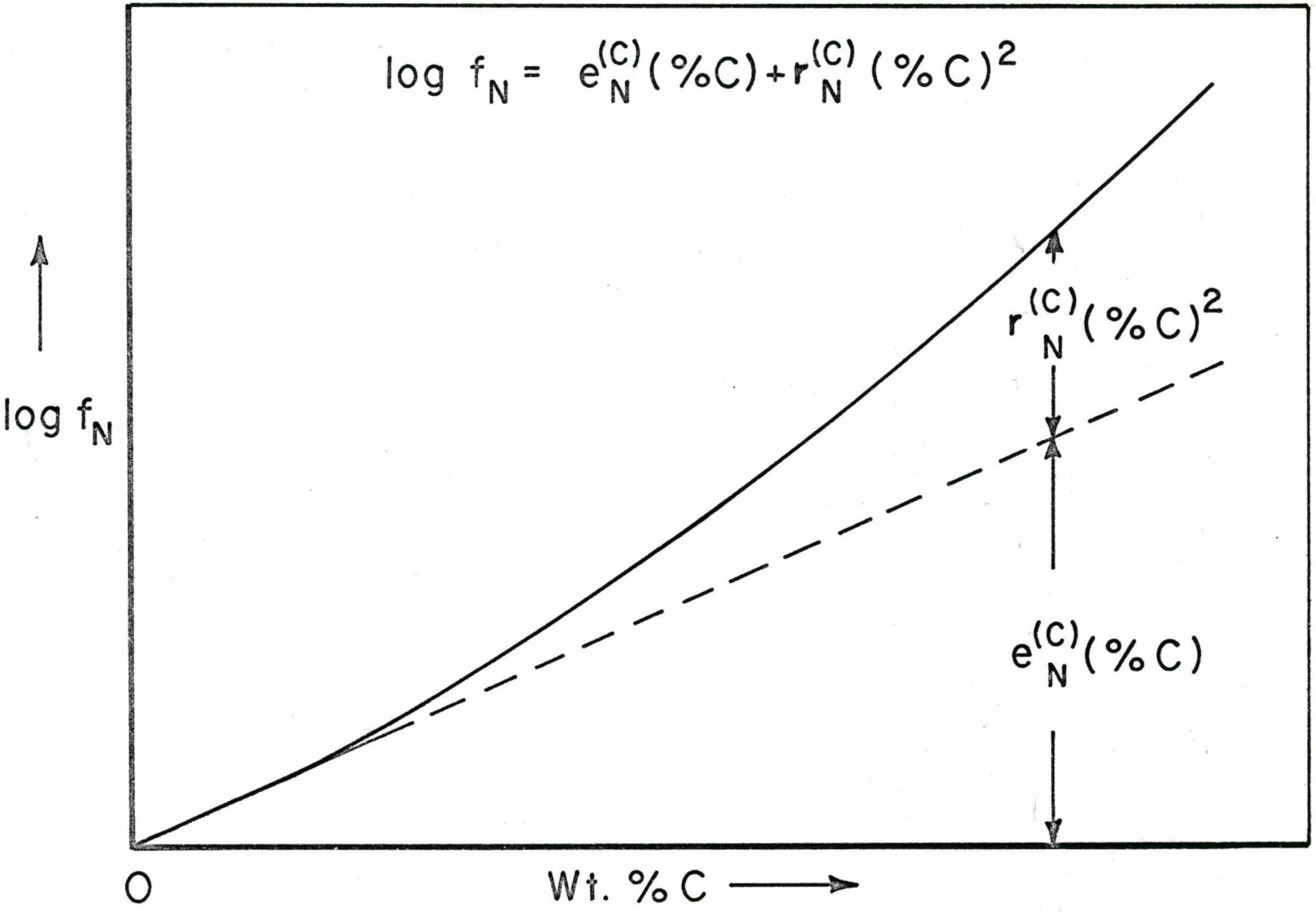


Fig. 28. Schematic diagram demonstrating first and second order free energy interaction parameters.

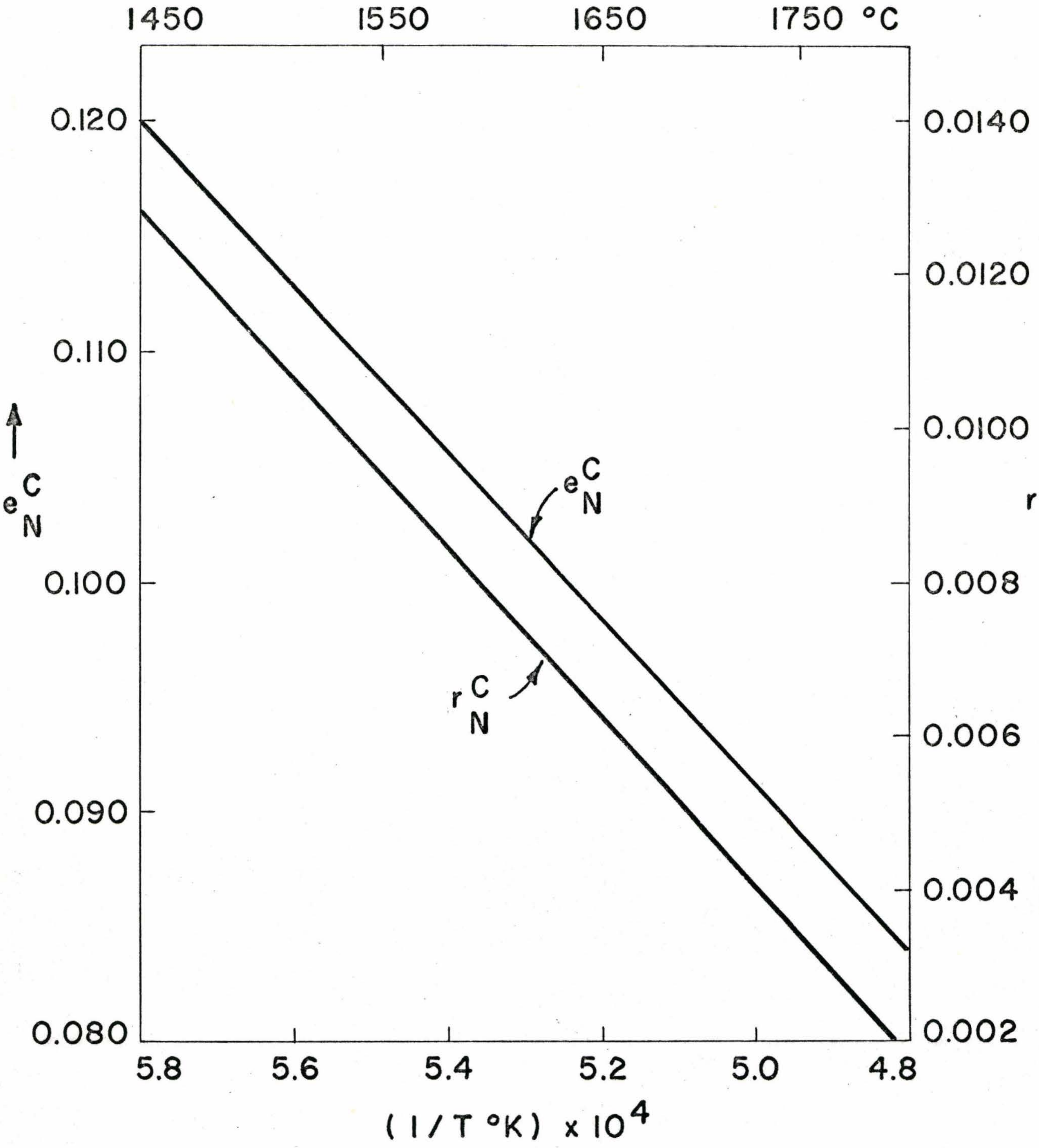

1450
1550
1650
1750 °C
0.120
0.110
0.100
0.090
0.080
0.0140
0.0120
0.0100
0.008
0.006
0.004
0.002
e_N^C
r_N^C
e_N^C
r_N^C
5.8
5.6
5.4
5.2
5.0
4.8
(1/T °K) x 10⁴

Fig. 29

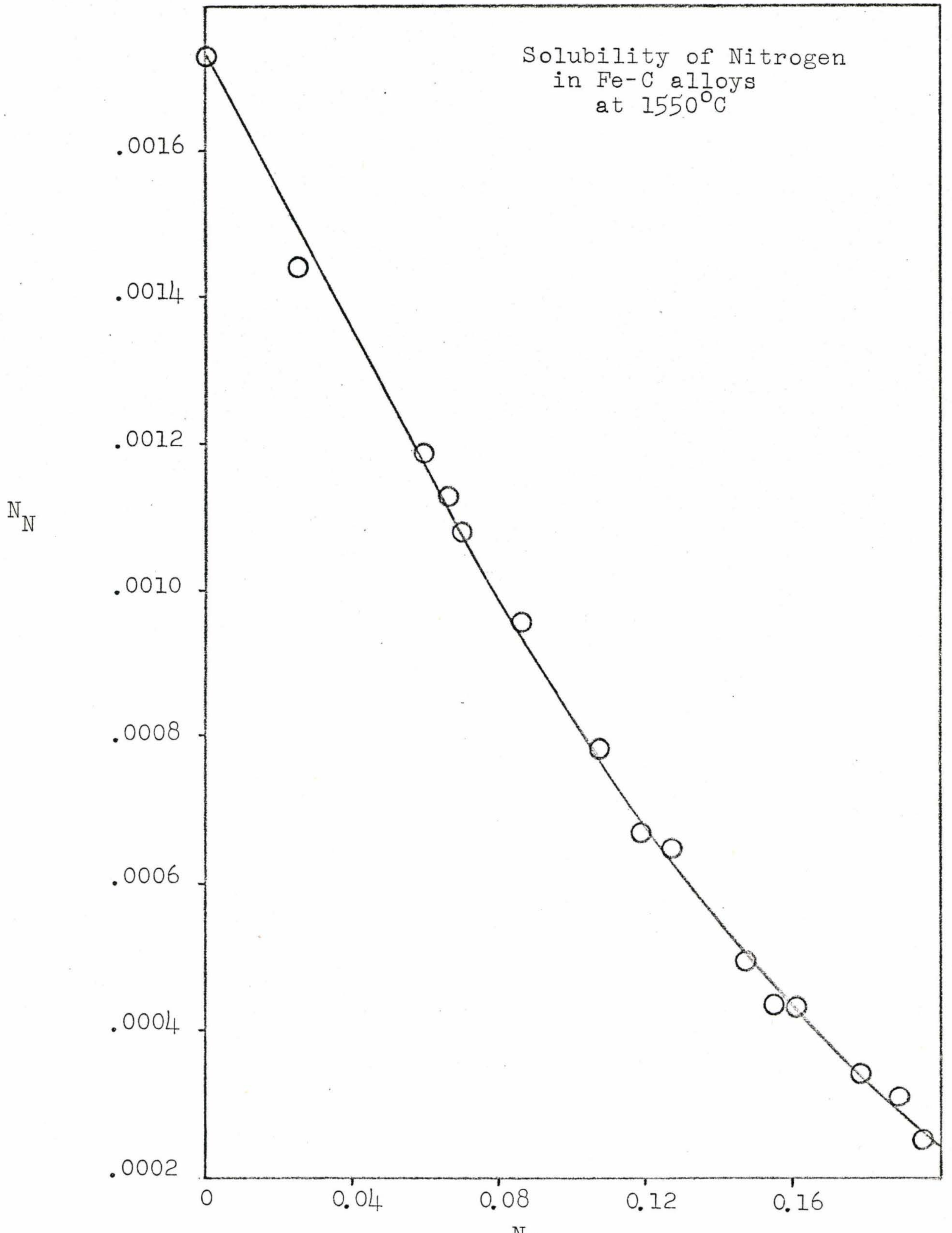

Solubility of Nitrogen
in Fe-C alloys
at 1550°C
.0016
.0014
.0012
.0010
.0008
.0006
.0004
.0002
N_N
0
0.04
0.08
0.12
0.16
N_C

Fig. 30

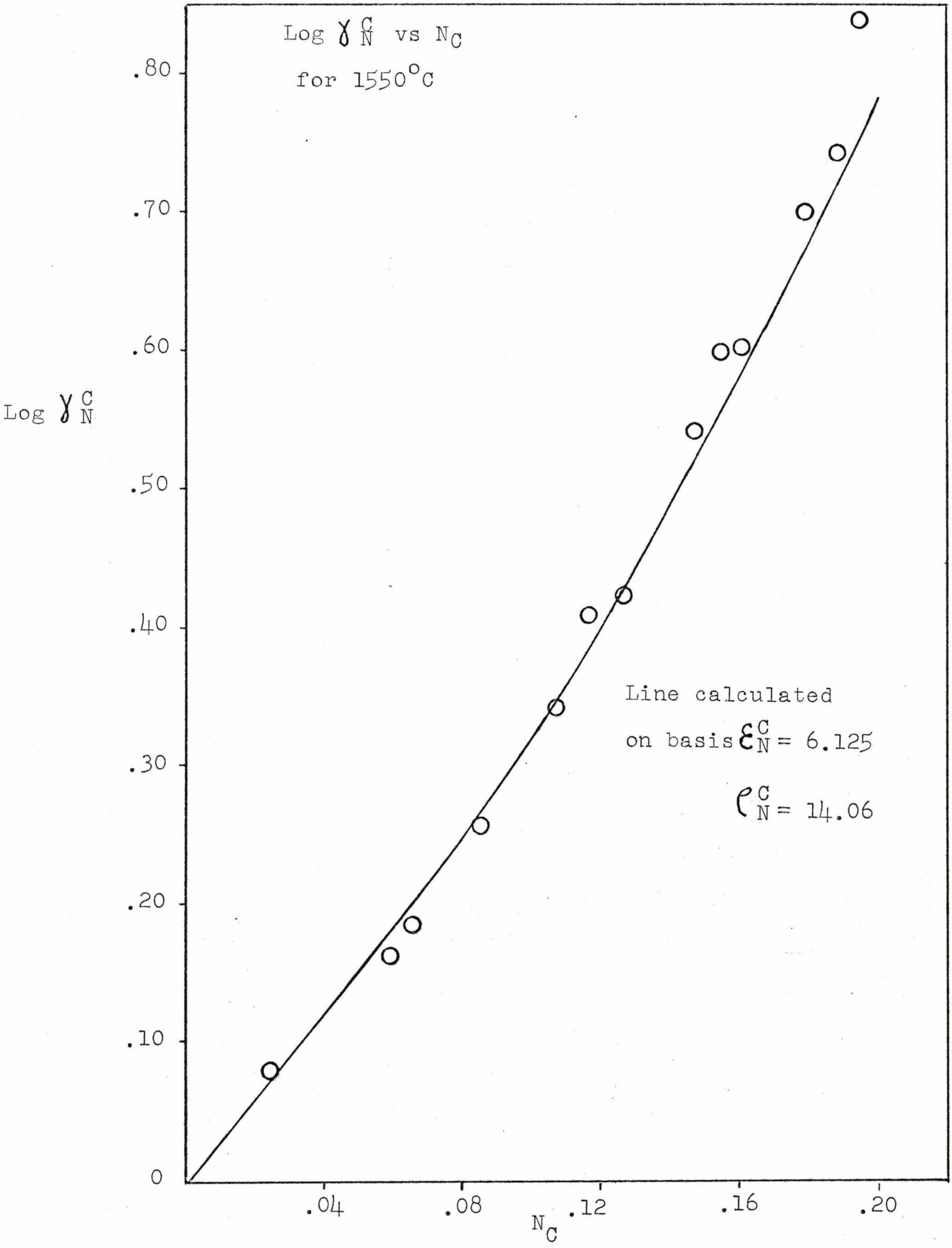
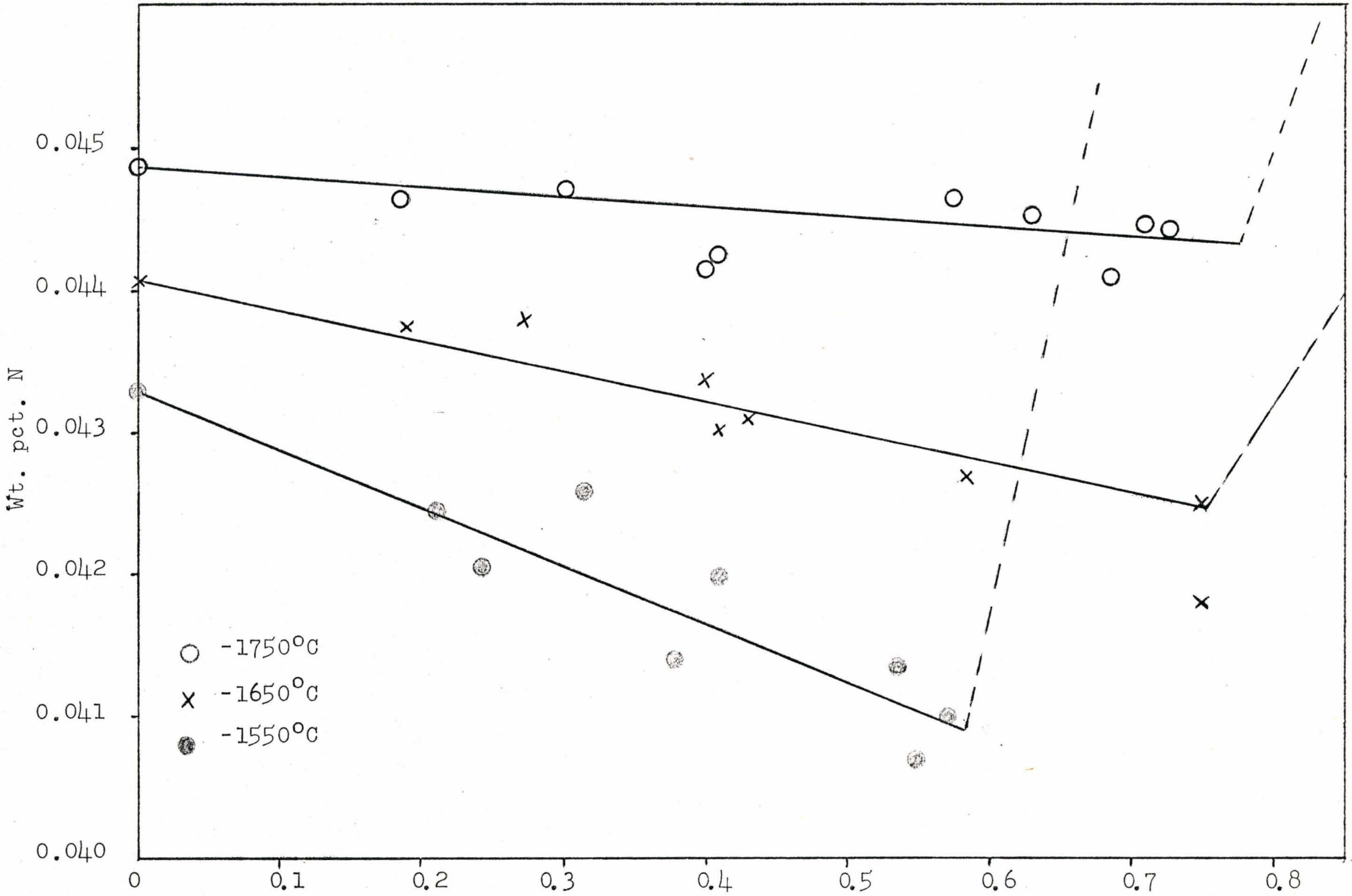

Log γ_N^C vs N_C
for 1550°C
Line calculated
on basis $\varepsilon_N^C = 6.125$
$\rho_N^C = 14.06$
Log γ_N^C
N_C
0
.10
.20
.30
.40
.50
.60
.70
.80
.04
.08
.12
.16
.20

Fig. 31

Solubility of Nitrogen in Fe-Al alloys.



Wt. pct. Al.

Fig. 32

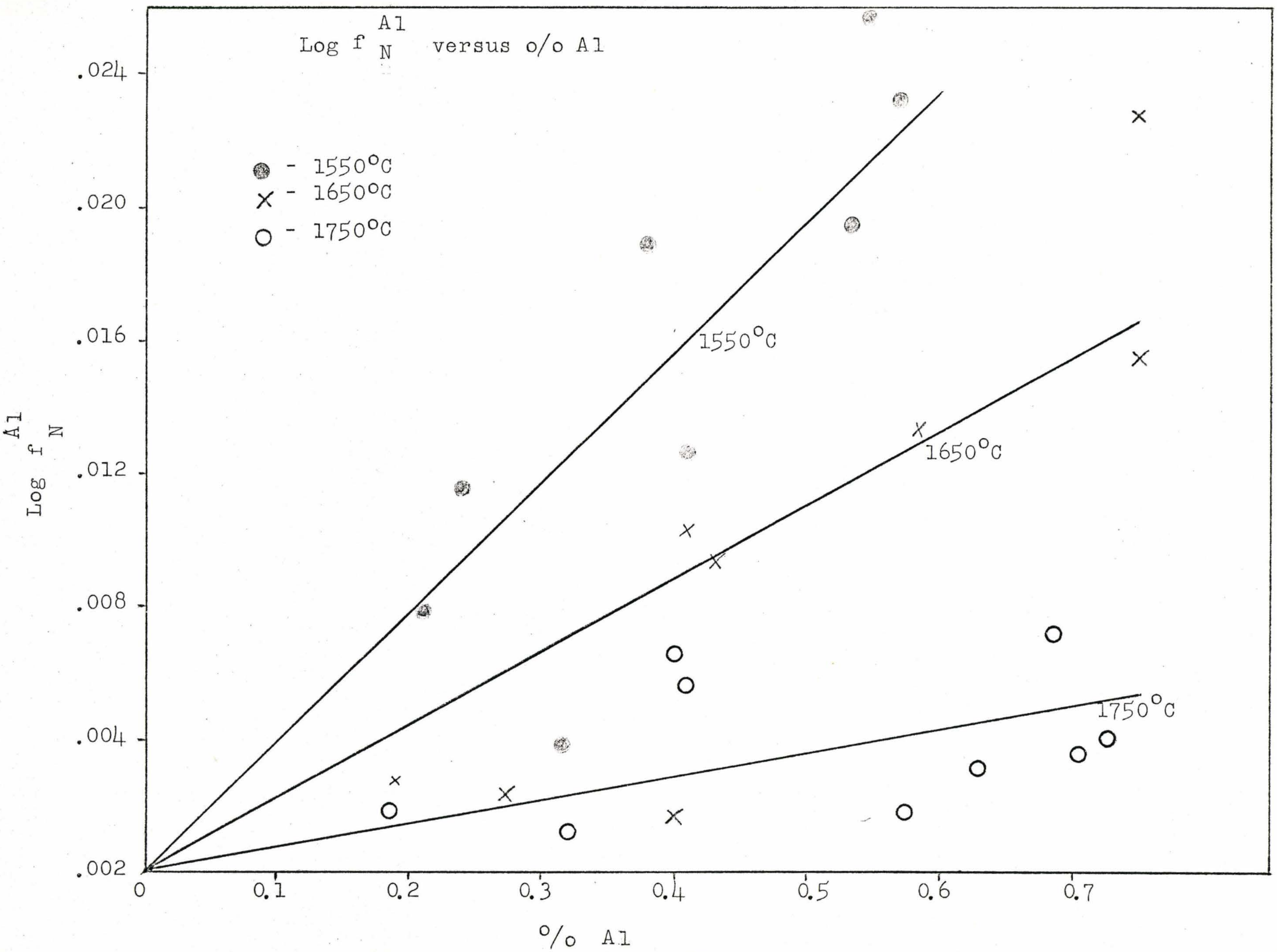

Log f_N^{Al} versus o/o Al
● - 1550°C
× - 1650°C
○ - 1750°C
1550°C
1650°C
1750°C
Log f_N^{Al}
.024
.020
.016
.012
.008
.004
.002
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
°/o Al

Fig. 33

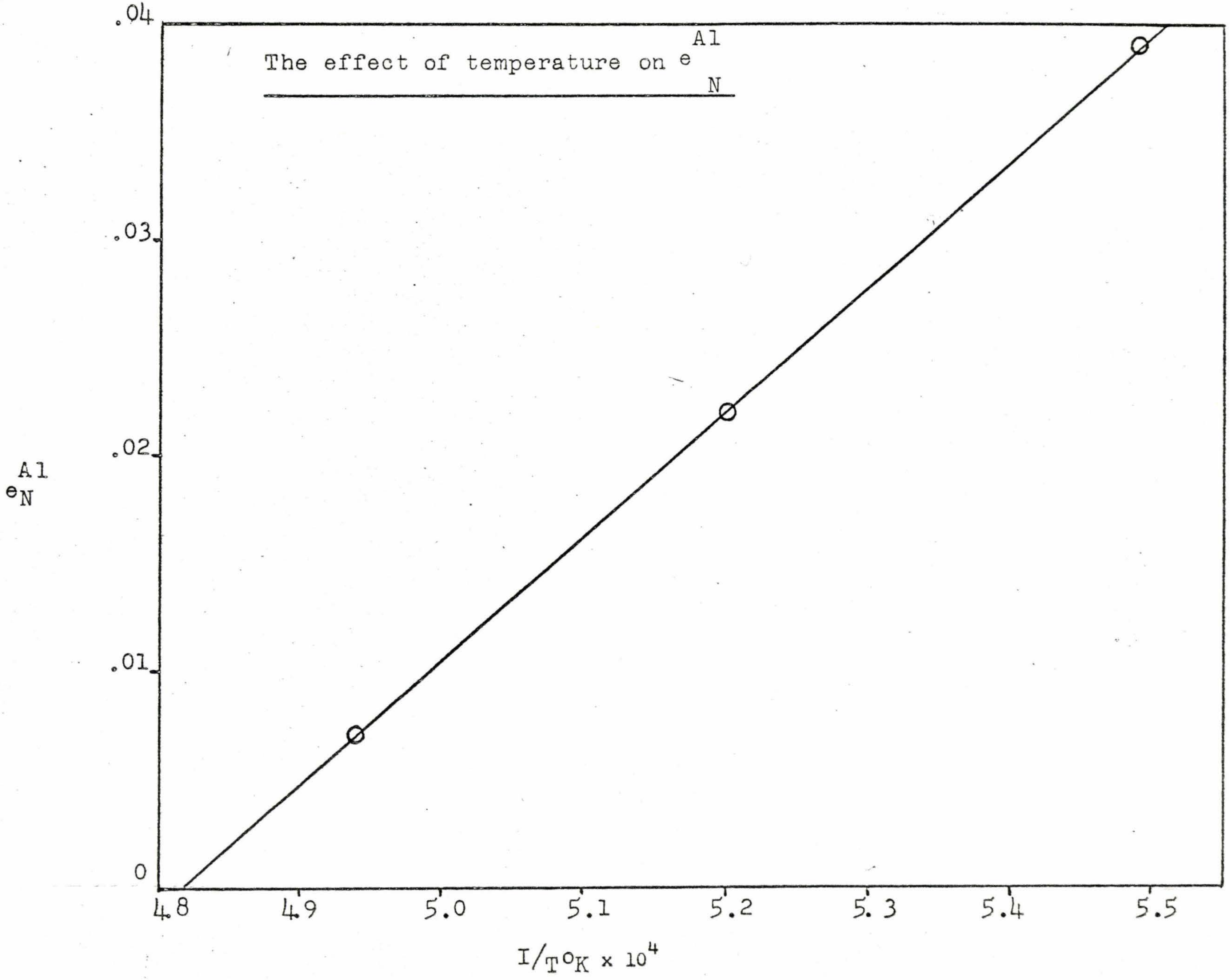
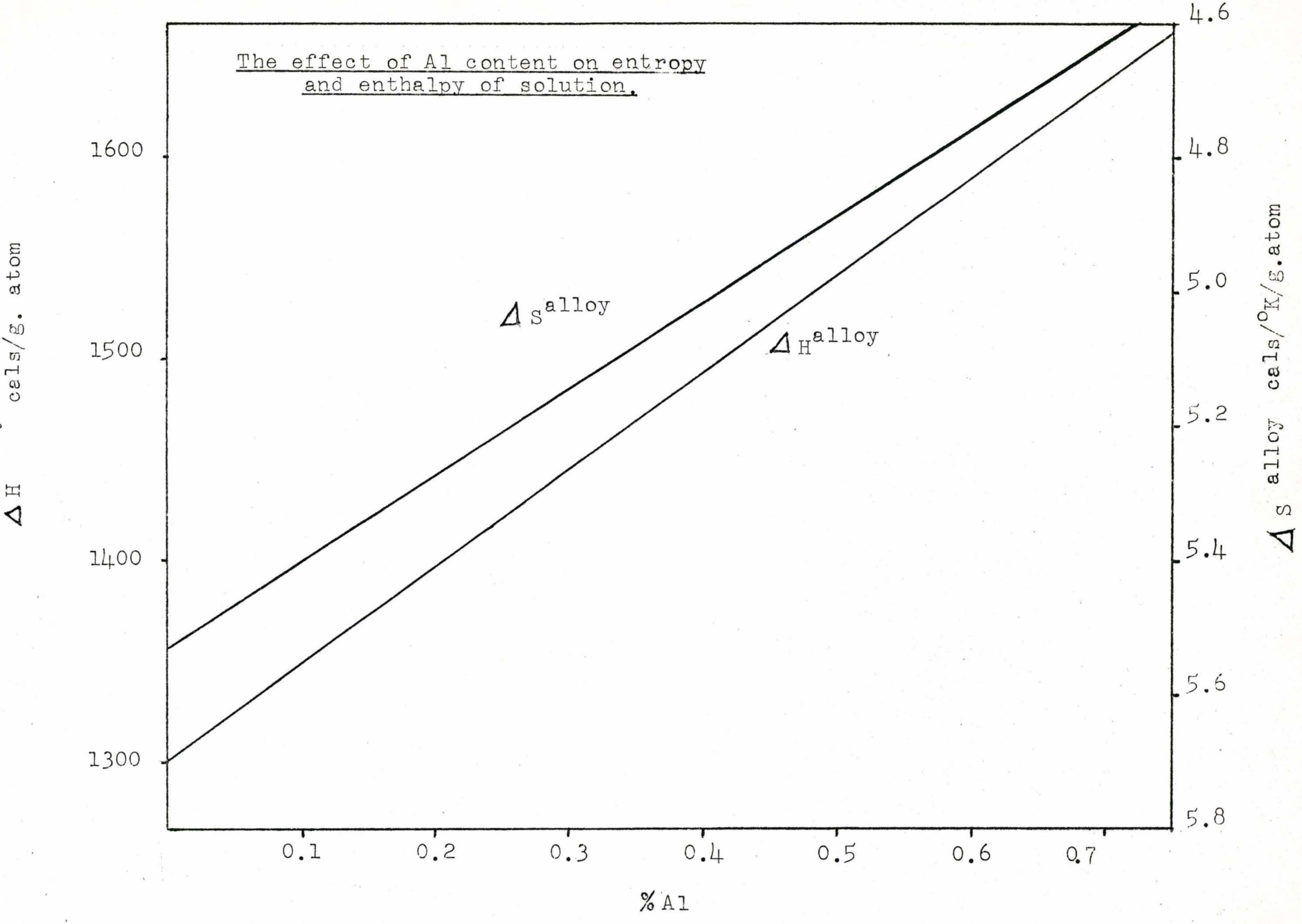

The effect of temperature on e_N^{Al}
.04
.03
.02
.01
0
e_N^{Al}
4.8
4.9
5.0
5.1
5.2
5.3
5.4
5.5
$I/T\,^oK \times 10^4$

Fig. 34



The effect of Al content on entropy and enthalpy of solution.
ΔH^{alloy} cals/g. atom
1600
1500
1400
1300
ΔS^{alloy}
ΔH^{alloy}
4.6
4.8
5.0
5.2
5.4
5.6
5.8
ΔS alloy cals/°K/g.atom
0.1
0.2
0.3
0.4
0.5
0.6
0.7
%Al

Fig. 35

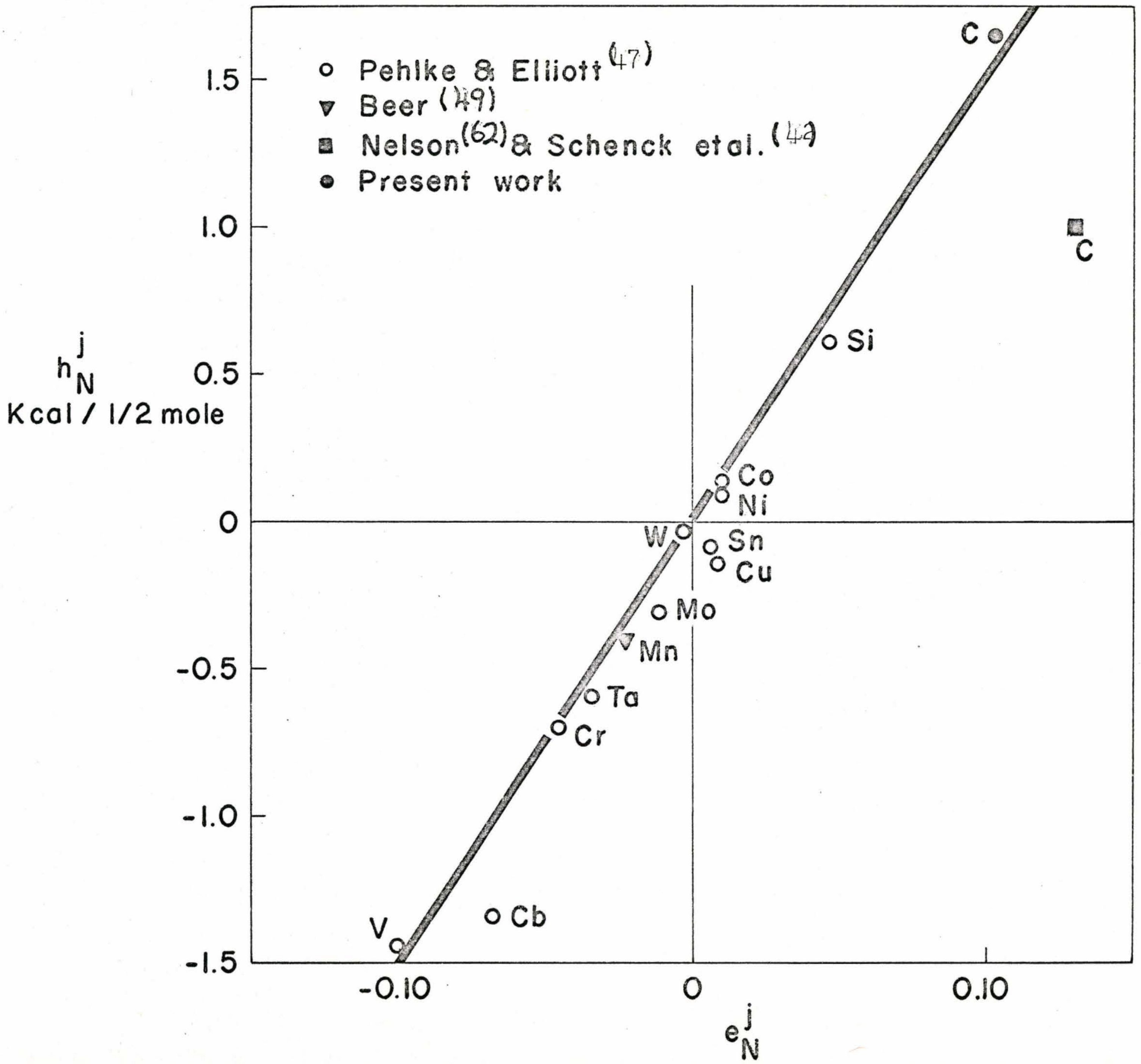

○ Pehlke & Elliott (47)
▼ Beer (49)
■ Nelson(62) & Schenck et al. (42)
● Present work
h_N^j
Kcal / 1/2 mole
1.5
1.0
0.5
0
-0.5
-1.0
-1.5
-0.10
0
0.10
e_N^j
C
C
Si
Co
Ni
W
Sn
Cu
Mo
Mn
Ta
Cr
V
Cb

Fig. 36

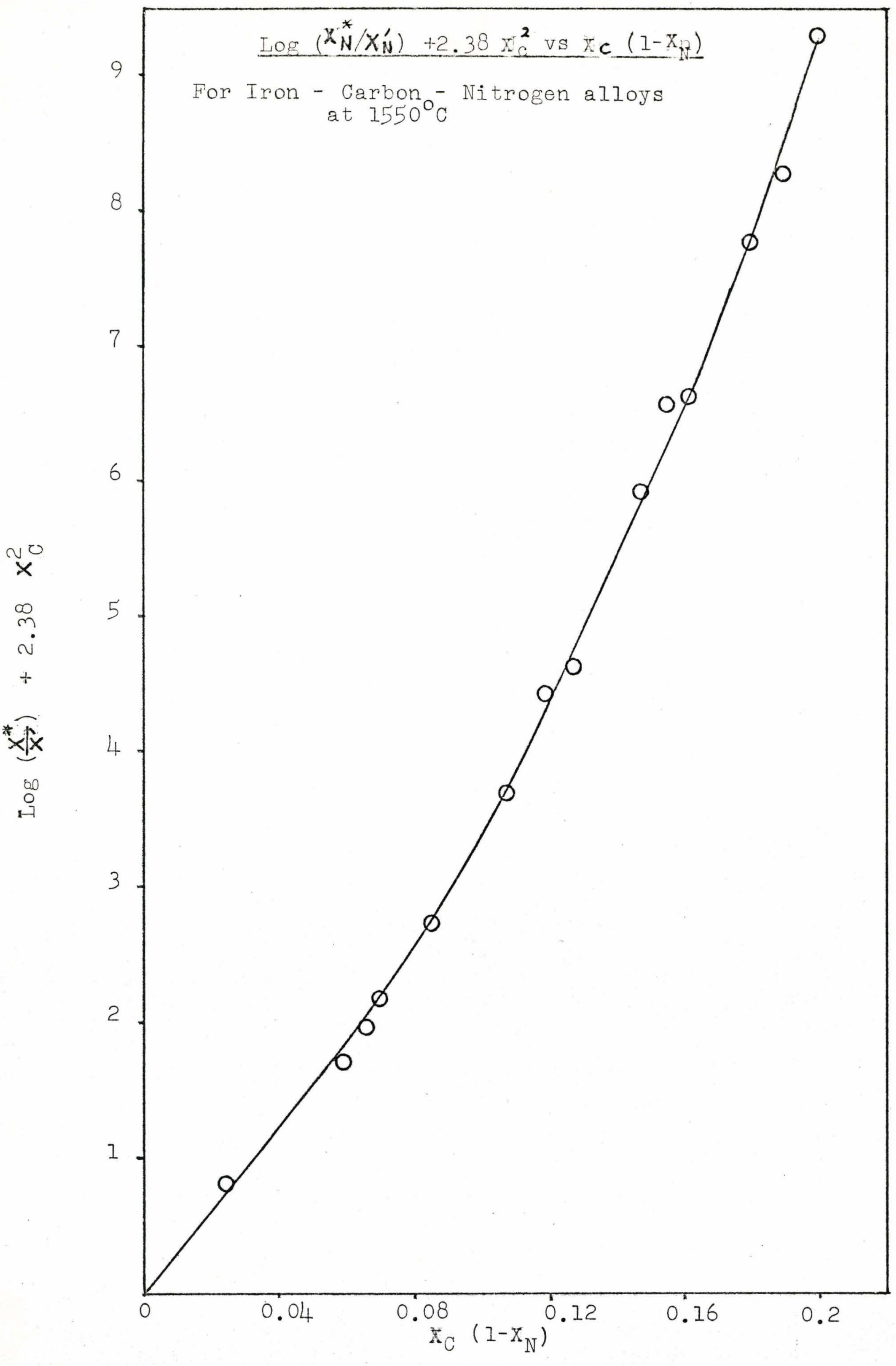

Log (X_N^*/X_N') +2.38 X_C^2 vs X_C (1-X_N)
For Iron - Carbon - Nitrogen alloys at 1550°C
Log ($\frac{X^*}{X'}$) + 2.38 X_C^2
X_C (1-X_N)
9
8
7
6
5
4
3
2
1
0
0.04
0.08
0.12
0.16
0.2

Fig. 37

Log ψ_N^C vs Z_C at 1450°C

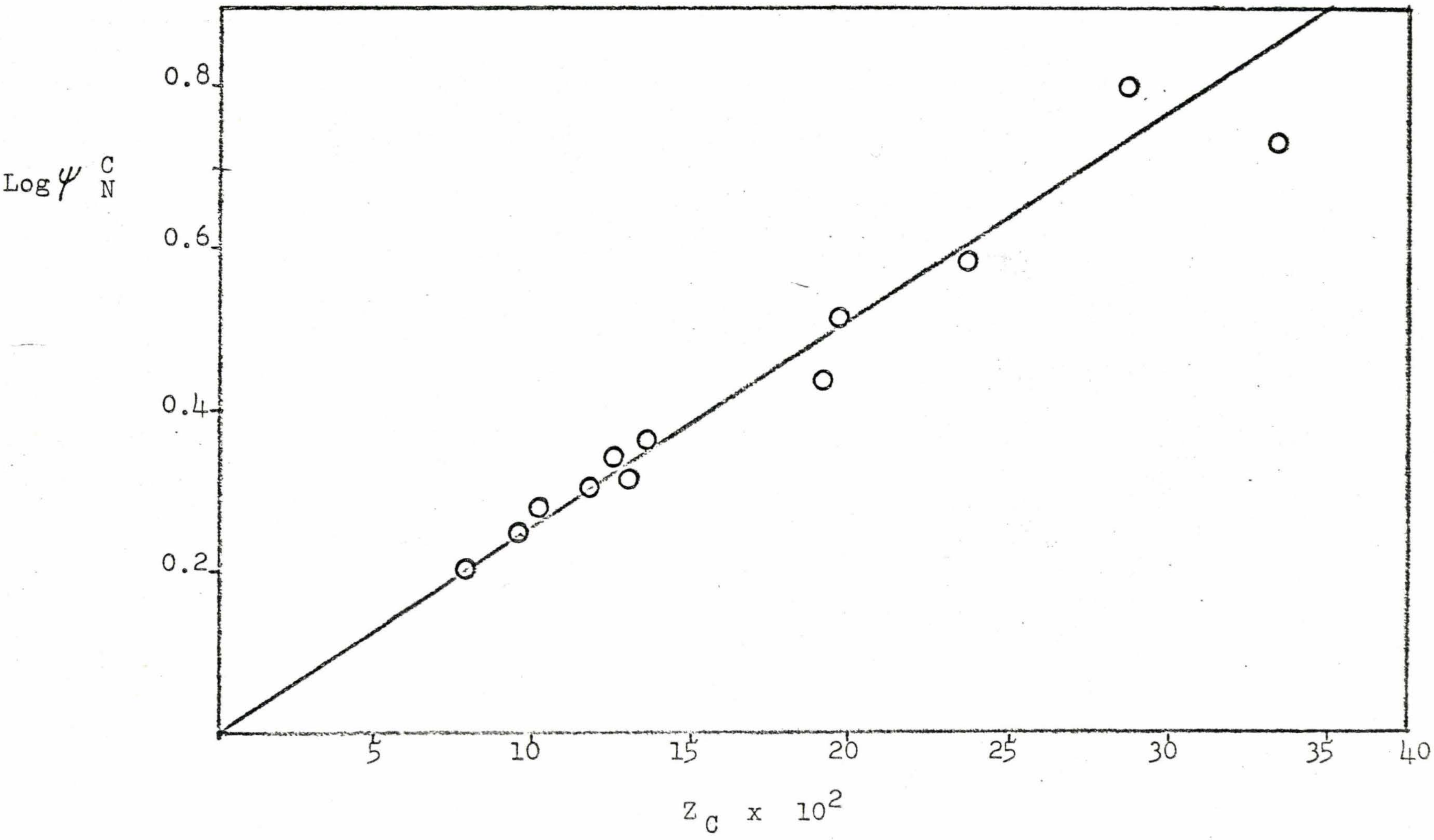


Fig. 38

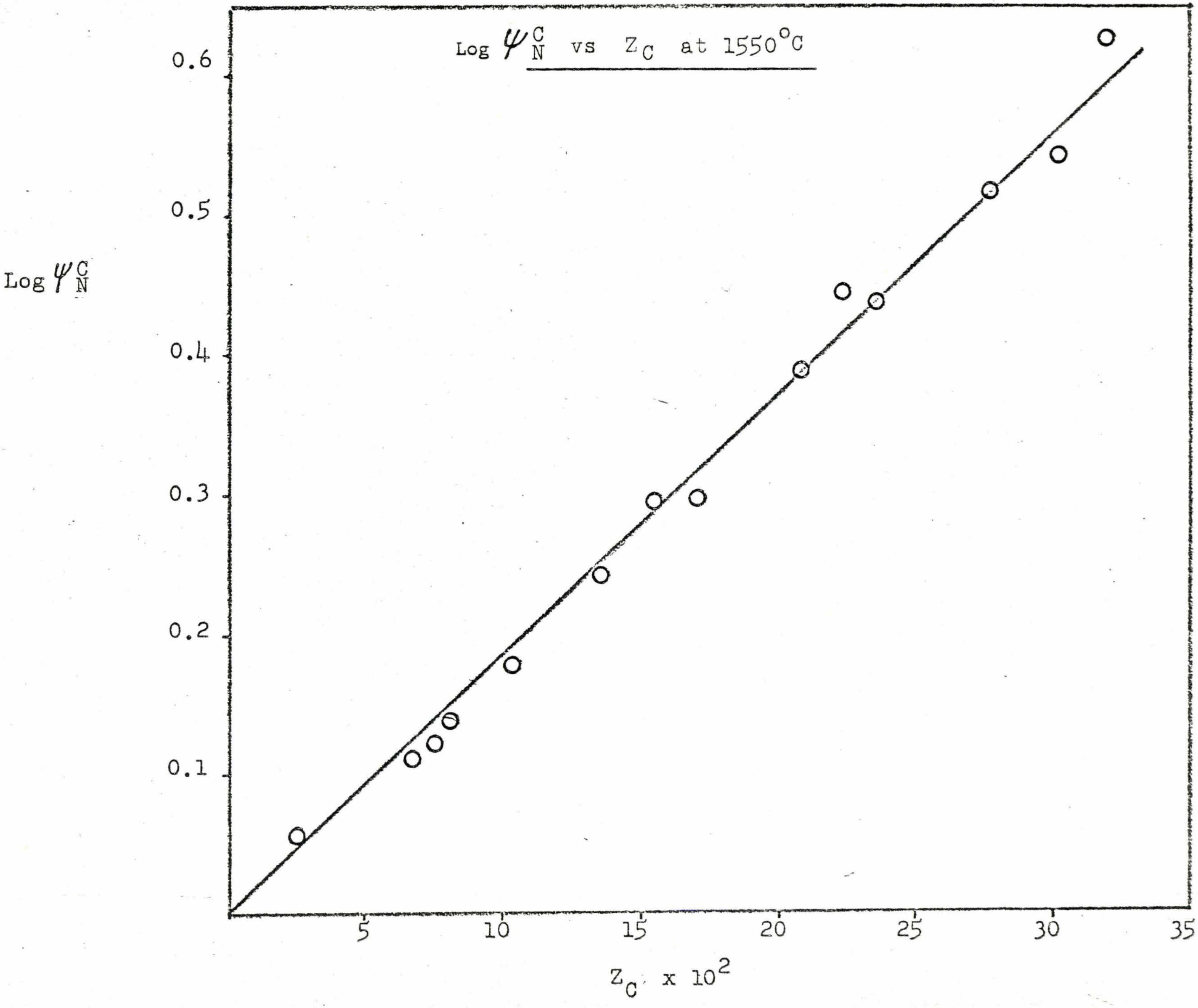

Log ψ_N^C vs Z_C at 1550°C
Log ψ_N^C
0.6
0.5
0.4
0.3
0.2
0.1
5
10
15
20
25
30
35
$Z_C \times 10^2$

Fig.

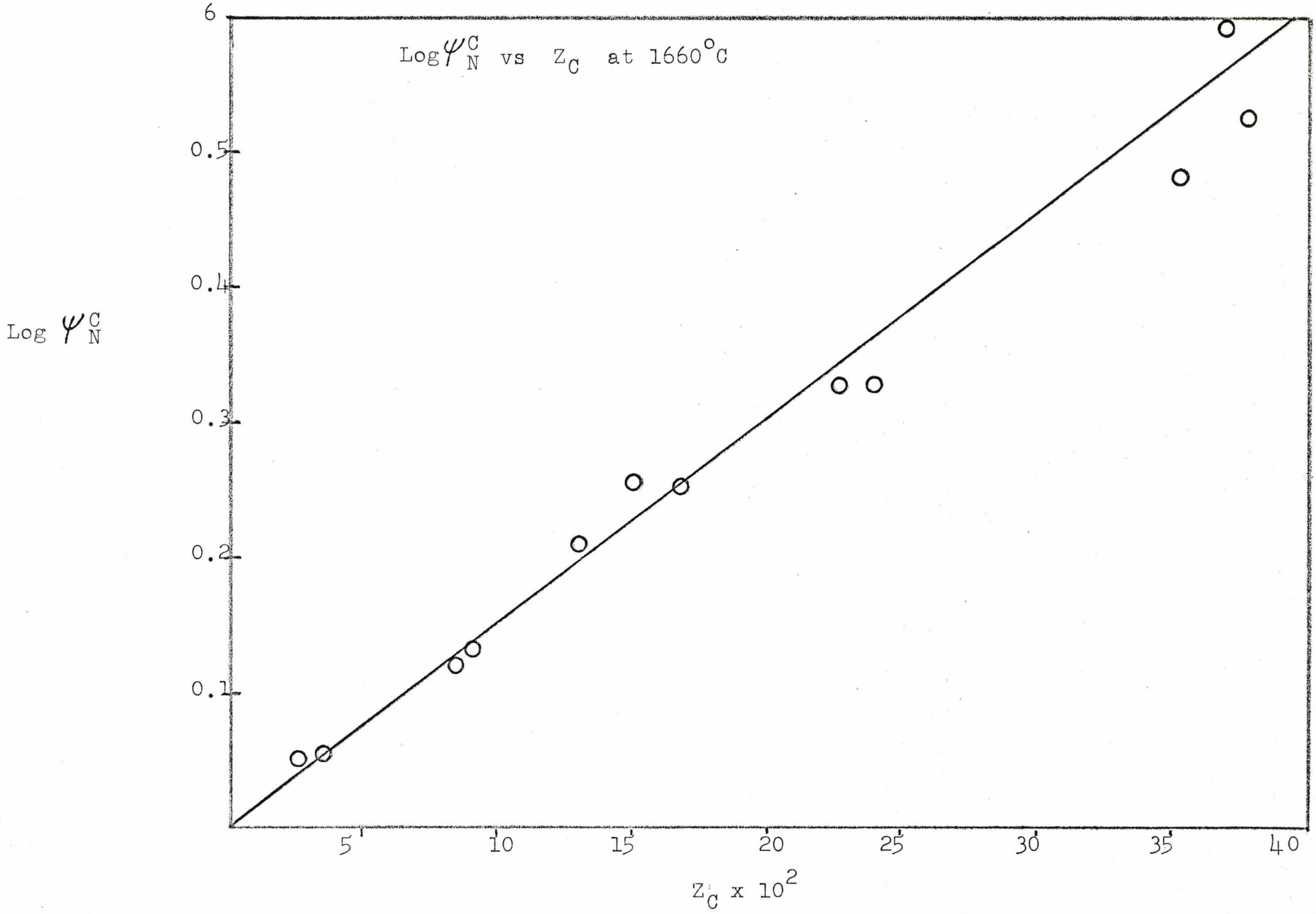

Logψ_N^C vs Z_C at 1660°C
6
0.5
0.4
0.3
0.2
0.1
Log ψ_N^C
5
10
15
20
25
30
35
40
Z_C x 10^2

Fig. 40

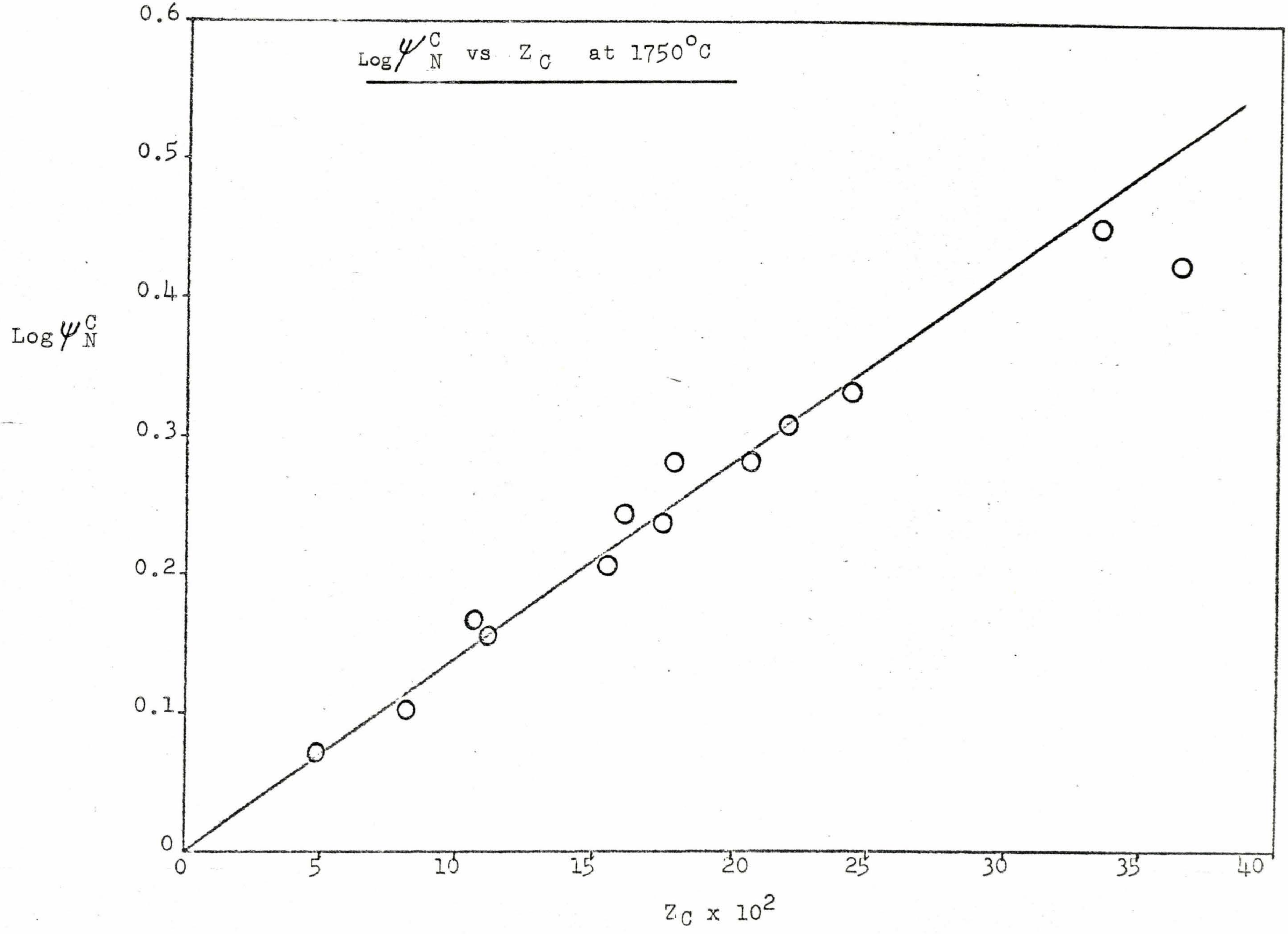

$\text{Log}\,\psi_N^C$ vs Z_C at 1750°C
0.6
0.5
0.4
0.3
0.2
0.1
0
$\text{Log}\,\psi_N^C$
0
5
10
15
20
25
30
35
40
$Z_C \times 10^2$

Fig. 41

Log Z_N vs Z_C

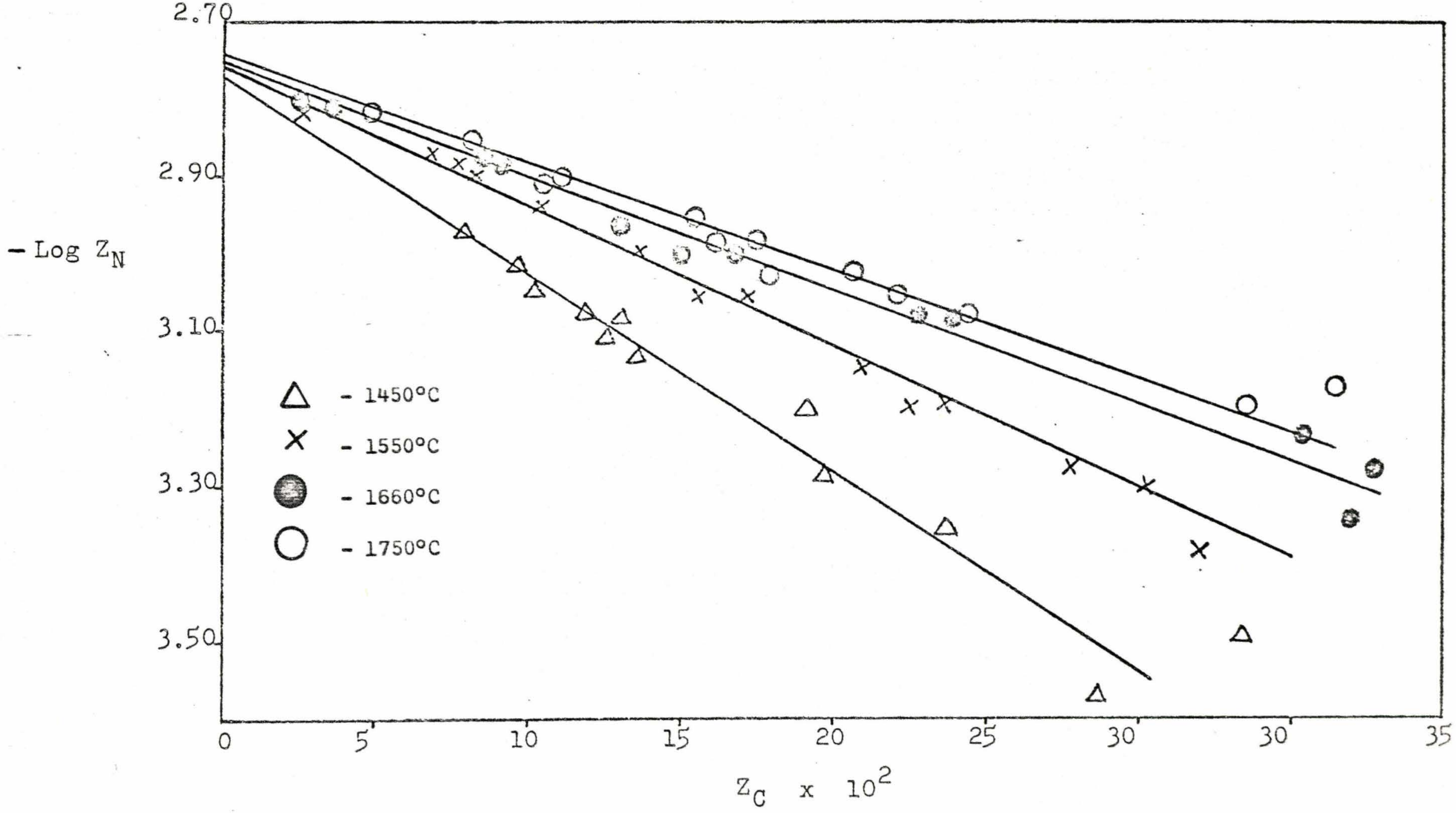


Fig. 42

TABLE I

SOLUBILITY OF NITROGEN IN LIQUID IRON

Author	Date	Press. mm Hg.	Temp. °C.	%N at 1 atm. 1600°C	Wt.% /°C×10^5	Techn.	Ref.
Chipman & Murphy	1935	735-743	1540-1760	0.040	1.5	Quenched Ingot Analysis	30
Sieverts & Zapf.	1935	760	1540	0.031 (1540)	-	Sieverts	31
Eklund	1939	760	1550-1700	0.042	1.0-2.0	Sampling	32
Vaughan & Chipman	1939	760	1600-1660	0.041	-	Sieverts	33
Brick & Creevy	1940	760	1590	0.038	-	Ingot Analysis	34
Kootz	1941	300-760	1560-1750	0.046	3.4	Sieverts	35
Karnaukhov & Morozov	1947		1550-1860	0.0521	0.2	Sieverts	36
Saito	1949	760	1550-1750	0.039	1.4	Sieverts	37
Saito	1949	760	1550-1750	0.044	-	Sampling	38
Wentrup & Reif	1949	760	1600-1700	0.046	+ve	Sampling	39
Kasamatu & Matoba	1957	30-1750	1560-1740	0.044	2.1	Sampling	40
Kashyap & Parlee	1957	50-750	1500-1900	0.042	1.5	Sieverts	41
Schenck et al	1958	100-760	1550-1650	0.044	-	Sampling	42
Fedotov & Samarin	1958	760		0.0444	8.9	Sampling	43
Maekawa & Nakagawa	1958	150-760	1550-1700	0.040	1.2	Sampling	44
Busch & Dodd	1960	760	1600	0.0395	-	Sieverts	45
Humbert & Elliott	1960	760	1500-1800	0.0438	0.77	Sieverts	46
Pehlke & Elliott	1960	76-760	1550-1730	0.0451	0.8	Sieverts	47
Fischer & Hoffmann	1960	50-500	1600	0.042		Sieverts	48
Beer	1961	152-760	1550	0.045 (1550)		Sampling	49
Dodd & Gokcen	1961	760	1550	0.040 (1550)		Sampling	50
Turnock & Pehlke	1966	760	1600-1800	0.045		Sieverts	51
Present Investigation	1967	760	1540-1800	0.0434		Levitation	

TABLE 2

Aluminium - nitrogen interaction parameters in liquid iron.

Temperature	e_N^{Al}	Reference
1600	-0.0103	(32)
1600	+0.006	(44)
1600	+0.0025	(47)
1600	-0.028	(53)
1650	-0.044	(53)
1700	-0.051	(53)
1750	-0.062	(53)

TABLE 3

Time at temperature (1550°C) Mins.	Nitrogen content Wt. pct. N
2	0.0430
4	0.0435
8	0.0433
16	0.0434

TABLE 4

SOLUBILITY OF NITROGEN IN PURE IRON

Wt. pct. N*	Temp. °C	Log (wt. pct. N)	$1/T$ °K $\times 10^4$
0.04506	1780	-1.3462	4.871
0.04482	1725	-1.3485	5.004
0.04448	1720	-1.3518	5.017
0.04457	1720	-1.3510	5.017
0.04411	1660	-1.3555	5.181
0.04385	1645	-1.3579	5.215
0.04365	1625	-1.3599	5.268
0.04381	1610	-1.3584	5.310
0.04360	1595	-1.3605	5.353
0.04351	1550	-1.3614	5.486
0.04294	1530	-1.3671	5.547
0.04328	1550	-1.3637	5.486
0.04303	1550	-1.3662	5.486
0.04340	1550	-1.3625	5.486

* The reproducibility in the analysis for nitrogen is about ± 3 ppm.

TABLE 5

SOLUBILITY OF NITROGEN IN IRON - CARBON ALLOYS
on a Wt. pct. scale

For 1750°C

% Carbon	% Nitrogen	Log f_N
0	0.04485	--
0.98	0.03579	0.09793
1.59	0.03183	0.14887
2.03	0.02720	0.21724
2.14	0.02760	0.21085
2.80	0.02348	0.28103
2.90	0.02170	0.31535
3.12	0.02146	0.32015
3.155	0.01933	0.36549
3.54	0.01890	0.37531
3.74	0.01740	0.41129
4.03	0.01618	0.44280
5.12	0.01133	0.59759
5.44	0.01187	0.57727

For 1660°C

% Carbon	% Nitrogen	Log f_N
0	0.04410	--
0.58	0.03800	0.0715
0.75	0.03686	0.0651
1.65	0.03033	0.1626
1.76	0.02927	0.1781
2.42	0.02340	0.2753
2.73	0.02080	0.3264
3.00	0.02070	0.3284
3.83	0.01640	0.4296
3.99	0.01600	0.4403
5.31	0.01030	0.6316
5.48	0.00783	0.7507
5.57	0.00920	0.6807

TABLE 5 (continued)

For 1550°C

% Carbon	% Nitrogen	Log f_N
0	0.04325	--
0.54	0.03675	0.07071
1.34	0.03120	0.1418
1.49	0.02980	0.1618
1.58	0.02860	0.17961
1.97	0.02567	0.2266
2.52	0.02150	0.3036
2.80	0.01856	0.3674
3.04	0.01810	0.3674
3.57	0.01406	0.4880
3.77	0.01238	0.49768
3.95	0.01239	0.54288
4.46	0.01003	0.63471
4.75	0.00922	0.67125
4.95	0.00742	0.76558

For 1450°C

% Carbon	% Nitrogen	Log f_N
0	0.04250	--
1.54	0.02450	0.23931
1.86	0.02150	0.29601
1.95	0.01990	0.32958
2.23	0.01850	0.36119
2.33	0.01690	0.40052
2.42	0.01770	0.38039
2.50	0.01600	0.42423
3.34	0.01280	0.52114
3.41	0.01050	0.60726
3.95	0.00850	0.69897
4.57	0.00490	0.93817
5.10	0.00567	0.87483

TABLE 6

PREVIOUS VALUES OBTAINED FOR e_N^c at 1600°C

Author	Reference	e_n^c
Pehlke & Elliott	(47)	0.25
Schenk et al	(42)	0.125
Maekawa & Nakagawa	(44)	0.135
Saito	(37, 38)	0.135
Kootz	(35)	0.13
Eklund	(32)	0.15
This Study		0.103

TABLE 7

Mole Fraction		Wt. Pct.	
Symbol	Value	Symbol	Value
ε_N^C	5.86*	e_N^C	0.103*
ρ_N^C	11.69*	r_N^C	0.007*
σ_N^C	7.2	s_N^C	0.409
π_N^C	113.3	p_N^C	0.233
η_N^C	35,270	h_N^C	1646
λ_N^C	260,000	l_N^C	504

*Values at 1600°C

TABLE 8

VARIATION OF SOLUBILITY OF NITROGEN WITH TEMPERATURE FOR FIXED LEVELS OF CARBON IN IRON

% C	% N	T °C	$^{1}/_{T}\,^{\circ}K \times 10^{4}$	-Log % N
1%	0.0300	1450°C	5.80	1.52288
	0.0335	1550	5.49	1.47496
	0.0348	1660	5.17	1.45842
	0.0354	1750	4.94	1.45100
2%	0.0201	1450	5.80	1.69680
	0.0251	1550	5.49	1.60033
	0.0270	1660	5.17	1.56864
	0.0288	1750	4.94	1.54061
2.5%	0.0166	1450	5.80	1.77989
	0.0225	1550	5.49	1.64782
	0.0235	1660	5.17	1.62893
	0.0245	1750	4.94	1.61083
3%	0.0135	1450	5.80	1.86967
	0.0178	1550	5.49	1.74958
	0.0203	1660	5.17	1.69250
	0.0215	1750	4.94	1.66756
3.5%	0.0109	1450	5.80	1.96257
	0.0147	1550	5.49	1.83121
	0.0175	1660	5.17	1.75696
	0.0187	1750	4.94	1.72700
4%	0.0084	1450	5.80	2.07572
	0.0123	1550	5.49	1.91187
	0.0151	1660	5.17	1.82102
	0.0162	1750	4.94	1.79049
4.5%	0.0062	1450	5.80	2.20761
	0.0100	1550	5.49	2.0000
	0.0129	1660	5.17	1.88941
	0.0141	1750	4.94	1.85078
5%	0.0045	1450	5.80	2.34679
	0.0078	1550	5.49	2.10237
	0.0108	1660	5.17	1.96658
	0.0122	1750	4.96	1.91364

TABLE 9

HEAT OF SOLUTION OF NITROGEN AS A FUNCTION OF CARBON CONTENT

% C	ΔH K cals	Error K cals
0	1.300	± 0.5
1	3.720	± 3.8
2	7.969	± 7.0
2.5	8.445	±12.3
3	10.605	± 8.7
3.5	12.471	± 8.7
4	15.139	±11.6
4.5	18.890	±14.9
5	22.930	±16.6

TABLE 10

ENTROPY OF SOLUTION AS A FUNCTION OF CARBON CONTENT

% C	ΔS	Error
0	-5.53	±0.03
1	-4.77	±0.08
2	-3.06	±0.15
2.5	-3.11	±0.26
3	-2.31	±0.18
3.5	-1.65	±0.19
4	-0.59	±0.25
4.5	+1.02	±0.32
5	+2.74	±0.35

TABLE 11

SOLUBILITY OF NITROGEN IN IRON - CARBON ALLOYS
ON THE MOLE FRACTION SCALE

Temperature 1750°C

Mole Fract. C	Mole Fract. N
0.000	
0.044	0.00138
0.070	0.00120
0.088	0.00101
0.092	0.00102
0.118	0.00085
0.122	0.00078
0.130	0.00077
0.132	0.00069
0.146	0.00067
0.153	0.00061
0.163	0.00056
0.201	0.00038
0.211	0.00039

Temperature 1550°C

Mole Fract. C	Mole Fract. N
0.000	0.00173
0.025	0.00144
0.059	0.00118
0.066	0.00113
0.070	0.00108
0.085	0.00095
0.107	0.00078
0.118	0.00067
0.127	0.00065
0.147	0.00050
0.154	0.00043
0.160	0.00043
0.178	0.00034
0.188	0.00031
0.195	0.00025

Temperature 1660°C

Mole Fract. C	Mole Fract. N
0.026	0.00148
0.034	0.00143
0.072	0.00114
0.077	0.00110
0.103	0.00086
0.115	0.00075
0.126	0.00074
0.156	0.00057
0.162	0.00056
0.207	0.00034
0.212	0.00026
0.215	0.00030
0.000	

Temperature 1450°C

Mole Fract. C	Mole Fract. N
0.000	
0.068	0.00092
0.081	0.00080
0.085	0.00074
0.096	0.00068
0.100	0.00062
0.103	0.00065
0.106	0.00058
0.138	0.00045
0.141	0.00037
0.160	0.00030
0.182	0.00017
0.200	0.00019

TABLE 12

THE ACTIVITY OF NITROGEN IN FE-C ALLOYS AT 1550°C ON THE HENRIAN SCALE (γ_{n}^{c})

Mole Fract. C	γ_{N}^{C}	Log γ_{N}^{C}
0.025	1.2021	0.0799
0.059	1.4546	0.1628
0.066	1.53185	0.1853
0.070	1.6013	0.2044
0.085	1.8068	0.2569
0.107	2.1994	0.3422
0.118	2.5720	0.4103
0.127	2.6589	0.4247
0.147	3.4828	0.5420
0.154	3.9793	0.5998
0.160	3.9976	0.6019
0.178	5.0173	0.7004
0.188	5.5303	0.7427
0.195	6.8964	0.8386

TABLE 13

SOLUBILITY OF NITROGEN IN LIQUID IRON - ALUMINUM ALLOYS

Temperature 1750°C

% Al	% N	Log f_N^{Al}
0.185	0.04465	0.0019
0.302	0.04470	0.0013
0.401	0.04415	0.0066
0.410	0.04425	0.0057
0.575	0.04465	0.0019
0.630	0.04452	0.0031
0.686	0.04410	0.0072
0.710	0.04447	0.0036
0.727	0.04442	0.0041
* 0.83	0.04570	

Temperature 1650°C

0.190	0.04374	0.0028
0.274	0.04380	0.0024
0.400	0.04347	0.0017
0.410	0.04302	0.0103
0.430	0.04310	0.0094
0.585	0.04269	0.0134
0.750	0.04250	0.0228
0.750	0.04180	0.0155
* 0.85	0.04392	

Temperature 1550°C

0.210	0.04245	0.0079
0.240	0.04205	0.0116
0.318	0.04259	0.0039
0.380	0.04140	0.0189
0.410	0.04200	0.0127
0.535	0.04135	0.0195
0.547	0.04070	0.0257
0.570	0.04100	0.0232
* 0.70	0.0544	

* ALN assumed to be stable

TABLE 14

Temp.	e_N^{Al}	$10^4/T°K$
1550°C	0.039	5.485
1650°C	0.022	5.200
1750°C	0.007	4.943

TABLE 15

INTERSTITIAL SOLUTIONS

Exptl. 1st order parameter	Exptl. 2nd order parameter	Predicted values for e_i^j Lupis & Elliott (23)	Interstiti Model
$\varepsilon_S^C = 6.4$	12.0	3.0	12.8
$\varepsilon_S^P = 6.0$	9.5	2.0	12.0
$\varepsilon_S^{Si} = 8.1$	21.0	7.5	16.2
$\varepsilon_N^{Si} = 5.9$	9.7	3.7	11.8
$\varepsilon_H^B = 3.1$	3.8	-1.2	6.2
$\varepsilon_H^C = 3.8$	8.0	-1.1	7.6
$\varepsilon_H^S = 1.5$	5.8	1.3	3.0
$\varepsilon_N^C = 5.86$	11.69	2.7	11.72