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THE THERMODYNAMICS AND KINETICS OF INTERSTITIAL SOLID SOLUTIONS

by

José Roberto Gonçalves da Silva

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Thesis Director's Signature:

Rex B. McElhan

Houston, Texas

April, 1976
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This work is the result of effort dispensed by many people and institutions.

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To all of you "MUITO OBRIGADO".
THE THERMODYNAMICS AND KINETICS OF
INTERSTITIAL SOLID SOLUTIONS

José Roberto Gonçalves da Silva

ABSTRACT

CHAPTER I - The Thermodynamics of the Hydrogen-Iron System

New data have been presented for the temperature variation of the hydrogen solubility in polycrystalline iron in equilibrium with \( \text{H}_2 \) gas at one atmosphere pressure. An analysis of these data and previous solubility measurements have shown a deviation from Arrhenius behavior. In the temperature range from \(-300^\circ\text{C}\) up to the \(\alpha/\gamma\) transformation temperature the solubility is largely insensitive to chemical composition and the presence of grain boundaries. The curved Arrhenius plot has been discussed in terms of several possible mechanisms including the formation of H-H-complexes, the presence of trapping sites, and the simultaneous occupation of both tetrahedral and octahedral sites in the bcc lattice by H-atoms.

CHAPTER II - The Solubility of Hydrogen in Super Pure Iron Single Crystals

An equilibrate-quench-analyze technique has been used to measure the temperature dependence of hydrogen solubility in a super pure iron single crystal. The non-linearity of the Arrhenius plot of the solubility, which had been previously found in the case of
super pure polycrystalline iron, was also determined for the single crystal.

The new data provides evidence that the non-Arrhenius behavior in the temperature range measured is not due to the trapping of H-atoms at dislocations, grain boundaries or dissolved impurity atoms.

CHAPTER III - The Thermodynamic Functions of Hydrogen in Solid Solutions of the Group V Metals Nb, Ta and V.

The large volume of available data for the isotherms characterizing the dissolution of H from H₂ gas into the Group V metals Nb, Ta, and V has been reviewed.

Both the temperature and composition variation of the partial molar and relative partial molar enthalpies and entropies have been discussed in terms of theoretical models in which the H-atoms in solution can possess degrees of translational freedom. The relative invariance of the relative partial enthalpy $\Delta H_u$ to temperature and the change in $\bar{H}_u$ with temperature are in accord with this concept.

The variation of $\bar{H}_u$ with solute composition has been used in conjunction with recent elastic data for H-Nb, H-Ta, and H-V solid solutions to discuss the form of the H-H interaction in these systems.

CHAPTER IV - Diffusion of Carbon and Nitrogen in BCC Iron

It is shown that there is a positive deviation in Arrhenius plot of $\ln D$ vs. $1/T$ both for C and N in bcc Fe. The diffusion data for C and N in bcc Fe were reviewed and it is shown that the deviation
in the case of C is approximately twice as much as that in the case of N, that agrees with the ferromagnetic model.

CHAPTER V - The Solubility of Hydrogen in \( \alpha \)-Manganese.

New data of hydrogen solubility in \( \alpha \)-manganese are presented using the equilibrate-quench-analyze technique. It shows a slight increase with decreasing temperature, and the relative partial enthalpy of hydrogen changes sign with temperature. The variation of \( R_u \) and \((S^x_S + \ln \beta)\) with temperature seems to indicate a change in the H-Mn interaction with temperature, supported by the behavior of the paramagnetic susceptibility in phase \( \alpha \).
TABLE OF CONTENTS

ABSTRACT

ACKNOWLEDGEMENTS

PROLOGUE

GENERAL INTRODUCTION

CHAPTERS

I. The Thermodynamics of the Hydrogen-Iron System .......... 1

II. The Solubility of Hydrogen in Super Pure Iron Single Crystals ................. 24

III. The Thermodynamic Functions of Hydrogen in Solid Solutions of the Group V Metals Nb, Ta and V ............. 34

IV. Diffusion of Carbon and Nitrogen in BCC Iron ............ 49

V. The Solubility of Hydrogen in α-Manganese .............. 61

APPENDIX I: Experimental-Determination of Hydrogen in Metals ................. 69
PROLOGUE

The chapters of this thesis are being published as shown:


Chapter V will be submitted for publication, and will be presented at the Materials Conference to be held at Universidade Federal de São Carlos (Brasil) from June 27/July 4, 1976.
GENERAL INTRODUCTION

This work is composed mainly of studies of hydrogen/metal systems where the hydrogen is dissolved in a solid solution.

The hydrogen in solution being considered as screened proton, moves rapidly and dissolves in large concentration ranges, permitting the study of the thermodynamics of very dilute solutions (like in iron) to very concentrate solutions (like in Pd or some intermetallic compounds).

Here, we studied in Chapters I and II the system Fe-H by exploring solubility data, with samples of very high purity. Despite previous investigations of the Fe-H systems, there was not much done on single crystals, either. Another reason was to explore previous findings of solubility dependence on purity made in this laboratory.

With variation on the gas pressure, the solute concentration can be increased up to atom ratio almost equal to one in metals like Nb, Ta, V. The isotherms taken that way permit the evaluation of the classical thermodynamic functions for the solute. This experiment was done very carefully by Veleckis and others; and their results were used in Chapter III.

Another topic of importance is the positive deviation of diffusivity vs. reciprocal temperature from a Arrhenius behavior for C and N in bcc metals. The case of bcc iron was reviewed taking into account recent data from internal friction experiments by Beshers et al. at high temperatures supporting the ferromagnetic model of Wuttig.
In Chapter V one reviewed and measured hydrogen solubility in electrolytic α-manganese that shows an anomalous behavior represented by slight increase in solubility with decreasing temperature in the temperature range 150° - 500°C, and a slight decrease in the range 500° - 680°C, acting both as an endothermic and an exothermic occluder of hydrogen.
CHAPTER I
THE THERMODYNAMICS OF THE HYDROGEN-IRON SYSTEM

Introduction

The iron-hydrogen system is of basic importance both from the viewpoint of the thermodynamics and kinetics of interstitial solid solutions and because of the often drastic effect of hydrogen on the chemical and mechanical properties of ferrous engineering materials. In spite of the large extent of research effort centering on the thermodynamic and kinetic behavior of hydrogen in iron, a large degree of uncertainty and confusion remains. The object of the present investigation is to present new data for the temperature variation of the solubility of hydrogen in iron in equilibrium with H₂ gas at atmospheric pressure, measured using polycrystalline sample, and to analyze these data together with previous data in the light of theoretical models for the iron-hydrogen solid solution.

A considerable degree of confusion arises because the solubility data for well-annealed iron exhibit, by and large, a considerable degree of mutual conformity but the plot of lnθ vs. 1/T for bcc iron, where θ is the atomic ratio of hydrogen dissolved, is not linear. This can be seen clearly in Fig. (1) in which lnθ vs. 1/T is plotted from the results of the present investigation and older data.

The degree of confusion increases on considering the diffusivity of H in Fe. The variation of the diffusion coefficient D with temperature has recently been reviewed by Völkl and Alefeld (1). In the
FIGURE 1. Plot of the hydrogen solubility in iron as a function of temperature.
temperature region from the \(\alpha/\gamma\) transformation down to \(-300^\circ C\) the data show scatter of about one order of magnitude. Below this temperature the degree of scatter becomes incredibly large and the reported data at \(-25^\circ C\) span a range of more than 4 orders of magnitude. Several investigators have ascribed this anomalous diffusion behavior to the presence of trapping sites in the metal. If this mechanism is effective, the question of the effect of presence of such sites on the thermodynamic properties of the system naturally arises. The relationship between trapping sites, measured permeability and diffusion data derived therefrom is also a cardinal question.

**Solubility Measurements**

The solubility measurements were made by the equilibrate-quench-analyze technique using an apparatus described in Appendix I and in previous reports \{2\}, \{3\}. The iron samples in the form of cylinders were equilibrated in a stream of super pure hydrogen gas (nominal purity 99.9995 vol. % and less than 1 ppm by volume of hydrocarbons).

After equilibration the samples were quenched and their hydrogen contents measured using a hot extraction technique \{2\}, \{3\}. The known data for the diffusivity of H in Fe \{1\} were used to ensure that at all temperatures the samples were equilibrated for sufficient time to ensure saturation with hydrogen. The solubility data are given in Table 1 and depicted graphically in the form of plots of \(\ln \theta\) vs. \(1/T\) in Fig. (1). The available older data are also indicated in this plot to the extent that actual solubility data, and not just representative equations or graphical
# Table 1

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>ø x 10^4</th>
<th>ø x T^{7/4}</th>
</tr>
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<tr>
<td>400</td>
<td>0.217</td>
<td>1.93</td>
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<tr>
<td>450</td>
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<tr>
<td>500</td>
<td>0.309</td>
<td>3.50</td>
</tr>
<tr>
<td>550</td>
<td>0.414</td>
<td>5.24</td>
</tr>
<tr>
<td>600</td>
<td>0.475</td>
<td>6.66</td>
</tr>
<tr>
<td>630</td>
<td>0.559</td>
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</tr>
<tr>
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<tr>
<td>830</td>
<td>1.620</td>
<td>34.28</td>
</tr>
<tr>
<td>850</td>
<td>0.953</td>
<td>20.75</td>
</tr>
<tr>
<td>860</td>
<td>0.995</td>
<td>22.03</td>
</tr>
<tr>
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<td>44.47</td>
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<tr>
<td>1030</td>
<td>2.130</td>
<td>60.19</td>
</tr>
</tbody>
</table>
illustrations, are available. The data points from each separate investigation are marked with a different symbol and the corresponding number gives the reference to the original paper \{4-8, 23\}.

It can be seen that there is good general accord between the present data and the previous measurements. The current data for $\gamma$-iron are slightly lower than most of the previously measured solubilities.

It can also be seen that the data for the $\alpha$-field deviate slightly from linearity. This positive deviation from Arrhenius behavior is small and most noticeable at low temperatures.

It has been the normal practice to represent the solubility data by constraining the $\ln \Theta$ vs. $1/T$ plot to be linear. In view of the small degree of curvature, the data can be represented by such a scheme in the temperature range $-400^\circ$C up to the $\alpha$-$\gamma$ transition. Such an equation has been given by Oriani \{9\}. The solubility in the $\delta$-region obtained by extrapolating this relation is however almost twice as small as the measured solubility. This is illustrated in Fig. (1) by the dashed line.

Discussion
a) Degree of Purity

For many of the older determinations, little indication of the purity grade of the iron was given. However, the available information is contained in Table (2). The impurity contents are given in ppm and the symbols used at the left-hand side of the table correspond to those
<table>
<thead>
<tr>
<th>Impurity element</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>S</th>
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<th>Mn</th>
<th>Sn</th>
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<th>Cu</th>
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<th>Si</th>
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<td>&lt;10</td>
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<td>-</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>3.5</td>
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<td>Luckemeyer-Hasse and Schenck</td>
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<td>-</td>
<td>-</td>
<td>2.7x10⁴</td>
<td>3x10⁴</td>
<td>-</td>
<td>2x10⁴</td>
<td>-</td>
<td>4x10⁴</td>
<td>-</td>
<td>10⁴</td>
<td>10⁴</td>
<td></td>
</tr>
<tr>
<td>Sieverts, Zapf, and Moritz</td>
<td>3x10⁴</td>
<td>-</td>
<td>-</td>
<td>2x10⁴</td>
<td>2x10⁴</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5x10³</td>
<td>3x10³</td>
<td></td>
</tr>
<tr>
<td>Martin</td>
<td>7x10³</td>
<td>2x10³</td>
<td>-</td>
<td>1.8x10³</td>
<td>8x10³</td>
<td>-</td>
<td>-</td>
<td>7.5x10³</td>
<td>-</td>
<td>6x10²</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Armbruster</td>
<td>10⁴</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Contents are given in ppm
- = analysis not available
used in Fig. (1). It can be seen that in many instances the irons used were very impure. The single crystal used in [23] was relatively free of interstitial impurities but contained quite high levels of substitutional impurity elements. In recent work by Louthan et. al. [10] the solubility of deuterium and tritium were measured in zone-refined iron single crystals of MARZ-grade purity. The data are in reasonable accord with those of Fig. (1). Since these measurements were made at much lower temperatures than the other data, they have been illustrated in Fig. (2), which shows the data of Louthan et. al. using the symbols ○ (deuterium) and □ (tritium). The lowest solubilities were measured at -150°C but these were not included because of the large uncertainty in the diffusivity at this temperature and the concomitant question as to the achievement of equilibrium. Some of the samples used were cold-worked and then annealed. The different treatments are indicated by the modified symbols (see caption to Fig. (2)). The open circles in Fig. (2) refer to all the other data points of hydrogen solubility from other investigators.

It is clear that in the temperature range from the α/γ transformation down to -350°C, the purity of the iron does not play a significant role in affecting the hydrogen solubility of iron. If impurity atoms act as trapping sites for H-atoms it is not observed in the solubility above 350°C.

b) Effect of Grain Size

It can be assumed that the average grain size of the irons used in the data collection represented by Fig. (1) differed from sample
FIGURE 2. Plot of the solubility of H, D and T in bcc iron as a function of temperature. The data of the previous investigations as in Fig. (1) are represented by open circles. The low temperature data of Louthan et al. are included and the symbols have the following meanings:

- deuterium
- tritium
- single crystal
- polycrystalline (cold-worked and annealed)
- 90% cold-worked
- cold-worked and annealed at 800°C
- 90% cold-worked
- annealed at 800°C
- annealed at 300°C
to sample. Furthermore it is clear from the present investigation and that of Louthan et. al. (10) that the solubility data obtained using single crystal and polycrystalline samples are in good mutual accord.

It seems to be clear that the presence and extent of grain boundaries has little influence on the H-solubility in iron at least above 400°C. This behavior is in contrast to that of Ni where the plot of lnθ vs. 1/T obtained using polycrystalline samples shows much more positive curvature at low temperatures than that exhibited by the solubilities obtained using Ni single crystals (11).

In the case of the H-Ni system plots of lnθ vs. 1/T for polycrystalline samples are much more distinctly curved than the corresponding plot in Fig. (1) and part of the curvature in the H-Ni-solubility plot has been ascribed to the presence of extra low-energy sites for H-atoms associated with grain boundaries. It is clear from Fig. (1) that in the temperature range considered this does not happen in the H-Fe system. However, there is no reason to expect a plot of lnθ vs. 1/T, spanning large ranges of temperature, to be linear anyway, especially when data at low temperatures are involved.

The solubility of H in a metal with respect to H₂ gas at a pressure P can be expressed in two ways. In one representation

\[ \theta = \beta \exp \left( -\frac{\Delta H_u}{kT} \right) \exp \left( \frac{\Delta S_{uS}}{k} \right) \]  

\[...........................(1)\]
where \( \Delta R_u = \bar{R}_u - \frac{1}{2} \bar{H}_u^{0} \), and \( \Delta S_u^{xs} = S_u^{xs} - \frac{1}{2} \bar{S}_u^{0} \) are the relative partial molar enthalpies and excess entropies of dissolved hydrogen. In the other representation the standard state thermodynamic functions of the \( H_2 \) gas are written explicitly, resulting in the solubility equation (12),

\[
\theta = \frac{\beta p^{\frac{1}{2}} \lambda}{T^7/4} \exp \left( - \frac{\bar{H}_u - \frac{1}{2} E_D^{0}}{kT} \right) \exp \left( \frac{S_u^{xs}}{k} \right) \]

where \( \lambda \) is a known constant \{12\} and \( E_D^{0} \) is the dissociation energy of the \( H_2 \) molecule at 0K. The partial molar enthalpy \( R_u \) in these equations is measured with respect to a temperature-independent reference state (that of an \( H \) atom at rest in a vacuum). In deriving these equations it is assumed that the dilute solution is quasi-regular and that the \( H \)-atoms are randomly distributed in the interstitial sites having the occupation number \( \beta \), defined as the number of such sites per metal atom. Although \( R_u \) can be extracted from the data without knowledge of \( \beta \), this positional information is obviously required to obtain the excess entropy. In this work it has been assumed that the \( H \)-atom occupies the tetrahedral site in bcc iron so that \( \beta = 6 \). This choice is in accord with general indications for site occupancy but it is by no means certain. Indeed for \( H \) in bcc Cr, Picrauz and Vook \{13\} have determined that \( H \) occupies the octahedral sites by ion channeling measurements.
Now it is clear from equ. (1) that, since $H_{H_2}^{O}$ and $S_{H_2}^{O}$ both vary with temperature, especially at low temperatures, plots of $\ln \theta$ vs. $1/T$ spanning low temperature data regions will not in general be linear unless $A_u$ and $S_{u}^{xs}$ exhibit a temperature dependence such that the relative quantities $\Delta A_u$ and $\Delta S_{u}^{xs}$ are virtually constant. Such behavior is not generally to be expected however. Both $H_{H_2}^{O}$ and $S_{H_2}^{O}$ increase with increasing temperature. Now $A_u$ can be split into a part $A_{u}^{OS}$ arising from the vibrational energy of the dissolved H-atom and $A_{u}^{M}$ arising from the interaction between the H atom and the matrix. If the vibrations of the dissolved H atom are approximately harmonic, $A_{u}^{OS}$ is given as

$$\bar{A}_{u}^{OS} = 3kT \psi \left\{ 1 + (e^{\psi} - 1)^{-1} \right\} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots (3)$$

and the corresponding entropy is,

$$\bar{S}_{u}^{OS} = 3k \left\{ \psi (e^{\psi} - 1)^{-1} - \ln(1 - e^{-\psi}) \right\} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots (4)$$

where $\psi = h\nu/kT$ and $\nu$ is the frequency of the H atom. With reasonable values of $\nu$ ($1-2 \times 10^{13}$ sec$^{-1}$), both $A_{u}^{OS}$ and $S_{u}^{OS}$ increase with temperature in approximately the same way as $H_{H_2}^{O}$ and $S_{H_2}^{O}$. However $A_{u}^{M}$ almost certainly decreases with increasing temperature. Despite the details of the H-metal atom electronic interaction, there will be a contribution to $A_{u}^{M}$ arising from the elastic distortion of the matrix. The partial
molar volume of H in bcc iron is surprisingly large (2.0 cc/s/mol. H \{14\}). Classical elasticity calculations indicate that the distortional energy is proportional to the shear modulus of the matrix which is a decreasing function of temperature.

Thus the approach taken is to use equ. (2) to analyze the data. It is worthwhile pointing out that the temperature variation of $S_{u}^{xS}$ and $\bar{R}_{u}$ cannot be obtained from isobaric measurements of solubility as a function of temperature. For this purpose it is necessary to measure several P-θ isotherms so as to obtain the chemical potential $\mu_{u}$ of the dissolved H as a function of temperature at a fixed composition.

Accordingly a plot of $\ln θT^{7/4}$ vs. $1/T$ has been made and is depicted in Fig. (3). It can be seen that the curvature is more pronounced than in Fig. (1). It should also be noted that taking cognizance of the curvature in Fig. (1) and Fig. (3) brings the data points from the α and δ-iron regions into coincidence. The corresponding curve containing the data of Louthan et. al. is shown in Fig. (4).

A least-squares fitting routine was used to fit the data for the α-region to both modes of representation. It was found that,

$$\ln \theta = 4.3300 - 0.5204 \times + 0.0079 \times^2$$ \hspace{1cm} (5)

and $\ln(\theta T^{7/4}) = 9.5249 - 0.8095 \times + 0.0137 \times^2$ \hspace{1cm} (6)

where $x = 10^4/T$.

This curvature in the plot of $\ln \theta T^{7/4}$ has several possible origins. Aside from the question of an intrinsic dependence of $\bar{R}_{u}$ and $S_{u}^{V}$ on
temperature there are three obvious sources which may give rise to such an effect. One is the presence of "trapping" sites, another is the dual occupancy of interstitial sites by lattice atoms, and a third possibility is the formation of H-atom clusters. These three effects will be considered individually.

c) **Complex Formation**

Rosales and Ono \(^{15}\) attempted to account for the low temperature anomaly in the diffusivity of H in \(\alpha\)-iron by supposing that H-H di-interstitials associated with a binding energy of \(-10\) k.cals/mole are formed. These are relatively immobile and would lead to the drastic reduction in \(D\) observed at low temperatures \(^{1}\). Rosales and Ono calculated that the presence of such H-H pairs would give rise to a slight curvature of the plot of \(\ln \theta\) vs. \(1/T\) of about the extent observed experimentally.

This model has however been criticized by Oriani \(^{9}\) who has pointed out that the di-interstitial formation would be an intrinsic property of the thermodynamic state of the H atoms in solid solution and the huge range of \(D\)-values \((10^{-4} \text{ to } 5 \times 10^{-9})\) recorded at \(25^\circ\text{C}\) is difficult to explain from such a concept.

Complex formation with H in iron and other interstitial atoms (C, N and O) has been detected by magnetic disaccommodation measurements \(^{16}\) \(^{17}\) but the binding energies involved are all much lower than \(10\) k.cal/mole and the trapping effects are observed only below -200\(^\circ\text{K}\).

Furthermore one may be sure that the formation of di-interstitials
FIGURE 3. Plot of $\ln\theta^{7/4}$ vs. $1/T$ for hydrogen in iron.
FIGURE 4. Plot of $\ln nT^{7/4}$ vs. $1/T$ for H, D, and T in bcc iron.
is not responsible for the curvature in the plot \( \ln \sigma T^{7/4} \) vs. \( 1/T \) in the case of Ni since the data for Ni single crystals yield a corresponding plot which is linear (11).

d) **Dual Site Occupancy**

The H-atoms dissolved in bcc iron have both octahedral (O) and tetrahedral (T) sites available to them. If one kind of site is energetically more favorable for occupation, this site will be preponderantly occupied at low temperatures. However at high temperatures where the TS-term in the free energy begins to dominate the thermodynamic behavior of the system, alternative sites will be simultaneously occupied on account of the large increase in entropy ensuing from the dual occupancy. The thermodynamic properties of such solutions, where the total solute concentration is small, have been discussed previously (18).

If the total number of solute atoms is \( N_u \), \( N_u^O \) atoms must be distributed in the octahedral (O) sites, and \( N_u^T \) in the tetrahedral (T) sites such that,

\[
N_u = N_u^T + N_u^O
\]

The distribution at any given temperature \( T \) is given by (18).

\[
\frac{N_u^O}{N_u^T} = \frac{\beta_o}{\beta_T} \exp \left( \frac{\Delta H}{kT} \right) \exp \left( -\frac{\Delta S}{k} \right) \quad \cdots \cdots \cdots \quad (7)
\]
where $\beta$ is the position number for each type of site, $\Delta R = R^T_u - R^O_u$ is the difference in enthalpy between an H-atom in a T-site and one in an O-site, and $\Delta S = S^T_u - S^O_u$ is the corresponding excess entropy difference.

Thus at low temperatures the chemical potential of the dissolved H-atoms is,

$$\mu_u = \frac{H^T_u}{T} - TS^T_u + kT \ln \left( \frac{\theta_u}{\beta T} \right) \quad \text{...............(8)}$$

where $\theta_u$ is the H-atom concentration. At higher temperatures where both sites are occupied (mixed), the chemical potential is \cite{18},

$$\mu_u^m = kT \phi \ln \left( \frac{N^O_u}{N^T_u} \cdot \frac{N^T_v}{N^T_v^2} \right) + kT \ln \left( \frac{N^T_u}{N^T_v \beta T} \right) +$$

$$+ T \phi \Delta S + \phi \Delta H + \frac{H^T_u}{T} - TS^T_u \quad \text{...............(9)}$$

where $N_v$ is the number of solvent atoms, and $\phi$ is the fraction of solute atoms at O-sites. Using the distribution function \cite{7}, $\mu_u^m$ can be written in terms of the H-concentration in this range,

$$\theta_u^m = \frac{N^O_u + N^T_u}{N_v} \quad \text{...............(10)}$$
in the form,

\[ \mu_u^m = kT \ln \left[ \frac{\epsilon_u^m}{\left\{ \frac{\beta_o}{\beta_T} \exp \left( \frac{\Delta H}{kT} \right) \exp \left( - \frac{\Delta S}{k} \right) + 1 \right\} \beta_T} \right] + \frac{\mu_u^T}{T} - TS_u^T \]  \hspace{1cm} (11) 

If the solution were constrained such that only T-sites could be occupied, the chemical potential would be given by equation (8), and \( \theta_u \) would be the corresponding H-solubility in equilibrium with a second phase. Thus \( \theta_u \) is the solubility given by extrapolating the experimental data from the \( \alpha \)-iron range (virtually complete T-occupancy) into the high temperature \( \delta \)-range. The experimentally determined solubility measured in the \( \delta \)-range corresponds with the partial potential of equation (11). If the real (mixed) and constrained (only T occupancy) solutions are equilibrated in the same H\(_2\) atmosphere at the same temperature in a thought experiment, \( \mu_u^m \) and \( \mu_u \) are equal and equations (11) and (8) lead to

\[ \frac{\epsilon_u^m}{\theta_u} = 1 + \frac{\beta_o}{\beta_T} \exp \left( \frac{\Delta H}{kT} \right) \exp \left( - \frac{\Delta S}{k} \right) \]  \hspace{1cm} (12) 

Now, by definition \( \Delta H \) must be negative and it is also physically plausible that \( \Delta S \) is negative since one would expect the lattice displacement surrounding an H-atom in a O-site to be larger than that corresponding to T-site occupancy and thus the dilational entropy to
be greater. Using values of $\Delta A = 7.0 \text{k.cal/mole}$ and $\Delta S/k = -3.0$
values of the ratio $\theta_u^m/\theta_u$ have been calculated for various temperatures. Using the solubility data of Fig. (1) and approximating the data of the lowest 200°C to be linear in the $\ln \theta$ vs. $1/T$ representation enables $\theta_u$ to be obtained by extrapolation to higher temperatures. The calculated values of $\theta_u^m$ are indicated by the circles in Fig. (5). It can be seen that they agree well with the upper curve which represents the best fit to the actual solubility data. The percentage of 0-sites occupied at 1450°C corresponding to the values of $\Delta S$ and $\Delta A$ chosen is 50% and at 1023°C it is 23% and at 300°C it is 2%.

It is clear that the observed solubility behavior of H in Fe is compatible with the dual occupancy of sites by H atoms. This does not of course imply that this mechanism is indeed responsible for the curvature in the plots of $\ln \theta T^{7/4}$ vs. $1/T$ but it is clear that the dual occupancy of sites is a thermodynamic necessity and it is only the degree to which it occurs that is open to question.

e) Trapping Models

The phenomenon of trapping has been discussed many times in respect to the behavior of H in $\alpha$-iron, particularly the anomalous diffusivity. McNabb and Foster (19) developed a general treatment of the phenomenon of diffusion in the presence of trapping sites, and Orian (20) has reformulated this treatment invoking a local equilibrium between H atoms at trapping sites and at normal lattice sites.
FIGURE 5. Comparison of the measured solubility data for H in bcc iron and the behavior predicted from considering the dual occupancy of sites in the bcc lattice by H-atoms.
Oriani (20) applied his model to a series of experimental investigations of the permeation of H through both cold-worked and annealed irons and steels. The results showed that, despite the approximations made in the analysis and the diversity in the chemical composition of the material, the calculated trapping depth was surprisingly constant (~ -8.0 k.cals/mole) and the density of traps for non-cold-worked material was ~ $10^{19}$ sites per cm$^3$. However in surveying all the evidence Oriani concluded that the observations could not be explained by a single type of trapping site and that there was a multiplicity of such sites.

The fact that many different sites may be effective as traps for H-atoms in Fe is also indicated by more recent work. Kummick and Johnson (21) studied H transport through both annealed and deformed Armco iron. The results obtained were interpreted in terms of two kinds of traps. Type 1 traps could not be removed by annealing prior cold-worked Fe and those were thought to be microwoids. Type 2 traps were also induced by deformation but they could be removed by annealing and were ascribed to the dislocation cell structure caused by the deformation.

The low temperature solubility data of Louthan et. al. (10) contain much scatter but give some support to the presence of trapping sites in cold-worked iron. In the deuterium solubilities the $\theta$-values are higher than the Oriani equation for cold-worked iron. However in the case of tritium, heavy cold-working gave rise to only a small increase in solubility. It is interesting to note that D-solubility
measured using single crystals which were then cold-worked and annealed were little different to those found using the original single crystals. This indicates that grain boundaries are not effective trap sites in iron. Indeed the higher temperature data in Figs. (1-4) show no significant difference between solubilities determined by using single crystal and polycrystalline samples.

The evidence for trapping sites in the case of well-annealed pure iron is somewhat confusing. However it is useful to pose the following question. If certain trapping sites are present in well-annealed relatively pure polycrystalline iron, perhaps giving rise to the enormous discrepancies in the low temperature transport data, what would be their effect on the solubility? The answer to this question is complicated by the fact that meta-stable traps operative at low temperature can become unstable at higher temperatures. However it is interesting to presuppose the existence of such traps, relatively stable at temperatures higher than 500OK, and calculate the meta-stable solubility curve.

Assume that the iron contains \( N_v \) "normal" lattice sites and \( N_x \) extra trapping \((x)\) sites. The total number of sites is thus,

\[
N_s = N_v + N_x \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdOTS

The \( N_u \) H-atoms are distributed such that \( N_u^x \) are in \( x \)-sites and \( N_u^n \) in "normal" sites. The enthalpy of the solution is,
\[ H = N_u^x \bar{H}_u^x + N_u^n \bar{H}_u^n + N_v H_v^O \] ........................................ \(14\)

where \( \bar{H}_u^x \) and \( \bar{H}_u^n \) are the enthalpy changes accompanying the insertion of an H-atom into an x-site or an n-site and \( H_v^O \) is the enthalpy per atom of iron. The partial enthalpy is thus,

\[ \bar{H}_u = \left( \frac{\varepsilon N_u^x}{\varepsilon N_u} \right)_{P,T} \bar{H}_u^x + \left( \frac{\varepsilon N_u^n}{\varepsilon N_u} \right)_{P,T} \bar{H}_u^n \] ................................ \(15\)

Assuming that H-atoms located on the subsets of n and x-sites do not interact, the canonical partition function is,

\[ \Omega_c = \frac{(N_v^\beta)!}{(N_v^\beta - N_u^n)!} \cdot \frac{N_x^!}{(N_x - N_u^x)!} \frac{N_u^n^!}{N_u^n!} \Omega (g) \]

\[ \exp \left\{ - \frac{1}{kT} (N_v H_v^O + N_u^x \bar{H}_u^x + N_u^n \bar{H}_u^n) \right\} \] ................................ \(16\)

The factor \( \Omega(g) \) is the sum over states for the internal degrees of freedom and

\[ k \ln \Omega(g) = (N_u^x S_{u}^{vx} + N_u^n S_{u}^{vn} + N_v S_v^{O}) \] .......................... \(17\)
where \( S^{\text{vx}}_u \) and \( S^{\text{vn}}_u \) are the partial excess entropies associated with inserting an H-atom into \( x \) and \( n \) sites and \( S^0_v \) is the entropy per atom of pure Fe.

Obtaining the configurational free energy \( F_c = -kT \ln \Omega_c \) and minimizing this with respect to \( N^x_u \) leads to the distribution function,

\[
\frac{N_u - N^x_u}{N^x_u} \cdot \frac{N_v \psi - N^x_u}{N_v \beta} = x = \exp \left\{ \frac{1}{kT} \left( \Delta \bar{E}_u - T \Delta \bar{S}_u \right) \right\}
\]

(18)

where \( \psi \) is the trap density \( N_x / N_v \), \( \Delta E_u \) is the trap depth \( R^x_u - R^n_u \) and \( \Delta S_u \) is the corresponding entropy term \( S^{\text{vx}}_u - S^{\text{vn}}_u \). Using the condition \( N_v \beta \gg N^x_u \) and the conservation equation (13), leads to the following expressions for the enthalpy, entropy, and chemical potential of a dissolved H-atom,

\[
\bar{H}_u = \bar{H}^n_u + \frac{1}{2} \Delta \bar{E}_u \kappa \quad \text{.......................... (19)}
\]

\[
\bar{S}_u = \bar{S}^{\text{vn}}_u - k \ln \left( \frac{N^n_u}{N_v \beta - N^n_u} \right) + \Delta \bar{E}_u \kappa / 2T \quad \text{............... (20)}
\]

\[
\mu_u = \bar{H}^n_u - T \bar{S}^{\text{vn}}_u + kT \ln \left[ \frac{\theta^*}{\beta} \left( 1 - \frac{\psi}{x \beta} \right) \right] \quad \text{............... (21)}
\]
where \[ \kappa = 1 - \frac{\theta - (\psi - \chi \beta)}{\left( (\psi + \chi \beta - \theta)^2 + 4\theta \chi \beta \right)^{\frac{1}{2}}} \] \hspace{1cm} (22)

Now at high temperatures where virtually only n-sites are occupied \( n^n_u = n_u \) and \( s^{vn}_u = s^{xs}_u \). Thus the solubility equation corresponding to chemical potential (21) is,

\[ \theta' = \frac{\beta \lambda P^{\frac{1}{2}}}{(1 - \frac{\psi}{\chi \beta}) T^{7/4}} \exp \left( - \frac{\mu'_u - \frac{1}{2}E_D^o}{kT} \right) \exp \left( \frac{s^{xs}_u}{k} \right) \] \hspace{1cm} (23)

Comparing this with (2) we get

\[ \frac{\theta'}{\theta} = \delta = \left( 1 - \frac{\psi}{\chi \beta} \right)^{-1} \] \hspace{1cm} (24)

Taking Orian's values of \( \Delta E_u = -8 \text{ k. cal/mole} \) \( \Delta s_u = c \) for simplicity and \( \psi = 2.25 \times 10^{-4} \) (corresponding to \( 2 \times 10^{19} \) traps per cm\(^3\)), the solubility \( \theta' \) can be calculated from (24). At 1000\(^o\)K, \( \delta = 1.002 \); at 600\(^o\)K, \( \delta = 1.032 \); at 500\(^o\)K \( \delta = 1.134 \), and at 450\(^o\)K \( \delta = 1.407 \).

This indicates that, for the trap density and depth used in the calculation, a deviation from Arrhenius behavior in the solubility would not be experimentally observable above 300\(^o\)C. Since it is clear that this trap density would have a large effect on the true diffusivity below 300\(^o\)C, it is safe to assume that trapping sites of this depth and less do not play an observable role in the solubility above 300\(^o\)C.
As Völkl and Alefeld have pointed out [1], no surface-independent method except for internal friction and magnetic disaccommodation has been applied to the study of H-transport through bcc iron and surface independent measurements are needed before the effect of traps or imperfections can be assessed. This was also pointed out previously by Gonzalez [22].

Conclusions
(a) New data for the temperature dependence of the H-solubility in iron are in good agreement with the previous data.
(b) Plots of lnθ vs. 1/T and lnθT^7/4 vs. 1/T are curved in the α-iron region. Taking cognizance of this curvature shows that solubility data measured in the α-iron range are in good agreement with those measured in the high temperature δ-range.
(c) The solubility data in the range 300°C up to the α/γ transformation are not markedly affected by the purity of the iron.
(d) The solubility data in the range 300°C up to the α/γ transformation are insensitive to the presence of grain boundaries.
(e) The departure from the Arrhenius behavior in the solubility is consistent with the simultaneous occupation of both tetrahedral and octahedral sites in the bcc iron lattice.
(f) It has been shown that the effect of meta-stable trapping sites of a depth of ~8.0 k.cal/mole would have no measurable effect on the solubility behavior above ~300°C in the case of well annealed iron.
Acknowledgement

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References


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CHAPTER II
THE SOLUBILITY OF HYDROGEN IN SUPER PURE IRON SINGLE CRYSTALS

Introduction

Recent measurements \{1\} of the temperature dependence of the solubility of hydrogen in annealed iron at atmospheric pressure using both single crystals and polycrystalline material of varying grades of purity have shown that the solubility is essentially independent of purity and the presence of grain boundaries and dislocations in the different polymorphic forms of iron. It was also concluded that plots of \( \ln \theta \) vs. \( 1/T \), where \( \theta \) is the atom ratio of hydrogen dissolved in the iron, were not linear in the bcc range and exhibited a positive curvature.

The purpose of the present experiment was to extend these measurements to include a super pure iron single crystal.

The equilibrate-quench-analyze technique has been used to measure the temperature variation of the hydrogen solubility in bcc \( \alpha \)-iron in the temperature range 282 to 903\(^\circ\)C.

Experimental Technique

The equilibration and quenching apparatus used are described in Appendix I and in previous reports \{2\}, \{3\}. The iron single crystal, whose purity is given in Table I, was obtained in the form of a cylinder 5.5 cm long and 2 mm in diameter. This cylinder was spark-cut into three smaller cylinders of equal length and the sample
for equilibration prepared by spot-welding thin iron wires (of negligible mass compared with the crystals) around the three cylinders.

The single crystal was grown from material provided by Johnson Matthey and Co. Ltd.. The initial nitrogen content (200 ppm) and carbon content (17 ppm) were removed by a treatment involving annealing in H₂ atmosphere for 100 hours at 800°C, and then annealing in vacuum at 750°C for 3 hours at <10⁻⁹ Torr. The subsequent N and C contents were below 0.5 ppm as indicated by magnetic aftereffect measurements. This information about the sample was given by Professor H. Kronmüller, who kindly offered us the iron single crystal.

The sample was equilibrated in a stream of super pure hydrogen gas (nominal purity 99.9995 vol. % and less than 1 ppm by volume of hydrocarbons).

**TABLE 1**

Impurities of iron single crystal, in ppm by weight

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>Mo</th>
<th>Al</th>
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After equilibration the samples were quenched and their hydrogen contents measured using a hot extraction technique (2), (3). On completing the measurements in the bcc α region in the temperature range 282 to 903°C, one of the three cylinders was used to measure
the hydrogen solubility in fcc $\gamma$-iron (from 977 to 1352°C) and also in the bcc $\delta$-iron phase (from 1400 to 1440°C).

Repeated measurements using different equilibration times were performed to ensure that equilibration was carried out for sufficiently long times to achieve equilibrium.

Because of the relatively large length of the sample, the high-frequency induction coil used to maintain the iron at the equilibration temperature was designed so as to achieve uniform heating. This was established empirically and checked by measuring temperatures along the specimen length by a series of Pt/Pt-13%Rh thermocouples.

The solubility data obtained are given in Table II, and illustrated in the form of a plot of $\ln \theta$ vs. $1/T$ in Fig. (1). The data ensuing from the super pure single crystal are indicated by filled circles (■) and the data points in $\gamma$-region by filled squares (■), and in the $\delta$-region by filled triangles (▲). The remaining symbols indicate older data using a series of polycrystalline irons of differing grades of purity and also relatively impure single crystals. The chemical compositions of the various irons have been shown in Chapter I.

Discussion

It is immediately obvious that the new data are in good agreement with the previous measurements and that the plot of $\ln \theta$ vs. $1/T$ is not linear. The dashed line in Fig. (1) represents the linear fit given by Oriani (4) to the older data. It predicts a much lower
FIGURE 1. Plot of $\ln\theta$ vs. $1/T$. The symbols have the following meaning:

- ● - super pure Fe single crystal (this investigation)
- □ - fcc $\gamma$-phase data of this investigation
- ▲ - bcc $\delta$-phase data of this investigation
- ◻ - impure single crystal (Ref. 12)
- ◼ - impure polycrystal (Ref. 12)
- ○ - pure polycrystal (Ref. 1 and Chapter 1)
- □ - impure polycrystal (Ref. 7)
- ○ - impure polycrystal (Ref. 8)
- ▽ - impure polycrystal (Ref. 9)
- ◻ - impure polycrystal (Ref. 10)
- ▲ - impure polycrystal (Ref. 11)
Oriani's equation

\[ T^{-1} \times 10^4 \left( ^\circ K^{-1} \right) \]
### TABLE II

<table>
<thead>
<tr>
<th>$T(\text{OC})$</th>
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<th>$\theta \times T^{7/4}$</th>
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(continued)

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solubility in the δ-iron range than is actually found. The fact
that this curvature is not a consequence of using a temperature de-
pendent standard state for the relative partial quantities, a con-
sequence of representing the data in the form of plots of lnθ vs. 1/T,
is illustrated in Fig. (2) in which lnθ T^{7/4} vs. 1/T is plotted.
The curvature in Fig. (2) is still apparent. Fig. (1) corresponds
to the solubility equation

\[
\ln \theta = \ln \beta - \frac{\Delta \bar{H}_u}{kT} + \frac{\Delta \bar{S}^{XS}_u}{k} \quad \text{.......................... (1)}
\]

and Fig. (2) corresponds to the solubility equation (5)

\[
\ln(\theta T^{7/4}) = \ln(\beta P^{1/2}_r \lambda) - \left( \frac{\bar{H}_u - \frac{1}{2}E_D^0}{kT} \right) + \frac{\bar{S}^{XS}_u}{k} \quad \text{........ (2)}
\]

In these equations β is the number of interstitial sites per
metal atom (β = 6 for the bcc structure, assuming tetrahedral site
occupation, and β = 1 for the fcc structure assuming octahedral
occupation (6)). The quantities Δ\bar{H}_u = \bar{H}_u - \frac{1}{2}H_2^0 and Δ\bar{S}^{XS}_u = \bar{S}^{XS}_u - \frac{1}{2}S_2^0
are the relative partial molar enthalpy and excess entropy relative
to gaseous H_2, P is the H_2 pressure, λ a known constant (5), and E_D^0
is the dissociation energy of the H_2 molecule at 0°K.

A least square fitting technique was used to fit all the data
given in Figs. (1) and (2). The resulting representations are
FIGURE 2. Plot of $\ln \theta T^{7/4}$ vs. $1/T$. The symbols have the same significance as in Figure 1.
\[ \ln \theta = 4.3225 - 0.5303x + 0.0087x^2 \] \[ \text{...............}(3) \]

and

\[ \ln(\theta T^{7/4}) = 9.4807 - 0.8121x + 0.0142x^2 \] \[ \text{.........}(4) \]

where \( x = 10^4/T \).

The new data obtained using the super pure single crystal support a series of conclusions made previously \{1\} ∗ Chapter I.

1) The solubility data in the range \(-300^\circ\text{C}\) up to the \(\alpha/\gamma\) transformation temperature are not markedly affected by the purity grade of the iron;

2) The solubility data in the range \(-300^\circ\text{C}\) up to the \(\alpha/\gamma\) transformation temperature are insensitive to the presence of grain boundaries;

3) The departure from the Arrhenius behavior in the hydrogen solubility is consistent with the simultaneous occupation of both tetrahedral and octahedral sites in the bcc iron lattice \{1\}. The curvature observed is consistent with an energy difference between an H-atom in a tetrahedral and octahedral site of \(-7\) kcal/mole. At low temperatures \((<600^\circ\text{C})\) virtually all the H-atoms occupy
tetrahedral sites. A least squares regression to equation (2) in this temperature range leads to
$R_u = -42.29 \text{ kcal/mole and } S_u^{xs}/k = 2.57.$

4) The observed curvature is not due to the presence of meta-stable trapping sites of a depth of
-8 kcal/mole. Such traps would manifest themselves in the thermodynamic data only at tempera-
tures below 300°C.
Acknowledgements

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References


CHAPTER III
THE THERMODYNAMIC FUNCTIONS OF HYDROGEN
IN SOLID SOLUTIONS OF THE GROUP V METALS Nb, Ta, AND V

Introduction

Many recent investigations have dealt with the thermodynamic properties of hydrogen in the Group V metals Nb, V, and Ta. This is a topic of considerable importance in the understanding of interstitial solid solutions. One reason for this is the fact that, in contrast with most interstitial solutions, the Group V metals absorb H-concentrations corresponding to an atom ratio $\theta$ greater than unity in equilibrium with $H_2$ gas at atmospheric pressure. Thus knowledge pertaining to the $H$-$H$ interaction can be extracted from the partial thermodynamic functions of the dissolved $H$-atoms in the concentrated solid solutions. Another reason for the importance of such solutions is that it is difficult to reconcile the degree of mobility of $H$ in solution with the conventional bound oscillator models. Baker and Birnbaum (1) give a value $\sim 10^{-5}$ cm$^2$/sec for the diffusion coefficient of $H$ in Nb at 3000 K. The corresponding value for C in bcc iron is $10^{-17}$ cm$^2$/sec. In setting up models for solid solutions, it is expedient to ensure that the predictions of the model are compatible with both the thermodynamic and kinetic behavior of the system. Thus a knowledge of the variation with composition and temperature of the relative partial entropy $S_u$ and relative partial enthalpy $H_u$ is desirable.
Almost all the recent investigations have lead to the conclusion that the relative partial enthalpy $\Delta R_u = R_u - \frac{1}{2} H_{H_2}^0$ is virtually independent of temperature and varies only to a relatively small extent with H-concentration. However, a recent investigation of the H-Nb system [2] yielded results showing that $R_u$ varied strongly with temperature and were more strongly dependent on composition than the previous data indicate.

The purpose of the present work is to reexamine the temperature and composition variation of the thermodynamic functions of H in the Group V metals and compare them with a theoretical model for such solutions which is compatible with the remarkably high mobility of H in these solutions.

Temperature Variation of $R_u$ and $\Delta R_u$

Burch and Francis [2] have analyzed their recent pressure-composition isotherms for the H-Nb-system using a modification of a technique proposed by Langeberg and McElhan [3], in which a temperature-independent standard state is used. This technique is capable of revealing a temperature dependence of $R_u$ provided that such changes are not masked by the inherent scatter in the data. Burch and Francis [2] indicate that, at a composition of $\theta = 0.05$, $R_u$ changes from $-56.7$ k.cals/gm at H at 10000K to $-51.2$ k.cals/gm at H at 5000K, a change of $\Delta R_u = 2.5$ k.cals/gm at H. The change in $\Delta R_u$ in the same T-range is much smaller.

This large variation of $R_u$ with temperature is interesting but
it is not entirely supported by other investigations. Kleppa,
Dantzer and Mel nichak \{4\} measured the thermodynamic functions of
H in V and Nb. Their analysis showed that $\Delta H_u$ is very nearly in-
dependent of temperature. The T-range encompassed by their data
was smaller than that of the measurements of Burch and Francis \{2\}.
The data of Kleppa, Dantzer and Mel nichak \{4\} for H in V and Nb
are in excellent agreement with those of Veleckis and Edwards \{5\}.
The data of Veleckis and Edwards \{5\} for the H-Nb system span the
T-range 352 - 671°C (again smaller than that of Burch and Francis,
349 - 849°C), and the analysis of Langeberg and McLellan \{3\} in-
dicated that $\Delta H_u$ was independent of temperature at least in that T-
range. In the previous analysis \{3\}, representational equations
were derived for the isotherms of Veleckis and Edwards \{5\} and the
chemical potential $\mu_H$ for H in the bcc solid solutions computed
from these equations for a given composition. This analysis has
been undertaken again using the actual data points to obtain values
of $\mu_u$ at a series of different compositions. Now, $\mu_u$ is given by \{3\}

$$
\mu_u = \frac{E^D_0}{2} + kT \ln \left( \frac{\psi P^{1/3}}{T^{7/4}} \right)
$$  \hspace{1cm} (1)

where $E_0^D$ is the dissociation energy of the H$_2$ molecule at 0°K, $P$
is the H$_2$-pressure, and $\psi$ is a known constant \{3\}. Plots of $\mu_u$
vs. T taken from the isotherms of Veleckis and Edwards are shown in
Fig. (1). It is clear that they are linear. A least-squares re-
gression of the data points shows that the standard deviations are
FIGURE 1: Plots of the chemical potential $\mu$ vs. $T$ taken from the isotherms of Veleckis and Edwards (5), for the case of Nb.
0.0245, 0.0177, 0.0236 and 0.0149 in decreasing order of \( \theta \). The instantaneous slopes of these plots at any temperature give the partial entropy \( S_u \) since \( S_u = -(\partial H_u / \partial T)_p \). Thus the data of Veleckis and Edwards indicate that both \( H_u \) and \( S_u \) are temperature independent. The \( S_u \)-values taken from the slopes of Fig. (1) are given in Fig. (2). The upper curve denotes the \( S_u \)-values taken from the previous analysis [3] and the solid curve is taken from the results of Kleppa et al. [4] for the H-Nb system at 440\(^\circ\)C.

This invariance of \( \Delta H_u \) with respect to temperature is also seen in the data for the other Group V metals. Mallet and Koehl [6] measured P-\( e \)-isotherms in the T-range 300 - 700\(^\circ\)C for H-Ta and found linear plots of \( T \) vs. relative partial free energy. Those authors concluded that \( \Delta H_u \) was constant in the T-range 300 - 700\(^\circ\)C. The same conclusion was reached by the following sets of investigators:

(1) Veleckis and Edwards [5] for H-V (245 - 554\(^\circ\)C) and H-Ta (350 - 631\(^\circ\)C),

(2) Kofstad, Wallace and Hyv"onen [7] for H-Ta (164 - 402\(^\circ\)C),

(3) Kofstad and Wallace [8] for H-V (165 - 456\(^\circ\)C),

(4) Pryde and Tsong [4] for H-Ta (38 - 211\(^\circ\)C),


The investigations cited above seem to contain contradictions. It should be noted that the authors [4], [6], [7], [8], [9], [10] extracted \( \Delta H_u \) from their data and not \( H_u \) directly. It is clear that the data of Veleckis and Edwards [5] is not in agreement with those of Burch and Francis [2]. However, the exhaustive data of Kleppa
FIGURE 2: Plots of the partial molar entropy of H in Nb. The upper curve is taken from the data of Veleckis and Edwards (5) and the lower solid curve from those of K·eppa et al. (4). The remaining curves are calculated configurational entropies.
Data of Kleppa et. al. for Nb at 440°C

Data of Veleckis Edwards for Nb

\( S_u/k \) vs \( \theta \)
et al. {4} can perhaps help to clear up the discrepancies. These authors report that whereas $\Delta R_u$ is virtually independent of temperature, $S_u$ is not. Their curves of $S_u$ vs. $\theta$ (see Fig. (2)) indicate a T-dependence in $S_u$ which is at variance to the results of Veleckis and Edwards. In the case of H-Ta their curves show an increase of $\sim0.75$ e.u. on going from 300 to 434°C. The data for H-Nb show a similar increase in $S_u$ with T but the change is smaller because the temperature range is smaller. This variation of $S_u$ with T implies that $R_u$ (but not necessarily $\Delta R_u$) also varies with temperature because of the relation,

$$
\left( \frac{\partial H_u}{\partial T} \right)_P = T \left( \frac{\partial S_u}{\partial T} \right)_P \quad \text{................. (2)}
$$

While it is not possible to integrate this equation directly, it is clear that the temperature variation of $S_u$ found by Kleppa et al. {4} implies a temperature variation in $R_u$.

In analyzing the data, Burch and Francis {2} plotted $\ln P/T^{7/2}$ vs. $1/T$. From equation (1) it can be seen that the instantaneous slope of such a plot is,

$$
\frac{\partial \left( \ln \frac{P}{T^{7/2}} \right)}{\partial \left( \frac{1}{T} \right)} = \frac{2}{R} \left[ \frac{\partial \left( \frac{H_u}{T} \right)}{\partial \left( \frac{1}{T} \right)} - \frac{E_D^0}{2} \right] = \frac{2}{R} \left( \frac{H_u - E_D^0}{2} \right) \quad \text{(3)}
$$
Their plot, combining their own data with those of Veleckis and Edwards (5) and Pryde and Titcomb (10), is linear in the temperature range -340 to 800\textdegree K and there is a change of slope only in the range 800 to 1100\textdegree K. This implies that, as far as these data are concerned, $\bar{R}_u$ is independent of temperature at low temperatures, and a temperature variation becomes observable at higher temperatures.

In summary the following conclusions can be drawn:

(1) Virtually all the data are consistent with the fact that $\Delta R_u$ is essentially independent of temperature.

(2) $\bar{R}_u$ appears to depend on temperature but to a smaller degree than suggested by Burch and Francis (2). The data of Veleckis and Edwards (5) and Pryde and Titcomb (10) do not exhibit any variation of $\bar{R}_u$ with temperature, but a T-dependence is revealed by combining these data with those due to Burch and Francis (2). A variation of $\bar{R}_u$ with T is also consistent with the temperature variation of $S_u$ recorded by Kleppa et al. (4).

Composition Dependence of $\bar{R}_u$ and $S_u$

The composition dependence of $\Delta R_u$ for the Group V metals V, Ta, and Nb taken from several sources is illustrated in Fig. (3). The solid lines for Nb and V are taken from Kleppa et al. (5) and
FIGURE 3: Variation of $\Delta G_u$ with composition for H in Nb, V, and Ta.
$\bar{H}_u - \bar{H}_u^0$ for C in f.c.c. Iron

\( -\Delta H_u \) (Kcal/moleH)

\( \Theta \)
that for Ta from Kleppa, Melnichak, and Charlu {11}. The symbols □ represent the data points of Kofstad, Wallace and Hyvönen {7} for Ta, and Kofstad and Wallace {8} for V. The mean temperature of the data, for which $\Delta \bar{R}_u$ is temperature independent, is given in brackets. The symbols ○ give the points corresponding to the plots of Fig. (1) taken from the data of Veleckis and Edwards {5}. Since there is no $T$-dependence of $\bar{R}_u$ observable in these data, it is legitimate to estimate $\Delta \bar{R}_u$ from $\bar{R}_u$ using the relation,

$$\Delta \bar{R}_u = \bar{R}_u - \frac{1}{2} E_0^D - \frac{7}{4} kT \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots 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for $T = 6290\text{K}$, the temperature to which the data of Kleppa et al. {5} refer. The large degree of conformity between the several investigations is immediately apparent. Furthermore the small change in $\Delta \bar{R}_u$ over very large concentration ranges is clear, especially for Ta and V. This small variation in $\Delta \bar{R}_u$ with solute concentration should be compared with that found in other interstitial systems such as C in fcc iron. The dashed line in Fig. (3) illustrates the variation of $\bar{R}_u - \bar{R}_u^\infty$ for C in austenite. The origin has been displaced to 9 k.cals/mol for ease of comparison. It should be noted that, provided the values of $\Delta \bar{R}_u$ have been correctly extracted from the isotherms, the composition dependence of $\bar{R}_u$ and $\Delta \bar{R}_u$ must of course be identical. The difference in the $\theta$-dependence of $\Delta \bar{R}_u$ and $\bar{R}_u$ reported by Burch and Francis {2} is difficult to understand.
Discussion

a) Temperature Variation of $R_u$ and $S_u$

It is often useful to visualize the dissolution of H in metals by considering the ionization of an H-atom and the subsequent insertion of a proton and an electron into the lattice [2], [12], [13]. It is, however, difficult to deduce anything about the temperature variation of $R_u$ from such an approach because the various contributions to $R_u$ may vary in an unknown manner with temperature. For example, the electronic work function of Ta has been found to vary by (-9 k.cal/mol) in the temperature range 273 to 1473°K [14].

It is simpler to consider the effect of temperature on the thermodynamic state of a dissolved H-atom. As has been pointed out by Kleppa et al. [4] the entropy curves in Fig. (2) reflect an entropy somewhat greater than the ideal configurational entropy even when the H-atoms can occupy all six tetrahedral sites per metal atom. The series of superlattices formed at $\theta \sim 1$ [15] indicate that at low temperatures there is a large degree of order present and the measured total entropy would be lower than the ideal entropy. This fact, coupled with the large mobility of H in Nb, lead Kleppa et al. [4] to suggest that the H-atoms are non-localized at high temperatures.

Such a model has been also proposed by McLellan [16]. At small H-concentrations the direct H-H-interaction is ignored and a Hamiltonian is written for the dissolved H-atom which contains a sinusoidal H-metal interaction leading to a severe restriction on the entropy at low temperatures and the formation of ordered structures
in keeping with measured low-temperature specific heat data in the H-solutions of the Group V metals (17). However at higher temperatures the H-atoms become delocalized and there is a concomitantly large increase in entropy. At such temperatures, to which the data discussed in this report apply, the partial enthalpy is given by,

\[ H_u = kT \left( \alpha T + \frac{3}{2} \right) + H_0 \] ........................(5)

where \( \alpha \) is the thermal expansivity and \( H_0 \) is the value of \( H_u \) at \( T \to 0 \). The term \( k \alpha T^2 \) is small so that \( H_u \) varies as \( \frac{3}{2} kT \). This is somewhat less than the variation deduced by Burch and Francis (2). However the relative partial molar enthalpy is,

\[ \Delta H_u = H_u - \frac{1}{2} H_{H_2}^0 \]

\[ = kT \left( \alpha T + \frac{3}{2} \right) + H_0 - \frac{1}{2} \left( -\frac{7}{2} kT + \mu D_0 \right) \] ........................(6)

\[ \cong -\frac{3}{2} kT + H_0 - \frac{\mu D_0}{2} \]

so that, in accord with virtually all the experimental data, \( \Delta H_u \) has a variation with temperature that would be hardly detectable.

The entropy at \( \theta \to 0 \) is given by (16)
\[
\frac{S'_{u\infty}}{k} = -\ln\left(\frac{\theta}{\phi' V^O_V}\right) + \frac{3}{2} \left[ 1 + \ln\left(\frac{2\pi mkT}{N_o^{2/3} h^2}\right)\right] \quad \ldots\ldots (7)
\]

where \(\phi'\) is a constant, \(V^O_V\) is the atomic volume of the solvent metal, \(N_o\) is Avogadro's number and \(h\) is Planck's constant. Thus, ignoring a small contribution from the temperature dependence of \(V^O_V\), \(S'_{u}\) varies as \(\ln T\) similar to an assembly of classical oscillators. This entropy change is in good agreement with that estimated from the curves given by Kleppa et al. \{4\}.

While it is clear that the excess entropy arising from non-configurational sources may be large, it should not vary strongly with temperature. Aside from the small electronic entropy term, there is an entropy associated with the shear strain in the lattice arising from the distortion due to the H-atoms but this is proportional to the temperature coefficient of the shear modulus and thus relatively invariant to temperature.

b) Composition Dependence of \(A_u\) and \(S_u\)

The variation of the measured \(S_u\)-data with composition taken from Kleppa et al. \{4\} and Veleckis and Edwards \{5\} for bcc Nb-H is shown in Fig. \{2\}. The ideal configurational entropy of an interstitial solution consisting of bound solute atoms in the tetrahedral sites in a bcc host lattice is,
\[ S_{id}^u = -k \ln \left( \frac{\theta/\beta}{1-\theta/\beta} \right) \]  \hspace{1cm} (8)

where \( \beta = 6 \). As can be seen in Fig. (2), this entropy is close to the total entropy found experimentally. If H-Nb is such a solution, the \( S_u \) curves imply that the excess partial entropy is small and that there is a tendency to ordering at higher \( \theta \)-values.

Now Kleppa et al. (4) adopted the position of defining the ideal entropy in the form

\[ S_{id}^u = -k \ln \left( \frac{C_u}{1-C_u} \right) \]  \hspace{1cm} (9)

where \( C_u \) is the atom fraction of H. This is equivalent to \(-k \ln \theta \) since \( C_u = \theta/(1+\theta) \). At low solute concentrations \(-k \ln \theta \) approximates the ideal configurational entropy of an interstitial solution containing one site per lattice atom. This is no longer true at larger values of \( \theta \) since the ideal configurational entropy of such a solution is given by equation (8) with \( \beta = 1 \). However the main point is that the enumeration of the excess entropy depends on the arbitrary choice of \( S_{id}^u \).

The adoption of equation (8) with \( \beta = 6 \) is logical in terms of traditional bound oscillator models since the bcc lattice contains 6 tetrahedral sites per metal atom and not one. This choice however constrains \( S_{xs}^u = S_u - S_{id}^u \) to be very small. On the other
hand the choice of Kleppa et al.\cite{4} constrains $\frac{\Delta S}{\Delta u}$ to be large, leading to the suggestion of a "communal entropy" to help account for the difference.

Unfortunately, the constant $\phi'$ in equation (7) of the "quasi-free" theory can not be calculated accurately so that once more the absolute entropy is not obtainable from the model.

Since all the curves in Fig. (2) have a similar $\theta$-variation, it is probably impossible to use the data to differentiate between the models suggested in view of the uncertainties in both experimental $\overline{S}_u$ measurements and calculated non-configurational entropies.

While it is difficult to calculate the electronic entropy of a concentrated solid solution at a high temperature, the change in entropy due to the expansion of the lattice may be obtained by the procedure outlined by Wagner \cite{18}. The change in entropy which would occur with composition if the volume were constrained to be constant is related to the $\overline{S}_u$ value by

$$\overline{S}_u = \overline{S}_u + a\overline{V}_u B \quad \ldots (10)$$

where $\overline{S}_u = (\partial S/\partial n_u)_{V,T}$, $\overline{V}_u$ is the partial molar volume, and $B$ is the bulk modulus. At infinite dilution this becomes

$$\overline{S}_u = \overline{S}_u^\infty + a\overline{V}_u B^0 \quad \ldots (11)$$
The recent elastic data of Fisher, Westlake, and Ockers (19) yields
\[ S^w_u - \tilde{S}^w_u = 1.46 \text{ k.} \] If the value of B varies linearly with \( \theta \), as these data imply, equation (10) can be written,

\[ \tilde{S}_u = \tilde{S}_u + (\tilde{S}^\infty_u - \tilde{S}^\infty_u) - \alpha \bar{V}_u \theta \frac{dB}{d\theta} \] .................(12)

Using the value (20) of \( \frac{dB}{d\theta} = -0.112 \times 10^{12} \) dyn/cm² the change in \( \tilde{S}_u - \tilde{S}_u \) on going from infinite dilution to \( \theta = 0.05 \) is only \(-0.03\)k. This implies that, at least at moderate solute concentrations, this entropy contribution changes with composition only slowly. However, this entropy change can not be ascribed only to a change in the non-configurational entropy since if the concentration is changed at constant volume the state of order would change in a different manner compared with the constant pressure case.

Turning to the composition dependence of \( \Delta H_u \), the state of affairs is shown in Fig. (3). The relative \( \theta \)-invariance of the three solid solutions is apparent, although it is less marked in the case of Nb. As Wagner has shown (18), it is not possible in general to deduce the form (sign) of the H-H mutual interaction from the variation of \( \Delta H_u \) with \( \theta \) since, as \( \theta \) and the solvent lattice parameter increase, both the H-H and H-solvent interactions are simultaneously changing with composition. However if the change in internal energy \( E \) with composition could be measured at constant volume, then for reasonably small concentrations the metal-H interactions will be
invariant to solute concentration and the variation of the quantity

$$
\bar{E}_u = \left( \frac{\partial F}{\partial n_u} \right)_{V,T,N_V} \quad \text{..........................}(13)
$$

will be predominantly determined by the solute atom mutual interactions. The counterpart of equation (12) is,

$$
\bar{E}_u = \bar{H}_u + (\bar{R}_u^\infty - \bar{E}_u^\infty) + T\alpha_v v_u \theta \frac{d\beta}{d\theta} \quad \text{..........................}(14)
$$

The data of Fisher et al. [19] show that for H-Nb the quantity $\bar{R}_u^\infty - \bar{E}_u^\infty$, representing the difference in energy necessary to insert an H atom into the lattice at constant pressure and constant volume is - 0.4 k.cal/mole [20].

Using the values of $\frac{d\beta}{d\theta}$ for H-Nb, H-V, and H-Ta indicates that the H-H interaction in Nb is probably slightly attractive but in the case of Ta and V it may be slightly repulsive [20]. The major point is that the interaction is weak in nature. It is understandable that the ordered Somerkow structures are only found at very low temperatures. Pick's [15] X-ray and neutron scattering data show that the ordered Somerkow structure is formed in H-Nb of $\theta = 1$ at - 175°C and a further cubic $\gamma$ superlattice is formed at - - 90°C.
References

CHAPTER IV
DIFFUSION OF CARBON AND NITROGEN
IN BCC IRON

Introduction

In recent years the behavior of the diffusivity $D$ of carbon in bcc iron as a function of temperature $T$ has been the object of much controversy, and many models have been proposed to account for the positive deviation in Arrhenius plots of $\ln D$ vs. $1/T$ occurring at high temperatures. The purpose of the present short report is to re-examine the diffusion data for both C and N in bcc iron in order to assess the plausibility of the various models which have been proposed.

Experimental Data

a) The Fe-C System

The plot of $\ln D$ vs. $1/T$ is seen in Fig. (1). The bulk of the experimental points were taken from the paper of Lord and Beshers (1), but other data are also included. It is to be noted that in all cases actual experimental data points were used and not points computed from representational equations. The references, corresponding to the various symbols used in Fig. (1), are listed in Table 1. The letters adjacent to the symbols in Fig. (1) indicate briefly the method used to determine the diffusion coefficients according to the scheme:
FIGURE 1: Plot of carbon diffusivity in bcc iron versus inverse of temperature.
<table>
<thead>
<tr>
<th>SYMBOLS</th>
<th>(514 - 786)</th>
<th>(503 - 865)</th>
<th>(353.)</th>
<th>(177.5)</th>
<th>(26.4 - 125)</th>
<th>(-35 - -10)</th>
<th>(23.7 - 74.2)</th>
<th>(-38 - -17)</th>
<th>(-39)</th>
<th>(648 - 702)</th>
<th>(408 - 430)</th>
<th>(616 - 844)</th>
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<td>MF</td>
<td>MF</td>
<td>IF</td>
<td>IF</td>
<td>IF</td>
<td>IF</td>
<td>EAE</td>
<td>IF</td>
<td>MAE</td>
<td>PAE</td>
<td>MF</td>
<td>IF</td>
</tr>
<tr>
<td>AUTHORS</td>
<td>Stanley</td>
<td>Smith</td>
<td>Lord and Beshers</td>
<td>Hasiguti and Kamoshita</td>
<td>Guillet and Hocheid</td>
<td>Wert</td>
<td>Wert</td>
<td>Thomas and Leak</td>
<td>Maringer</td>
<td>Rathenau</td>
<td>Ham</td>
<td>Lord</td>
</tr>
</tbody>
</table>

**TABLE 1**
MF = mass flow, IF = internal friction, EAE = elastic after effect, PAE = permeability after effect, MAE = magnetic after effect.

The curvature, noticeable as T increases, has been analyzed using a least-squares fitting technique involving a parabolic representation. The 83 separate data points can be represented by

\[ \ln D = -2.087 - 1.197x + 0.0037x^2 \quad \ldots \ldots \ldots (1) \]

where \( x = (10^4/T)0K^{-1} \). The mean square deviation is 0.022. A separate representation of the low-temperature diffusivity was obtained by taking only points below 740°C. These 23 points can be represented by,

\[ \ln D = -6.395 - 0.9413x \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2) \]

with a mean square deviation of 0.023. The values of the diffusion parameters defined by

\[ D = D_0 e^{-Q/kT} \]

corresponding to equation (2) are \( D_0 = 1.670 \times 10^{-3} \text{ cm}^2/\text{sec} \) and \( Q = 18.65 \text{ k.cal/mole} \).

b) The Fe-N System

The references taken for the diffusivity data are compiled in Table 2, and correspond with the symbols used in the plot of \( \ln D \) vs. \( 1/T \)
**TABLE 2**

<table>
<thead>
<tr>
<th>AUTHORS</th>
<th>REF.</th>
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<th>SYMBOLS</th>
</tr>
</thead>
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<td>MF</td>
<td>750 - 1470</td>
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</tr>
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<td>Fast and Verrijp</td>
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<td>MF</td>
<td>500 - 600</td>
<td>▽</td>
</tr>
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<td>Busby, Hart and Wells</td>
<td>27</td>
<td>MF</td>
<td>400 - 600</td>
<td>×</td>
</tr>
<tr>
<td>Podgurski and Gonzales</td>
<td>28</td>
<td>MF</td>
<td>322 - 398</td>
<td>☼</td>
</tr>
<tr>
<td>Lord and Beschers</td>
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<td>IF</td>
<td>163</td>
<td>⋆</td>
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<td>IF</td>
<td>91 - 162</td>
<td>○</td>
</tr>
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<td>Guillet and Hocheid</td>
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<td>IF</td>
<td>90 - 148</td>
<td>●</td>
</tr>
<tr>
<td>Thomas and Leak</td>
<td>20</td>
<td>IF</td>
<td>18.5 - 58.5</td>
<td>□</td>
</tr>
<tr>
<td>Wert</td>
<td>30</td>
<td>IF</td>
<td>-29 - 31</td>
<td>+</td>
</tr>
<tr>
<td>Fast and Verrijp</td>
<td>26</td>
<td>IF</td>
<td>10 - 21.5</td>
<td>▼</td>
</tr>
<tr>
<td>Wert and Keefer</td>
<td>31</td>
<td>EAE</td>
<td>-35 - 25</td>
<td>○</td>
</tr>
<tr>
<td>Bosman</td>
<td>32</td>
<td>PAE</td>
<td>-39</td>
<td>●</td>
</tr>
<tr>
<td>Maringer</td>
<td>33</td>
<td>MAE</td>
<td>-47 - 31.5</td>
<td>●</td>
</tr>
</tbody>
</table>
given in Fig. (2). This plot again shows a positive deviation from Arrhenius behavior as $T$ increases but the deviation is smaller than in the case of the Fe-C system.

The 52 data points were analyzed in the manner described for the Fe-C system with the result,

$$\ln D = -4.485 - 0.9979 x + 0.0014 x^2 \quad \text{.........(3)}$$

with a mean square deviation of 0.030. The low temperature range was taken to be less than 500°C and these 24 data points can be represented by,

$$\ln D = -6.676 - 0.8858 x \quad \text{.........................(4)}$$

with a mean square error of 0.037. The corresponding diffusion parameters are

$$D_0 = 1.26 \times 10^{-3} \text{ cm}^2/\text{sec and } Q = 17.54 \text{ k.cal/mole}$$

The coefficient of the quadratic term in equation (1) (C) is about 2.5 x larger than that in equation (3) (N).

Discussion

Three models which have been proposed to explain the diffusion anomaly in the Fe-C system will be discussed in terms of the facts revealed in Figs. (1) and (2).
FIGURE 2. Plot of nitrogen diffusivity in bcc iron versus inverse of temperature.
a) Interstitial-Vacancy Complexes

A model was proposed by Homan (2) in which the enhanced diffusivity at high temperatures is due to the greater mobility of C-atoms combined with vacant sites in the iron lattice in comparison with isolated solute atoms. This concept has been criticized by Beshers (3) in a recent review of interstitial diffusion, and also by McLellan, Rudee and Ishibachi (4), on the grounds that radiation damage studies indicate that C-vacancy pairs would not be stable at the temperatures where the diffusion anomaly is seen (5). However, a persual of Fig. (1) indicates that the internal friction measurements made at higher temperatures do not follow the extrapolated low temperature internal friction and MAE data, but are consistent with the diffusivities measured by mass-flow techniques. Since only a small fraction of the C-atoms are combined with lattice vacancies, the interstitial-vacancy theory would seem to predict that the higher temperature internal friction data should follow the dashed line in Fig. (1). Even in the case of N (Fig. (2)), there is some indication that the higher temperature diffusivities determined by internal friction (§, ◇, ☇) are beginning to show a positive deviation from the dashed line which represents equation (4).

A further objection to the interstitial-vacancy model is that the diffusion anomaly occurs at temperatures where the vacancy concentration would seem to be much too low to account for the effects observed.
Neglecting a small vibrational entropy factor, the ratio of complexed to isolated solute atoms is,

\[ f = \alpha C_v e^{B/kT} \]  \hspace{1cm} (5)

where \( \alpha \) is an orientational parameter depending on the vacancy-interstitial geometry, \( B \) is the binding energy, and \( C_v \) is the concentration of lattice vacancies. Mehl, Swanson and Pound (6) have given a value of 49.0 k.cal/mole for the vacancy formation energy in iron. This estimate is in good agreement with that obtained by the elastic method of McLellan (4) and is about half the latent heat of sublimation. Using this value of the vacancy formation energy and the value of \( B = 9.5 \) k.cal/mole proposed by Homan (2), equation (5) yields the value \( f = 10^{-10} \) at 8000K and taking \( \alpha = 6 \).

At this temperature \( D \) for \( C \) in bcc Fe is already \( \sim 5 \) x larger than the extrapolated low temperature diffusivity. Even if a value of only 30 k.cals/mole were taken for the vacancy formation energy in iron, the corresponding value of \( f \) of \( \sim 10^{-5} \) would be difficult to reconcile with the observed behavior.

b) **Dual Site Occupancy**

McLellan, Rudee, and Ishibachi (4) proposed a model in which the enhanced diffusivity at high temperatures was due to the occupation of the energetically less favorable tetrahedral sites by a fraction of the solute atoms. This fraction increases with temperature and, assuming that direct jumps between tetrahedral sites are
characterized by a smaller activation energy than those between octahedral sites, leads to an enhanced diffusivity. A similar model has been considered by Condit and Beshers \cite{8}.

The weaker enhancement of diffusivity shown for N in Fig. (2), with respect to C, is qualitatively in agreement with the dual occupancy model. The thermodynamic data show that C is more tightly bound to the bcc lattice than N. The partial enthalpies with respect to an atom at rest in a vacuum are $\bar{H}_C = -144.1$ k.cal/mole and $\bar{H}_N = -74.3$ k.cal/mole \cite{9} and the partial molar volume ($\bar{V}_N = 5.9$ cm$^3$, $\bar{V}_C = 6.3$ cm$^3$) are such that $\bar{V}_C > \bar{V}_N$ \cite{10}, \cite{11}. Thus it is reasonably safe to assume that the energy needed to transport a C-atom from an octahedral site in bcc iron into a neighboring tetrahedral site would be less than the corresponding energy for an N atom. Thus the observed diffusion anomaly should be greater in the Fe-C system than in the Fe-N system.

However it is difficult to reconcile the dual occupancy model with the observation that the D-values measured by internal friction agree with the mass-flow measurements. Notice particularly the points (\# + \&) in curve (1). It should be mentioned that the dual occupancy of different sites by interstitial atoms is a thermodynamic necessity because of the very large change in partial configurational entropy occurring when a second sub-assembly of sites begins to be occupied. The only factor in question is the magnitude of this effect. There is some evidence that this dual site occupancy is reflected in the thermodynamic behavior of the Fe-H system where
the energy needed to transfer an H atom from a tetrahedral site to
an octahedral site may be quite small \cite{12}, \cite{13}.

c) The Ferromagnetic Model

Wuttig \cite{14} explained the diffusion anomaly in the Fe-C system
by writing the free energy change accompanying the motion of an atom
into a saddle point configuration in the form,

$$
\Delta G^* = (1-\delta) \Delta G_s^* + \delta \Delta G_{\text{mag}}^* \quad \cdots \quad (6)
$$

where $\Delta G_s^*$ is due to the elastic distortion, $\Delta G_{\text{mag}}^*$ is due to the
magnetic exchange energy, and $\delta$ is a coefficient denoting that frac-
tion of $\Delta G^*$ which is not an elastic energy. The activation entropy

$$
\Delta S^* = -\left(\frac{\delta \Delta G^*}{\delta T}\right)_p \quad \cdots \quad (7)
$$

thus should vary with temperature since $\delta$ is approximately given by
the saturation magnetization. This effect obviously leads to a
positive deviation in the Arrhenius plot of $\ln D$ vs. $1/T$. Furthermore the magnetic model is consistent with the fact that the dif-
fusion anomaly is much smaller for N than for C because the pseudo
dipolar interaction of N with the lattice atoms is only half as strong
as that for C.

Fig. (2) shows that the diffusivities obtained in the $\delta$-iron
region seem to be in excellent agreement with the linear extrapolation
of the high-temperature data. Because of the small differences in-
volved it is difficult to quantify such arguments, but the implication
is that after the Curie temperature $T_C$ is reached no further enhancement of $D$ occurs. This is in keeping with the magnetic model since $\Delta G^* \rightarrow \Delta G_s^*$ as $T \rightarrow T_C$. Unfortunately no $D$-data exist for $C$ in the $\delta$-iron range where the anomaly is much larger than in the case of $N$.

However, perhaps the strongest argument in favor of the magnetic model is that it provides for single-stage diffusion mechanism where the diffusivities obtained from mass-flow measurements should be in agreement with those assessed from internal friction data. Consider the points in Fig. (1). Beshers [3] has criticized the Wuttig model on the grounds that the pseudo dipolar interaction is too small to account for the difference observed between $N$ and $C$. However it must be pointed out that this difference is really quite small and in fact in the past the non-linearity in the $N$-data has been ignored.
References


23. Private communication, cited by Stanley in (15).


28. Private communication, cited (1).


CHAPTER V
THE SOLUBILITY OF HYDROGEN IN α-MANGANESE

Introduction

Manganese is an interesting element in respect to the solubility of hydrogen in metals in that the low-temperature modification (α) appears to act, in different temperature ranges, both as an endothermic and an exothermic occluder of hydrogen.

The early work of Sieverts and Moritz [1] showed the H-solubility in α-Mn rapidly decreasing with increasing temperature in the range 100 - 500°C and then slightly increasing in the range 500 - 680°C. Qualitative agreement with this behavior was found by Iwasë and Fukusima [2], and the later data of Potter and Lukens [3] are in good agreement with those of Sieverts and Moritz [1], except that the rapid increase in H-solubility at low temperatures (100 - 300°C) was not so pronounced. The data of Potter and Lukens [3] and Sieverts and Moritz [1] are depicted in Fig. (1). The symbols ◯ represent electrolytic manganese, the symbols □ refer to repeatedly vacuum distilled manganese, and the symbols ⊔ indicate the data of Sieverts and Moritz. The large degree of hysteresis found by Potter and Lukens [3] in the α→β phase transformation was also found by Sieverts and Moritz [1].

The present H-Mn solubility measurements were undertaken in order to clear up the discrepancies between the sets of data revealed in Fig. (1) and to determine whether or not the sign of ΔH_y, the relative partial enthalpy of H in α-Mn changes with temperature.
Experimental Procedure

The apparatus used to measure the hydrogen solubility is of the equilibrate-quench-analyze type and has been described previously in reports on the measurement of hydrogen solubility in Rh, Ru, Ir and Ni [4] and in Appendix I. The Mn used was of 99.97% purity and chips of irregular shape were employed. The chips, weighing between 0.5 gm and 2.5 gm were equilibrated in a stream of super pure hydrogen (nominal purity of 99.9995 vol. % and less than 1 ppm by volume of hydrocarbons) at 1 atm pressure. The equilibrated samples were quenched and analyzed. It should be noted that the samples were very brittle and the spot-welding of the thermocouple directly onto the sample in many cases caused hairline cracks to appear in the material. Such samples were immediately rejected. It was also found that other samples developed cracks in the process of handling. However such chips exhibited H-solubilities of 10 - 100 x the expected value and it was a simple matter to detect and reject them.

Since no data for the diffusivity of H in Mn are available, the equilibrations were performed for times ample to ensure saturation. This was checked by subsidiary experiments. The lowest-temperature equilibration was held for 14 hours (at 140°C).

Experimental Results

The solubility results found are given in Table I and depicted in Fig. (1) (●). The solubility unit θ is the number of solute atoms per solvent atom.

It can be clearly seen that the present data for α-Mn are in
<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$\Theta \times 10^4$</th>
<th>$\Theta \times T^{7/4}$</th>
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</thead>
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<td>625</td>
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</table>
FIGURE 1. Plot of hydrogen solubility versus temperature.
good agreement with those of Potter and Lukens (3) and the very sharp increase in solubility at low temperatures found by Sieverts and Moritz (1) has not been confirmed. The present data were combined with those of Potter and Lukens (41 data points) and a least squares regression was made in order to fit the data to the polynomial

\[ \ln \theta = a + bx + cx^2, \text{ where } x = 10^{\frac{\theta}{T}}. \]

The following result was found,

\[ \ln \theta = 1.3666 + 0.0335x - 0.00008x^2 \]

(1)

A similar regression using the data of Potter and Lukens (3) for \( \beta \)-Mn yields,

\[ \ln \theta = 5.0380 - 0.4487x + 0.0205x^2 \]

(2)

The mean-square deviations corresponding to equations (1) and (2) are 0.079, and 0.0084.

**Discussion of Results**

In order to estimate the change in the partial enthalpy of a dissolved H-atom with temperature, the data have been evaluated using the expression (5)

\[ \theta = \frac{\beta_0 P^{\frac{3}{2}}}{T^3/4} \exp \left( - \frac{H_{li} - \frac{1}{2}F_D^O}{kT} \right) \exp \left( \frac{\Sigma S_{li}xs}{k} \right) \]

(3)
where

\[
\lambda = \left[ \frac{h^3}{(2\pi mk)^{3/2}} \cdot \frac{2h^2}{8\pi^2 I_k} \cdot \frac{1}{k} \right]^{1/2}
\]  \(........................(4)\)

and \(h\) is Planck's constant, \(m\) the mass of the hydrogen atom, \(I\) the moment of inertia of the \(H_2\)-molecule, and \(-\frac{1}{2}E_0^0\) is the dissociation energy of the \(H_2\) molecule at \(0^\circ K\). The partial molar enthalpy of the solute atoms with respect to an atom at rest in a vacuum is \(\bar{A}_u\) and the partial excess entropy is \(\bar{S}_u^{xs}\). The factor \(\beta\) is the number of solute atom sites per solvent atom. If \(\bar{A}_u\) and \(\bar{S}_u^{xs}\) are assumed to be independent of temperature, plots of \(\ln \sigma T^{7/4}\) vs. \(1/T\) should be linear. The data represented in Fig. (1) with the exception of that due to Sieverts and Moritz is shown in Fig. (2) in the form of plots of \(\ln \sigma T^{7/4}\) vs. \(1/T\). The \(\alpha\)-Mn-range spans a wide range of \(1/T\) and it can be seen that there is a positive curvature in the plot. A least-squares regression yields the relationship,

\[
\ln (\sigma T^{7/4}) = 5.7570 - 0.1455x + 0.0020x^2 \quad \ldots \ldots \ldots \ldots (5)
\]

in the \(\alpha\)-range and

\[
\ln (\sigma T^{7/4}) = 9.5117 - 0.5485x + 0.0143x^2 \quad \ldots \ldots \ldots \ldots (6)
\]
FIGURE 2. Plot of $\ln \theta T^{7/4}$ versus inverse of temperature.
in the $\beta$-range.

The slope of these curves gives the instantaneous value of $R_u$ and the corresponding intercept gives the value of $S_{u}^{xs} / k + \ln \beta$.

Due to the complex structures of $\alpha$ and $\beta$ manganese and the lack of neutron scattering data, the positional information needed to make a choice for $\beta$ is not known. Thus it is impossible to extract unambiguous data for the excess entropies from the solubility data.

The values of $R_u$ and $S_{u}^{xs} / k + \ln \beta$ obtained from the relations (5) and (6) are shown in Fig. (3).

The variation of $(S_{u}^{xs} / k + \ln \beta)$ with temperature is shown in Fig. (3), in the dashed line. This variation, and of course that of $R_u$, may reflect the fact that different interstitial sites in the complex $\alpha$-Mn lattice are being occupied according to a temperature-dependent distribution function. The structure of $\alpha$-Mn is b.c.c. but each lattice point is associated with a cluster of 29 atoms.

Alternatively, the variation in $(S_{u}^{xs} / k + \ln \beta)$ and $R_u$ with temperature may reflect a fundamental change in the H-Mn-interaction with temperature. Such an idea is supported somewhat by the parallel behavior of the paramagnetic susceptibility of $\alpha$-Mn with respect to $R_u$.

The magnetic susceptibility {6}, shown by the curve (---) in Fig. (3).

The value of $\Delta R_u$ does indeed change sign as the temperature is varied. The values of $\Delta R_u$ have been calculated from the relation,

$$\Delta R_u = R_u - \frac{1}{2} E_0^{D} - 7/4 kT \hspace{1cm} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)$$
FIGURE 3. Plots of the variation of the partial molar enthalpy, partial excess entropy of solute and paramagnetic susceptibility with temperature.
The values of $\Delta R_u$ are numerically close to $\frac{3}{2}E_D^O$. The variation of $\Delta R_u$ with temperature is shown in Fig. (4).
FIGURE 4. Plot of the variation of the relative partial molar enthalpy with temperature.
References

APPENDIX I
EXPERIMENTAL DETERMINATION OF HYDROGEN CONTENT IN METALS

The technique used to measure the solubility of hydrogen in metals in equilibrium with \( \text{H}_2 \) gas at a pressure of one atmosphere is the equilibrate-quench-analyze procedure described previously in many investigations (1-5).

A schematic diagram of the equilibration and analysis apparatus is shown in Fig. 1. A Lepel high frequency generator was used to heat up the specimens to the desired equilibration and outgassing temperatures that were measured by a Pt - Pt 13% Rh thermocouple which served as support wires during equilibrations.

The calibration of the thermocouple made by Stafford (5) applies to this work because the same thermocouple wires were used and re-checked. From 300°C to 900°C the readings are 2-4°C (± 4.0°C established error limits for Pt - Pt 13% Rh thermocouple) lower than the reference thermocouple (chromel-alumel referenced to 0°C). At ~1500°C an extrapolation would show a deviation of 6-12°C (± 4.0°C).

The power control of the high frequency generator permitted to maintain the sample temperature within ± 5°C of the desired temperature.

The metallic samples weighing between 0.3 to 2.0 grams were equilibrated in a stream of super pure hydrogen (nominal purity of 99.9995 volume % and less than 1ppm by volume of hydrocarbons) at 1 atm. pressure and after allowing for equilibrium they were quenched in methanol
FIGURE 1: Apparatus used to determine hydrogen solubility in metals.
or distilled water at -0°C by a break seal mechanism.

The samples were then rinsed in acetone and left to dry.

The partial pressure of $\text{H}_2$ gas evolved from the sample during hot extraction in vacuum was measured and analyzed by a modified LECO Hydrogen Analyzer. This is the same apparatus used in investigations {1-5}.

According to the analyzer catalog

$$\theta = \frac{\Delta P \times K}{m} \times W$$

where

- $\theta$ = solubility, in atom ratio,
- $\Delta P = P_1 - P_2$ = partial pressure of $\text{H}_2$, in microns of column of mercury,
- $P_1$ = total pressure of gas after outgassing and before analysis,
- $P_2$ = remaining pressure after analysis,
- $K = K_S$ or $K_L$, calibration constants used in case of a small or large volume of storage,
- $m$ = actual sample weight, in grams,
- $W$ = atomic weight of the element of the sample.

The calibration of the apparatus was done using standard non-alloyed Ti chips charged with hydrogen obtained from the National Bureau of Standards.

The analysis of $\text{H}_2$ gas is made by passing it through hot CuO pretreated powder, converting it into moisture that is absorbed by fine anhydrite powder contained in the same circuit as the CuO.
The system was opened, cleaned, reassembled and calibrated
three times during the course of this work.
References