Report #1845
C00-3166-73

PERMEATION OF HYDROGEN THROUGH ANNEALED
AND DEFORMED IRONS

by

Albert Joseph Kumnick

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Ph. D. Thesis
August 1972

Research Group:
Prof. H. H. Johnson
MSE

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

peg

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

Acknowledgements

The author would like to thank Professor H. H. Johnson for serving as his major advisor and Professors M. S. Burton and J. H. Freed for their service as special committee members.

Thanks are accorded to members of the Cornell staff for their technical abilities. Among these are G. Chevalier, J. Benard, and B. Addis.

The author acknowledges the Atomic Energy Commission and the National Defense Education Act for their support of his graduate work.

The author would like to thank his parents and J. Tester for their encouragement at the time of the decision to attend graduate school.

Special thanks are due to F. Mandigo for his technical competence and ready willingness to be helpful and to R. Rowlands for maintaining a refreshing degree of levity within the lab.

The author is most indebted to his wife, Sharon, for her financial support, patience and hard work on the preparation of this thesis.

TABLE OF CONTENTS

<u>Chapter</u>		<u>Page</u>
I	INTRODUCTION	1
	A. General Remarks.	1
	B. Phenomenology of Hydrogen Embrittlement.	1
	C. Hydrogen-Iron System	2
	D. Low Temperature Anomalies in Solubility and Diffusivity--the Trapping Concept. . .	9
	1. Experimental Results	9
	2. Theory	11
	E. Purpose.	15
II	EXPERIMENTAL	17
	A. Material.	17
	B. Method	17
	C. Specimen Preparation	20
III	RESULTS AND DISCUSSION	22
	A. Experimental Parameters.	22
	1. Palladium.	22
	2. Typical Data Recorded and Reproducibility.	24
	3. Surface vs. Volume Control	29
	4. Method of Data Analysis.	29
	B. Annealed Iron.	35
	1. Electrochemical vs. Gas Phase Charging	35
	2. Effective Diffusivity and Permeation Rate.	37
	3. Trapping in Annealed Iron.	43

<u>Chapter</u>	<u>Page</u>
C. Deformed Iron.	49
D. Thermal Treatment of Deformed Iron . . .	60
IV CONCLUSIONS.	70
REFERENCES	71

LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Diffusion Data for Iron.	5
II	Product of Steady State Flux and Specimen Thickness	36
III	Hydrogen Concentration Data for Annealed Iron.	48
IV	Hydrogen Concentration Data for Deformed Iron.	59
V	Activation Energy for Diffusion and D_0 as a Function of Deformation	62
VI	Trapped Hydrogen Concentrations Due to Type 2 Traps Determined from Absorption Transients	67

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Strain rate and temperature dependence of ductility in charged and uncharged 1020 steel.	3
2	Solubility of hydrogen in iron.	7
3	Diffusion coefficient of hydrogen in iron	8
4	Permeation cell and electrical circuit.	19
5	Typical absorption transient.	25
6	Typical evolution transient	26
7	Successive absorption transients.	27
8	Successive evolution transients	28
9	Steady state flux as a function of inverse thickness	30
10	Absorption transients as a function of specimen thickness.	31
11	Representation of concentration calculations from absorption transient	34
12	Comparison of electrochemical and gas phase charging.	38
13	Comparison of experimental results with theory for annealed iron	39
14	Effective diffusivity as a function of reciprocal temperature	40
15	Steady state flux as a function of reciprocal temperature	42
16	Effective diffusivity as a function of specimen thickness for electrochemical charging.	44
17	Effective diffusivity as a function of specimen thickness for gas phase charging	46

<u>Figure</u>		<u>Page</u>
18	Absorption transients for annealed and deformed iron	50
19	Absorption transients for annealed and deformed iron	51
20	Evolution transients for annealed and deformed iron	52
21	Evolution transients for annealed and deformed iron	53
22	Comparison of experimental results with theory for deformed iron.	54
23	Effective diffusivity as a function of specimen thickness	56
24	Normalized effective diffusivity as a function of percent reduction	57
25	Average dislocation density as a function of percent strain in iron	58
26	Effective diffusivity as a function of reciprocal temperature for varying per- cent reductions	61
27	Effective diffusivity as a function of annealing temperature	63
28	Hardness as a function of annealing temperature	64
29	Hydrogen concentration as a function of annealing temperature.	66
30	Effective diffusivity as a function of annealing time	69

ABSTRACT

The influence of deformation and annealing on the permeation of hydrogen through iron was studied. An electrochemical technique with a resolution of 10^{-13} moles $\text{H}/\text{cm}^2\text{sec}$ was used to monitor the hydrogen flux over 5-60°C. Hydrogen entry was effected with either cathodic polarization or hydrogen gas at 1 atm. pressure.

The activation energy for hydrogen diffusion was found to be 4.2 ± 0.5 kcal/mole for well annealed material over the temperature range mentioned above. The disagreement with high temperature results is accounted for in terms of trapping. The activation energy measured for permeation was 8.9 ± 0.5 kcal/mole. A thickness effect of the effective diffusivity was also accounted for on the basis of a trapping.

The effective diffusivity decreases with increasing plastic deformation. However, the effect of plastic deformation anneals out over the temperature range 100-400°C. Isochronal annealing studies are reported. The activation energy for the annealing process was determined for isothermal measurements to range from 15-48 kcal/mole.

The product of the steady state flux and specimen thickness was found to be independent of specimen condition.

I. INTRODUCTION

A. General Remarks

The ease with which hydrogen moves into and through iron and iron alloys has been observed for many years. Claire Deville and Troost⁽¹⁾ first reported in 1863 that a mild steel tube initially pressurized with hydrogen lost pressure when heated to a higher temperature in air. Around 1890 Bellati and Lussana⁽¹⁾ observed a 20 atm. pressure rise in a closed iron vessel when the external surface was cathodically polarized in an acid solution.

The presence of hydrogen in iron and iron alloys is generally regarded as detrimental. Among the problems it causes are flakes or hair-line cracks in cast and hot-worked steels, small blowholes in cast iron, cold cracking in welded sections, anomalous ductility effects in TRIP steels⁽²⁾, delayed brittle failure of high strength steel, and perhaps some stress corrosion problems.

B. Phenomenology of Hydrogen Embrittlement

Of the problems caused by hydrogen, delayed brittle failure, which is one aspect of hydrogen embrittlement, has probably received the most attention in recent years. The great interest in hydrogen embrittlement is a direct result of the severe restrictions it places on the strength level of steel which can be safely used in engineering applications.

Johnson⁽³⁾ has summarized most of the well-documented

observations on hydrogen embrittled material. He makes a strong case for the concept that hydrogen segregation, and hence diffusion, must occur within the material during straining if it is to become embrittled. This concept is suggested by the unusual strain rate and temperature dependence of hydrogen embrittlement, Fig. 1. The degree of embrittlement is inversely proportional to the strain rate⁽⁴⁾. In the limiting case of the impact test, hydrogen has virtually no effect on a material, presumably because there is insufficient time for hydrogen diffusion.

The embrittlement is most pronounced at temperatures near 300°K, completely disappearing at both lower and higher temperatures. At low temperatures the diffusion rate is presumed too low to allow significant diffusion. At high temperatures the explanation is still somewhat controversial, but a plausible suggestion is that hydrogen diffuses out of the material at these temperatures. It is perhaps significant that hydrogen has a maximum embrittling effect in the same temperature range where anomalies in both hydrogen solubility and diffusivity, to be discussed later, have been reported.

C. Hydrogen-Iron System

Many studies of solubility and diffusivity in the hydrogen-iron system have been reported. Because of differences in experimental technique and in material composition and processing, results are often not easily compared or generalized, and so progress in forming a unified, co-

Figure 1: Strain rate and temperature dependence of ductility in charged and uncharged 1020 steel

hesive picture of the hydrogen-iron system has been slow. None the less, some aspects of this system have been characterized. Sievert's⁽⁵⁾ Law, shown below, is obeyed at temperatures above 400°C and at pressures up to 100 atmospheres,

$$C = SP^{1/2} \quad (1)$$

C = concentration of hydrogen

P = hydrogen pressure

S = constant of proportionality

which indicates hydrogen enters iron in a dissociated rather than molecular form, and that the internal hydrogen is in random solution in the lattice.

There is substantial evidence that hydrogen in solution occupies an interstitial lattice site. This is suggested by the rather large partial molal volume of hydrogen in iron, 2.0 cm³/g atom, and the diameter of the hydrogen atom, 1.06Å⁽⁶⁾. At 1.06Å, the hydrogen atom is much smaller than an iron atom and, therefore, unlikely to have such a large and positive partial molal volume if it existed on a substitutional lattice position. In addition, the pre-exponential term D_0 in the expression for the diffusivity has been calculated by Wert and Zener⁽⁷⁾ for hydrogen in iron to be 1.6×10^{-3} cm²/sec, assuming interstitial diffusion. This value agrees reasonably well with experimentally observed values for D_0 from high temperature results as shown in Table I⁽⁸⁻¹⁸⁾. Finally, both Heller⁽¹⁹⁾ and Gibala⁽²⁰⁾ have observed Snoek relaxation peaks for hydrogen.

TABLE I
Diffusion Data for Iron

Source	Year	Material Purity	Temperature Range °C	D_0 ($\text{cm}^2 \text{sec}^{-1}$)	ΔH_D (cal)	$D_{27^\circ\text{C}}$ ($\text{cm}^2 \text{sec}^{-1}$)	Method
Geller & Sun (8)	1950	"pure" iron	400-900	4.6×10^{-2}	2900	1.76×10^{-5}	permeability
Stross and Tompkins (9)	1966	99.96	150-900	8.85×10^{-4}	3050	5.55×10^{-5}	evolution rate
Eichenauer, Kunzig & Pebler (10)	1958	α iron	200-774	9.3×10^{-4}	2700	1.02×10^{-5}	evolution rate
Johnson and Hill (11)	1960	99.9	200-750 25-200	1.4×10^{-3} 1.2×10^{-1}	3200 7820	6.70×10^{-6} 2.71×10^{-7}	evolution rate
Bryan and Dodge (12)	1963	>99.9	126-693	3.9×10^{-4}	1080	6.43×10^{-5}	permeability
Devanathan, Stachurski, and Beck (13)	1963	Armco Iron	25°C			8.3×10^{-5}	permeability
Wagner and Sizmann (14)	1964	99.8	250-600	1.42×10^{-3}	3270	6.40×10^{-6}	permeability
McBreen (15)	1965	Armco Iron	10- 75	6.0×10^{-4}	1330	6.70×10^{-5}	permeability
Wach, Miodownik, and Mackowiak (16)	1966	>99.98	80-180	1.1×10^{-2}	3610	2.54×10^{-5}	permeability
Heumann and Primas (17)	1966	>99.98	300-900	6.42×10^{-4}	1920	2.63×10^{-5}	permeability
Subramanyan (18)	1970	99.99	10- 70	2.51×10^{-3}	2200	6.50×10^{-5}	permeability

For temperatures below approximately 400°C, conflicting results for hydrogen solubility and diffusivity have been reported. Hill and Johnson⁽²¹⁾ have reported positive deviations from Sievert's Law. In addition, they showed that at lower temperatures, measured solubilities were substantially greater than the values predicted by extrapolation of high temperature data, Fig. 2.

Diffusivity studies on iron have also produced a significant amount of scatter and controversy, as indicated in Table I, which presents most of the experimental results produced over the last 25 years. It is impossible at present to completely account for the deviation in the results of Table I, but a few general comments are in order. The scatter is greater than simple experimental error and cannot be accounted for on the basis of composition variation of material tested. Low temperature (i.e., near room temperature) diffusivity data is scarce and extremely contradictory. Hill and Johnson⁽¹¹⁾ observe an anomalous break in the diffusivity vs. inverse temperature plot as shown in Fig. 3. This phenomenon was not observed by either Stross and Tompkins⁽⁹⁾ using a method similar to that of Hill and Johnson, or Bryan and Dodge⁽¹²⁾ using a quite different technique. In addition, the results shown in Table I show in general the measured diffusivities associated with permeability experiments to be larger than those associated with evolution experiments. This latter observation can be explained on the basis of the trapping concept which will be

Figure 2: Solubility of hydrogen in iron

16

Figure 3: Diffusion coefficient of hydrogen in iron

discussed in the following section.

D. Low Temperature Anomalies in Solubility and Diffusivity--The Trapping Concept

1. Experimental Results

Hydrogen delay, or trapping, in iron was first suggested by the permeation and evolution experiments of Darken and Smith⁽²²⁾. Annealed material exhibited an evolution rate slower than the absorption rate for the same sample. They also observed a pronounced increase in the solubility of hydrogen with increasing plastic deformation. Subsequent annealing at 800°C was found to decrease the solubility from that of the cold worked state but did not return the material to its original hot rolled condition with respect to hydrogen solubility.

Keeler and Davies⁽²³⁾ studied changes in density and occlusive capacity for high purity iron, ingot iron, and SAE 1020 steel. They were unable to cite any clear general trends. The high purity iron showed neither a density decrease nor any change in hydrogen occlusion with cold reduction, while the ingot iron showed a density decrease but no change in hydrogen occlusion with cold reduction. The SAE 1020 showed both a density decrease and an increase in hydrogen occlusion with increasing cold reductions. Annealing studies were also conducted on the three materials with varying results. No effect was observed on high purity iron. Ingot iron showed a partial density recovery but no change in hydrogen occlusion capacity, while the SAE 1020 showed a

complete density recovery and decreased occlusive capacity for hydrogen after annealing at 900°C.

Hill and Johnson⁽²⁴⁾ studied the cold working of iron-carbon alloys and found an increase in hydrogen solubility and a decrease in the diffusivity at temperatures up to 400°C as a result. The effects were observed to be more pronounced with increasing carbon content and degree of deformation. Internal friction work by Gibala⁽²⁰⁾ on cold worked iron charged with hydrogen suggests that hydrogen is bound to dislocations as well as being in solid solution. Subramanyan and Bockris⁽²⁵⁾ have observed anomalous permeation transients for permeation of hydrogen through iron charged at high current densities and suggest the creation of traps during the permeation process as the cause. Hancock⁽²⁶⁾ has observed high hydrogen concentrations at grain boundaries and internal surfaces in iron-carbon alloys charged with hydrogen at high current densities.

The exact nature of trapping sites is unclear, although many alternatives have been proposed on the basis of experimental work. Darken and Smith⁽²²⁾ described the traps as imperfections in the lattice. Hill and Johnson⁽²⁴⁾ concluded that traps are microcracks in which the hydrogen is chemisorbed. As indicated earlier, Gibala's⁽²⁰⁾ work suggests that dislocations are trapping sites. Hancock⁽²⁶⁾ states that all structural irregularities should be considered as candidate trapping sites. This includes grain boundaries, dislocations, vacancy clusters, and internal in-

terfaces.

In addition to observing the trapping process and commenting on possible trapping sites, some of the previously mentioned workers have estimated the energy associated with a trap. Hill and Johnson⁽²⁴⁾ state a value of 9.4 kcal/mole. Gibala⁽²⁰⁾ found the hydrogen-dislocation binding energy to be 6.4 kcal/mole. Subramanyan and Bockris⁽²⁵⁾ suggest a value of 14 kcal/mole.

2. Theory

The first theory to consider hydrogen diffusion in the presence of trapping was presented by Darken and Smith⁽²²⁾, who applied concepts developed to analyze internal oxidation. The hydrogen trap was presumed analagous to an internal oxide particle. On this basis it was possible to rationalize an effective diffusivity which was smaller in evolution than absorption.

A much more analytical approach was developed by McNabb and Foster⁽²⁷⁾. They considered trapping in terms of a potential energy well. Two equations were derived to describe hydrogen transport in a lattice with trapping and hydrogen interchange between lattice and trapped populations as shown below:

$$\frac{\partial C}{\partial t} + N \frac{\partial n}{\partial t} = \text{div} (D \text{ grad } C) \quad (2)$$

$$\frac{\partial n}{\partial t} = kC (1-n) - pn \quad (3)$$

C = concentration of diffusing atoms at instant considered

t = time

N = density of traps

n = fraction of traps occupied

D = lattice diffusivity

k = trapping constant; k atoms are trapped per second when $C=1$ and there is unit concentration of vacant traps

p = trapping constant; p atoms are released per second per unit volume from a region containing a unit concentration of occupied traps

The first equation is Fick's second law, modified to account for trapping by the additional term $N \frac{\partial n}{\partial t}$. The second equation describes the rate of interchange of hydrogen atoms between trapped and diffusing populations, and was derived from simple probability considerations.

The evaluation of the Foster and McNabb equations is not an easy task. Five unknowns must be evaluated in order to characterize a particular system. The five are N , D , k , p , and C_0 , where the first four are as described previously and C_0 is a reference concentration related to C by the equation shown below:

$$C = C_0 u \quad (4)$$

u = dimensionless concentration

A steady state permeation experiment could at best be used to determine C_0 , N , D , and the ratio k/p . Some form of decay rate experiment would be necessary to obtain independent values for k and p .

A most recent theory of hydrogen trapping is that developed by Oriani⁽²⁸⁾. This theory is really a reformulation of McNabb and Foster using the assumption of local equilibrium between hydrogen atoms in trapped sites (called extraordinary sites) and those in normal lattice sites (called ordinary sites). Mathematically this assumption is expressed as follows:

$$K = \frac{a_x}{a_L} \quad (5)$$

K = equilibrium constant

a_x = activity of hydrogen at an extraordinary site

a_L = activity of hydrogen at an ordinary site

$$a_i = \theta_i / (1 - \theta_i) \quad (6)$$

θ_i = fractional occupancy

For the case where no restraints are placed on the degree of coverage of extraordinary sites, the local equilibrium assumption leads to some simplification of the McNabb-Foster equations. This is primarily due to the fact that the ratio of the two trapping constants k and p can be expressed as follows:

$$\frac{k}{p} = \frac{K}{N_L} \quad (7)$$

K = equilibrium constant between ordinary and extraordinary sites

N_L = number of normal lattice sites per unit volume

If, however, the situation is such that a linear relationship between a_x and θ_x exists (i.e., $\theta_x \ll 1$), then the Oriani

treatment results in considerable simplification with regard to analyzing experimental data. Thus, when θ_x is very small, the true lattice diffusivity can be directly related to the diffusivity measured experimentally. For the case where the diffusivity is being measured from data on hydrogen permeability through a thin membrane of material, the following relationship holds:

$$D = D_L (1 + KN_x/N_L)^{-1} \quad (8)$$

D = diffusivity measured

D_L = true lattice diffusivity

K = equilibrium constant between ordinary and extraordinary sites

N_L = number of ordinary sites per unit volume

N_x = number of extraordinary sites per unit volume

This analysis also accounts for the difference between absorption and evolution behavior. The diffusivity measured for absorption is given by Oriani as $D = D_L C_L (C_T - \theta_x C_x)$ while that for evolution is $D = D_L C_L / C_T$. Hence, the predicted D (evolution) < D (absorption), as is observed experimentally.

Ellerbrock et.al.⁽²⁹⁾ have also developed a model to account for hydrogen trapping. The traps are assumed to be cavities into which hydrogen precipitates, and the following equation is said to apply:

$$\frac{\partial(C_1 + C_2)}{\partial t} = \text{div} (D \text{ grad } C_1) \quad (9)$$

C_1 = lattice hydrogen concentration

C_2 = cavity hydrogen concentration

t = time

D = lattice diffusivity

Using numerical methods on the above equation, Ellerbrock et.al.⁽²⁹⁾ have shown how the diffusivity calculated by rise time techniques will in general be smaller than the true lattice diffusivity. The difference between these two values is a function of temperature, total hydrogen concentration, pore volume, and degree of ideality assumed for hydrogen gas. At high temperatures the difference is small, independent of the other parameters involved. Near room temperature, the difference increases with increasing total hydrogen concentration and pore volume, and decreases as hydrogen deviates from an ideal gas.

E. Purpose

The purpose of this work is to better characterize the trapping of hydrogen in iron by studying the influence of room temperature deformation and annealing on the permeation of hydrogen through thin sheets of iron in the vicinity of room temperature.

Deformation causes alteration of the trap density while annealing studies may indicate the nature of the trap. In addition, some of the predictions of presently available theories can be tested.

To avoid hydrogen-induced structural damage during permeation, it was thought desirable to use small hydrogen fluxes. This minimizes the possibility of void or blister formation. The required sensitivity was obtained with an

electrochemical technique for measuring the hydrogen flux.

II. EXPERIMENTAL

A. Material

The material chosen for this study is a commercially available, reasonably high-purity iron designated Armco Ingot Iron H P. The as-received material was in sheet form, .080 inches thick, with actual composition as given below:

<u>Element</u>	<u>%</u>	<u>Element</u>	<u>%</u>
Carbon	.019	Nickel	..01-.05
Manganese	.01-.1	Molybdenum	<<.01
Phosphorus	.012	Silicon	<.01
Sulfur	.004	Iron	balance
Copper	.01-.1		

B. Method

The entry side of the membrane is exposed to hydrogen, either from the gas phase or by cathodic polarization; the amount of hydrogen coming through the exit side is measured as a function of time. The hydrogen is measured electrochemically by maintaining the exit side of the specimen at a constant anodic potential of +100 mV vs. standard calomel electrode with the aid of the Wenking electronic potentiostat. At the above potential any hydrogen reaching the exit surface is ionized. The current necessary for ionization of hydrogen without change in the potential of the specimen is supplied by the potentiostat. This current is a direct measure of the amount of hydrogen coming through the specimen and is recorded as a function of time with a Keithley Electrometer and Esterline Azas strip chart recorder. The

specimen has a constant cross-sectional area, thus the current can be converted to a current density and, using Faraday's Law of Electrolysis, expressed as a hydrogen flux using the following relation:

$$10^{-6} \text{ amp/cm}^2 = 1.04 \times 10^{-11} \text{ moles H/cm}^2 \text{ sec} \quad (10)$$

Fluxes as low as 10^{-13} moles H/cm²sec can be easily detected.

A schematic of the permeation cell and electrical circuit is shown in Fig. 4 for the case in which hydrogen is produced by cathodic polarization. When hydrogen gas is used to supply hydrogen to the membrane, no power supply or Pt electrode is needed. Hydrogen is simply allowed to flow into the cell.

The permeation cell consists of two 3-necked, spherical pyrex flasks which have a volume of 200 ml. They are connected to the specimen using flanged tubing with Viton o-rings. The specimen area exposed is about 1.2 square cm. Stirring of solutions is accomplished by bubbling nitrogen (99.99% pure) through the cell. Temperature control is accomplished by wrapping Calorex tubing (8 mm size) around the flasks and pumping water at the desired temperature through it. The temperature of the specimen can be varied from 5°-60°C and controlled to within $\pm 0.5^\circ\text{C}$. The water temperature is maintained with the aid of a Fisher Proportional Temperature Controller.

The solution used in the anodic compartment and cath-

SCHEMATIC OF PERMEATION CELL AND ELECTRICAL CIRCUIT

Figure 4: Permeation cell and electrical circuit

odic compartment when cathodic polarization was employed was .1 N sodium hydroxide. This solution was made with analytical reagent grade sodium hydroxide and Fisher double distilled water. The solutions were always de-aerated with nitrogen before use.

C. Specimen Preparation

As received material was first annealed at 850°C for four hours in Sen/pak heat treating containers. This technique allowed a reasonably large batch of material to be handled at one time without excessive oxidation. Various thicknesses and degrees of plastic deformation were obtained by cold rolling. Subsequent anneals of smaller amounts of material at 400°C and above were performed in vacuum at $<10^{-5}$ torr. Lower temperature anneals were performed in oil or molten salt baths.

After suitable heat treatment and/or plastic deformation, specimens were cut into squares approximately 2.5 cm on a side. They were then chemically polished using a one to two mixture by volume of hydrogen peroxide (30%) and phosphoric acid. Specimens subjected to only electrochemically produced hydrogen were then Pd plated on one side by placing a few drops of Pallamarse solution on the surface. This Pd coating protects the specimen from severe corrosion resulting from the imposed anodic polarization without hindering the flow of hydrogen. Specimens charged from the gas phase or by both gas phase and electrochemically produced hydrogen were plated on both sides with Pd. These

specimens were immersed in a warm solution (70°C) of 50% HCl and water after chemical polishing, rinsed quickly, then dipped in Pallamarse. Plating of both surfaces was found necessary for gas charging to be consistently reproducible.

III. RESULTS AND DISCUSSION

A. Experimental Parameters

1. Palladium

It is important to establish that the hydrogen flux is not influenced by the palladium applied to one or both sides of a specimen before permeation. Exit surfaces of all specimens were plated to retard the corrosion reaction which would occur upon exposure of iron to the anodic potential necessary to completely ionize the hydrogen reaching this surface. The plating does not appreciably alter the transport of hydrogen because it is very thin ($\approx 10^{-5}$ cm) and because Pd has a much higher solubility for hydrogen than does iron⁽³⁰⁾. An order of magnitude calculation for comparison of the potential flux across the Pd layer as compared with that across the specimen can be computed and thus show the Pd layer is not flux limiting. The steady state flux can be represented as follows⁽¹⁵⁾:

$$J_{\infty} = D \frac{C_0}{L} \quad (11)$$

	Fe	Pd
$D \text{ cm}^2/\text{sec}$	$\approx 10^{-5} \text{ (17)}$	$\approx 10^{-7} \text{ (31)}$
$C_0 \text{ arbitrary limits}$	1 (30)	100 (30)
$L \text{ cm}$	10^{-1}	10^{-5}

$$\frac{J_{\infty Pd}}{J_{\infty Fe}} = \frac{10^{-7}(100/10^{-5})}{10^{-5}(1/10^{-1})} = 10^4$$

Pd plating of the entrance surface makes gas phase charging consistently reproducible. The exact explanation for this situation is not clear and warrants further study. The most plausible explanation seems to be that in the absence of palladium, a film (possibly an oxide layer) forms on the surface and prevents hydrogen transport from the gas phase. An inhibiting influence of oxygen upon hydrogen transport into the gas phase has been demonstrated⁽³¹⁾.

Pd plating of the entrance surface for electrolytic hydrogen charging is not necessary, but when done, results in higher steady state flux values than in a similar specimen with no plating. Presumably the hydrogen produced electrochemically has a sufficiently high chemical potential or fugacity so as not to be affected by a slightly unclean entrance surface. The explanation of the higher fluxes with, than without, Pd plating is believed to be analagous to that for greater hydrogen transport into materials charged from solutions containing arsenic (As)⁽³³⁾. While studying the increased permeation of hydrogen through AISI 1010 steel charged from As containing solutions, McCright⁽³⁴⁾ found that the arsenic actually plated out onto the surface of the steel. It was thought to inhibit the recombination of hydrogen atoms to gaseous hydrogen and thus promote more absorption of hydrogen into the material being charged.

2. Typical Data Recorded and Reproducibility

The typical permeation curve has three distinct regions, Fig. 5. The first is the breakthrough time, whose length depends on diffusivity, the sensitivity of the measuring system, and thickness of the specimen. The second is a transient region showing an increase of hydrogen flux with time, while the third region shows a steady state situation. This steady state region is associated with a stable hydrogen concentration profile within the membrane; the magnitude of the steady state flux depends on lattice diffusivity, concentration of lattice hydrogen at the entrance surface, and thickness of the specimen, as indicated in Equation 11. If the cathodic current is interrupted or the hydrogen gas removed from the entrance surface, the evolution behavior observed at the exit surface is shown in Fig. 6.

Successive absorption and evolution transients recorded on the same specimen show good reproducibility as shown in Figs. 7 and 8 respectively. This suggests traps are not being introduced or enlarged during charging and is in contrast to some other works^(16,35) reporting a need to pre-charge with hydrogen to obtain consistent results. However, during both pre-charging and actually testing the current density and sulphuric acid concentration used in these other studies were higher than those at which McBreen⁽¹⁵⁾ observed anomalous absorption permeation transients. This suggests the possibility of a change in the initial trap structure of

Figure 5: Typical absorption transient

Figure 6: Typical evolution transient

Figure 7: Successive absorption transients

Figure 8: Successive evolution transients

the material during permeation if the charging conditions and associated fluxes are unnecessarily severe.

3. Surface vs. Volume Control

It is important to ascertain whether the measured permeation parameters are controlled by volume diffusion or surface processes. A suitable test is the measurement of the steady state flux as a function of the thickness L ; for volume control there should be a linear relation between the steady state flux and L^{-1} as shown in Equation 11. The results are shown in Fig. 9 for electrolytic hydrogen charging at 1.75 mA/cm^2 and gas phase charging at unit hydrogen partial pressure, indicating a diffusion controlled process.

If the thickness of the material is varied, the time involved and the steady state flux change, but the basic shape of the curve remains the same. Absorption permeation curves for three different thicknesses of annealed material charged with electrolytic hydrogen are shown in Fig. 10.

4. Method of Data Analysis

Since the process is diffusion controlled, an analysis of an absorption permeation transient, under the assumption that the transport of hydrogen obeys Fick's Law, allows the calculation of an effective diffusivity of hydrogen in iron. The boundary and initial conditions for this experimental geometry for hydrogen absorption are shown below⁽¹⁵⁾:

$$\begin{array}{lll} C = C_0 & x=0 & t \geq 0 \\ C = 0 & x=L & t \geq 0 \\ C = 0 & 0 < x < L & t < 0 \end{array}$$

Figure 9: Steady state flux as a function of inverse thickness

Figure 10: Absorption transients as a function of specimen thickness

The situation can be represented by Fick's second law for constant diffusivity as⁽¹⁵⁾:

$$\frac{\partial^2 C}{\partial x^2} - \frac{1}{D} \frac{\partial C}{\partial t} = 0 \quad 0 < x < L \quad (12)$$

Using the method of Laplace transforms on the above equation for the existing initial and boundary conditions, a series solution is obtained. The first term of this series gives results valid within 2% up to 96.5% attainment of the steady state permeation, and the time required to reach a certain fraction of steady state can be used to calculate the effective diffusivity. For example, when the flux reaches 83% of its steady state value, the following expression for the effective diffusivity is valid:

$$D_{\text{eff}} = \frac{.25L^2}{t_{83\%}} \quad (13)$$

The term effective diffusivity is used because later results will show this is not the true lattice diffusivity.

The activation energies for hydrogen diffusion and for hydrogen permeability can be calculated from permeation measurements at different temperatures. In addition, it is possible to calculate C_0 from the lattice diffusivity, the steady state flux, and the thickness of the specimen as shown in Equation 11.

It should also be possible to analyze evolution transients and get similar values to those predicted from absorption transients. The evolution situation, however, is somewhat complicated because the boundary condition at the en-

trance surface is not well defined when hydrogen charging is stopped. The two extremes for this boundary condition are that the concentration becomes zero immediately on the entrance surface, or that there is no flux of hydrogen across the entrance surface. The first of these extremes predicts a faster decay than the second one. Experimentally, the evolution occurs more slowly than predicted by either boundary condition, indicating the presence of traps and a smaller diffusivity than predicted from absorption transients. This latter result illustrates that calculated diffusivities are effective rather than true lattice diffusivities and agrees with predictions that the hydrogen transport process at low temperatures is not completely described by Fick's laws. This topic will be discussed in more detail in subsequent sections.

Absorption and evolution transients can be used to obtain additional information about the hydrogen concentration within the specimen. In the case of absorption transients, the situation is illustrated schematically in Fig. 11. Curve 1 is a typical, experimentally measured absorption transient, while curve 2 represents the result which would be measured in the absence of trapping (i.e., only lattice diffusion). The area between these curves, which is labeled region A in Fig. 11, is a measure of the trapped hydrogen concentration in the specimen. The units of the area are amp sec/cm^2 , which converts to a concentration when divided by the product of the specimen thickness and the

Figure 11: Representation of concentration calculations from absorption transient

Faraday constant. The fact that this area is directly proportional to the trapped hydrogen concentration will be used in the analysis of later results.

The results of Carslaw and Jaeger⁽³⁶⁾, modified for diffusion, or McBreen et.al.⁽³⁷⁾ can be used to calculate the concentration of lattice soluble hydrogen if the true lattice diffusivity of hydrogen in iron and the input hydrogen concentration are known. The region labeled 2 in Fig. 11 represents this calculation schematically. The area under evolution curves is a measure of the total (i.e., lattice plus trapped) hydrogen leaving the exit surface of the specimen.

On the basis of all of the available models for hydrogen transport, the steady state flux should be described by Equation 11 independent of the condition or microstructure of the material. Physically this means that the lattice and trapped hydrogen are in equilibrium at steady state. Thus, the product of the flux and the thickness of the iron should be a constant for constant charging conditions independent of the condition of the material. The experimental results are shown in Table II for specimens of varied mechanical and thermal histories. The average value of $J_{\infty}L$ within 95% confidence is $2.65 \pm .27 \times 10^{-13}$ moles/cmsec.

B. Annealed Iron

1. Electrochemical vs. Gas Phase Charging

As shown in Fig. 9, electrochemical charging in general results in larger hydrogen fluxes, presumably due to

TABLE II.

Product $J_{\infty} L$
 ($\times 10^{13}$ moles H/cm sec)

% Reduction at 300°K	No Anneal	100°C 1 Hr.	200°C 1 Hr.	300°C 1 Hr.	400°C 1 Hr.	600°C 1 Hr.	800°C 1 Hr.
8	1.26	2.62	2.79	2.77	3.40	5.05	2.89
40	3.10	4.24	2.62	2.56	2.79	3.70	3.72
50	2.39	2.84	2.25	2.25	2.29	3.48	3.17
63	2.28	2.33	2.15		2.02	2.91	2.49
75	1.68	2.12	1.72	2.06	1.66	1.85	2.16

$$\overline{JL} = 2.65 \pm .27 \times 10^{-13} \text{ moles H/cm sec}$$

95% confidence limits

the higher fugacity of electrochemical hydrogen. If the results are normalized, however, the absorption transients are similar for both methods of charging as shown in Fig. 12, where the ratio of the instantaneous flux to the steady state flux is plotted as a function of time for two specimens of different thickness. Despite the fact that the calculated or effective diffusivity shows an anomalous thickness effect, to be discussed later, the results for annealed materials are in reasonably good agreement with normalized theoretical results predicted by the first term of the Laplace transform solution for Fick's second law. These results are shown in Fig. 13.

2. Effective Diffusivity and Permeation Rate

A plot of effective diffusivity vs. reciprocal temperature is shown in Fig. 14 for three similar specimens, prepared and charged with hydrogen in the following manner:

- (1) Entrance surface not plated with Pd, charging current density = 1.75 mA/cm^2
- (2) Entrance surface plated with Pd, charging current density = 1.75 mA/cm^2
- (3) Entrance surface plated with Pd, hydrogen gas at unit partial pressure

A least squares fit of the data points gives an activation energy of $4.2 \pm .5 \text{ kcal/mole}$. This value is considerably higher than most values shown in Table I, and indicates that trapping is occurring in this annealed iron. Oriani⁽⁶⁾ predicts an activation energy of 1.9 kcal/mole in the absence of trapping.

The steady state flux was also observed as a function

Figure 12: Comparison of electrochemical and gas phase charging

Figure 13: Comparison of experimental results with theory for annealed iron

Figure 14: Effective diffusivity as a function of reciprocal temperature

of temperature and the results are shown in Fig. 15 for the three specimens described previously. A least squares fit of this data gives $8.9 \pm .5$ kcal/mole, which agrees reasonably well with much of the high temperature work in this area. Gonzalez⁽³⁸⁾ has recently summarized and statistically analyzed most of the available permeation data and arrives at an activation energy of $8.5 \pm .4$ kcal/mole within 90% confidence level between 130° and 900°C. Present results extend this temperature range down to 10°C.

The above results are in rather dramatic contrast with each other. The measured activation energy for diffusion is not in good agreement with literature values for lattice diffusion, while that for the steady state flux agrees reasonably well with literature values. This situation can be rationalized if we consider the difference in these two parameters. As mentioned earlier, measurement of the diffusivity involves the analysis of a structure sensitive property because of trapping. Hence, disagreement or scatter among different investigators can be expected. As mentioned earlier steady state permeation, however, is not influenced by trapping because at steady state the lattice and trapped hydrogen are in equilibrium and lattice diffusion is the dominant process. This is shown mathematically in the results of McNabb and Foster⁽²⁷⁾, Equation (2). Hence, it is not surprising that reasonable agreement with literature values for the permeation activation energy are obtained.

Figure 15: Steady state flux as a function of reciprocal temperature

3. Trapping in Annealed Iron

A puzzling but general observation is that specimen thickness has an effect on the diffusivity calculated from transient permeability experiments in which Fick's Law is assumed to be valid. Raczynski⁽³⁹⁾ found the diffusivity of mild steel to decrease with thickness at thicknesses below 0.09 cm, while it remained constant for thicknesses above 0.09 cm. He also observed a deviation from linearity of the steady state flux vs. inverse thickness plot. Radhakrishnan and Shreir⁽⁴⁰⁾, working with Swedish iron, found no thickness dependence of the diffusivity in as received material, but after annealing at 650°C for two hours, a substantial decrease of the measured diffusivity with decreasing thickness appeared. In both cases, the steady state flux varied linearly with the inverse thickness. Subramanyan⁽¹⁸⁾ showed Armco iron to exhibit a decrease of the effective diffusivity with decreasing thickness, while observing normal inverse thickness dependence of the steady state flux. Wach et.al.⁽¹⁶⁾ (also working with iron) have observed this same thickness dependence of the measured diffusivity.

In the present study, a pronounced decrease of the effective diffusivity with decreasing thickness was observed for annealed iron which had been reduced in thickness by room temperature rolling prior to annealing. This occurred independent of whether the material was annealed in the ferritic or austenitic region, as shown in Fig. 16, and is

Figure 16: Effective diffusivity as a function of specimen thickness for electrochemical charging

also observed for both electrochemical and gas phase charging, Figs. 16 and 17. However, the steady state flux was a linear function of inverse thickness for all charging and material conditions examined.

The earliest explanation for the thickness anomaly attributed it to surface control of the permeation process⁽⁴¹⁾, or damage to the specimen just below the surface layer by the action of hydrogen⁽⁴²⁾. Figure 9 shows the present results are representative of volume control and, in addition, the effect is observed for both gas phase and electrochemical charging. The reproducibility upon successive chargings shown in Figs. 7 and 8 is not compatible with a damaged surface layer.

A more recent and abstract explanation is due to Wach et.al.⁽¹⁶⁾ who postulated the formation of an "effective barrier" to hydrogen during the permeation process. This model can numerically correct much of the experimental data showing thickness effects, but the exact nature and real dimensions of the barrier are vague. As an explanation, it is in the same class as those postulating a surface layer of damaged material.

A probable explanation for the thickness effect is a higher density of traps in the thinner specimens; the traps presumably originate from cold working during material processing and are not removed by subsequent annealing. This concept is consistent with the data and observations cited earlier and is supported by an analysis of the present ab-

Figure 17: Effective diffusivity as a function of specimen thickness for gas phase charging

sorption and evolution transients for trapping behavior.

Comparison of absorption and evolution transients for the same specimen in all cases show a larger time constant for evolution than absorption. Hydrogen concentrations calculated from the area under evolution curves show an increase with decreasing thickness, indicating more trapping per unit volume as the specimen decreases in thickness. These results are shown in Table III.

Absorption transients were also used to measure trapping. The procedure involved the calculation of the area between two absorption curves as described earlier and shown in Fig. 11. Not knowing the true diffusivity for annealed iron, the effective diffusivity calculated for annealed iron .200 cm thick was used to generate absorption transients for different thickness specimens. The generated absorption transients were always to the left and above the experimentally measured transient; hence, the area between them was a measure of the increase of trapping with decreasing thickness. The trapped concentration calculated from these areas are also shown in Table III for comparison with concentrations calculated from evolution data. As before, the trapped concentration increases with decreasing thickness. The values measured from evolution data are larger than those measured from absorption data. This is to be expected because the evolution data measures both trapped and lattice hydrogen while the absorption data represents only the difference in trapping between two specimens. The absolute

TABLE III
Hydrogen Concentration Data for Annealed Iron

L (cm)	Hydrogen Conc. From Evolution Results ($\times 10^8$ atm fraction)	Trapped Hydrogen Conc. From Absorption Results ($\times 10^8$ atm fraction)
.188	4.1	0.5
.120	6.5	1.1
.102	9.4	1.2
.076	9.2	1.5
.049	21	1.8

accuracy of the concentration is probably only good to within a factor of 2, but the general trends are consistent.

Further support for the above reasoning is the very slight thickness dependence for material which was reduced by chemical polishing, Fig. 16.

C. Deformed Iron

Deformation greatly increased the hydrogen trapping capacity as measured by comparison of absorption and evolution transients with those of an annealed specimen of the same thickness. As received material .200 cm thick was first annealed (850°C, one hour in vacuum) and then, by rolling at room temperature, to varying degrees plastically deformed. Figures 18 and 19 show absorption transients for two different degrees of plastic deformation with a transient for a fully annealed specimen of the same thickness; evolution transients for the same specimens are shown in Figs. 20 and 21 respectively.

Effective diffusivities calculated for deformed material are much lower than those calculated for annealed material at the same thickness. In addition, greater deviation from the solution of Fick's Second Law for the experimental initial and boundary condition was observed, Fig. 22. The behavior of deformed material can be analyzed in terms of two species of traps; type 1 and type 2. Type 1 traps are the residual traps described earlier in the section on annealed iron. Type 2 traps are also deformation induced and, as will be described later, removed by annealing.

Figure 18: Absorption transients for annealed and deformed iron

Figure 19: Absorption transients for annealed and deformed iron

Figure 20: Evolution transients for annealed and deformed iron

Figure 21: Evolution transients for annealed and deformed iron

Figure 22: Comparison of experimental results with theory for deformed iron

The presence of type 2 traps causes the observed changes of the absorption and evolution transients from the annealed case.

The presence of type 2 traps also decreases the thickness anomaly. Four specimens were produced with different thicknesses, but the same percent reduction to final thickness. On the basis of the dual trap picture, these specimens should have an increasing density of type 1 traps with decreasing thickness, but nearly the same density of type 2 traps. The net result of this addition of type 2 traps is a higher, more uniform total trap density. This model agrees with the smaller and less thickness dependent effective diffusivity shown in Fig. 23.

The rather qualitative discussion so far of increased trapping with deformation is supported by a reasonable amount of quantitative information. The effect of deformation on the effective diffusivity is shown in Fig. 24. The ordinate of this plot is a ratio of effective diffusivities to eliminate the thickness effect caused by type 1 traps. This curve is compatible with dislocation density vs. percent strain measurements made by Keh, Fig. 25, suggesting that dislocations are the source of trapping behavior. Calculation of hydrogen concentration from hydrogen evolved at the exit surface shows an increase with increasing deformation, Table IV. Trapped hydrogen concentrations from absorption data also show similar trends, Table IV. As expected from Oriani's predictions, the activation energy mea-

Figure 23: Effective diffusivity as a function of specimen thickness

Figure 24: Normalized effective diffusivity as a function of percent reduction

Figure 25: Average dislocation density as a function of percent strain in iron

TABLE IV
Hydrogen Concentration Data for Deformed Iron

Percent Reduction	Hydrogen Conc. From Evolution Results ($\times 10^7$ atm fraction)	Trapped Hydrogen Due To Deformation From Absorption Results ($\times 10^7$ atm fraction)
8	1.6	0.8
40	4.8	2.5
50	5.6	4.8
62	8.0	5.9
75	8.5	12

sured from the effective diffusivity vs. inverse temperature increases with increasing deformation, Fig. 26. Table V shows the values of the activation energy and the pre-exponential term, D_0 , as a function of percent reduction.

D. Thermal Treatment of Deformed Iron

Deformation induced changes in the permeability of iron to hydrogen are readily altered by subsequent annealing. The effective diffusivity is plotted as a function of annealing temperature in Fig. 27. Two types of behavior are observed. At low temperatures (i.e., $<400^\circ\text{C}$), the effective diffusivity changes rapidly with temperature, while above 500°C it changes only slightly. On the basis of hardness vs. annealing temperature curves, Fig. 28, the most drastic change of the effective diffusivity is associated with the recovery stage of the annealing process. The slight change of the effective diffusivity with annealing temperature above the recrystallization temperature can be rationalized. Change of temperature in this region produces only slight alteration of grain size, which McBreen⁽¹⁵⁾ found to be a minor factor in influencing permeation behavior. Annealing above the recrystallization temperature, however, did return the pronounced thickness effect discussed earlier, Fig. 23. The effect persists to very high temperatures, also shown in Fig. 23.

Hydrogen concentrations calculated from absorption and evolution data exhibited a decrease with increasing annealing temperature. As in the case of the effective diffusivity,

Figure 26: Effective diffusivity as a function of reciprocal temperature for varying percent reductions

TABLE V
Activation Energy for Diffusion and D_0 as a
Function of Deformation

Percent Reduction	ΔH (kcal/mole)	D_0 cm ² /sec
0	4.2±.5	1.4±.3x10 ⁻²
40	5.2	1.2 x 10 ⁴
75	7.8	3.9 x 10 ⁶

Figure 27: Effective diffusivity as a function of annealing temperature

Figure 28: Hardness as a function of annealing temperature

the most pronounced change occurred below 400°C. Concentrations calculated from the area under evolution curves are shown as a function of annealing temperature in Fig. 29. The trapped concentration of hydrogen above that for fully annealed material was calculated from absorption transients as described earlier; the results are shown in Table VI.

The behavior noted above is consistent with a dual trap argument. The changes brought about by deformation are the result of the creation of type 2 traps which are sensitive to annealing. On the basis of the temperature range involved and other physical tests conducted on this iron, some possibilities for type 2 traps have been eliminated. Electrical resistivity measurements at 78°K show no significant change with annealing below 400°C, suggesting that type 2 traps are not point defects. Also, Cuddy⁽⁴⁴⁾ found vacancies introduced by deformation at 78°K annealed out below room temperature. Within 1 part in 10^4 , this material does not exhibit a density change during plastic deformation, thus it seems unlikely that the coalescence of microvoids could be causing the observed behavior. Ellerbrock et.al.⁽²⁹⁾ have suggested that void volumes below the detection limits of our density apparatus could account for significant trapping. The hydrogen concentration required for this, however, is much higher than that used in the experiment.

The activation energy for the process which is occurring at these lower annealing temperatures has been measured by performing isothermal annealing tests on material deformed

Figure 29: Hydrogen concentration as a function of annealing temperature

TABLE VI

Trapped Hydrogen Concentration ($\times 10^7$ atm fraction) Due to
Type 2 Traps From Absorption Transients

Percent Reduction	Cold Worked	200°C 1 Hr.	400°C 1 Hr.	600°C 1 Hr.
8	.8	.2	.01	0
40	2.5	.3	.1	0
50	4.8	.6	.1	0
62	5.9	3.3	.2	0
75	12.5	3.6	.4	0

75%. The effective diffusivity was measured as a function of time and temperature, as shown in Fig. 30. Using the method of cross-cut⁽⁴⁵⁾, the calculated value for the activation energy ranged from 15 to 48 kcal/mole, indicating a non-singly activated process. These values are similar to those obtained by Michalak and Paxton⁽⁴⁶⁾ on recovery studies in polycrystalline iron, which also suggests that the removal of traps created by rolling at room temperature is closely connected with the recovery process.

It appears probable that the number and arrangement of dislocations are important in determining the extent of trapping. This is based primarily on the comparison of the present work with that by Keh⁽⁴³⁾. As mentioned earlier, the effective diffusivity vs. percent reduction plot resembled the dislocation density vs. percent strain plot of Keh⁽⁴³⁾. Keh⁽⁴³⁾ also found joggy and nonuniformly distributed dislocations in deformed material, while fully recovered iron exhibited dislocation networks in regular arrays. These observations can account for the changes in the permeation behavior of deformed material with low temperature annealing. Joggy and nonuniformly distributed dislocations are very active trapping sites for hydrogen, but the change to dislocations networks in regular arrays with low temperature anneals reduces this number of trapping sites; hence, the observed changes in effective diffusivity and trapped hydrogen concentration. Detailed electron microscopy of the iron used in this study would of course be necessary to completely substantiate this line of reasoning.

Figure 30: Effective diffusivity as a function of annealing time

IV. CONCLUSIONS

1. Gas phase (H_2 at 1 atm pressure) and electrochemical (from .1N NaOH solution at 1.75 mA/cm^2) charging produce similar hydrogen permeation behavior in thin iron sheets.
2. Hydrogen trapping occurs in both annealed and deformed Armco Iron HP over the temperature range 5-60°C.
3. Two species of traps seem to exist. Both type 1 and type 2 are deformation induced; type 2 are easily removed by annealing while type 1 are not affected by annealing.
4. Room temperature deformation substantially increases the amount of hydrogen trapped and decreases the effective diffusivity. These results are reversible with annealing.
5. Evidence exists for suggesting that type 2 trapping is caused by dislocations.
6. The steady state flux through a given thickness of material within the accuracy of the experiment is not a function of the microstructure or condition of the material.

REFERENCES

1. M. Smialowski, Hydrogen in Steel, Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962.
2. E. Gold and T. J. Koppenaal, Trans. A.S.M., 62, 607 (1969).
3. H. H. Johnson, Proceedings of the Symposium on Stress Corrosion, Columbus, Ohio (September 1967).
4. E. E. Fletcher and A. R. Elsea, "Hydrogen Movement in Steel--Entry, Diffusion, and Elimination", DMIC Report 219, June 30, 1965.
5. A. Sieverts, Z. Metallkunde, 21, 37 (1929).
6. R. A. Oriani, Proceedings of the Symposium on Stress Corrosion, Columbus, Ohio (September 1967).
7. C. Wert and C. Zener, Phys. Rev., 76, 1169 (1949).
8. W. Geller and T. H. Sun, Arch. Eisenhuttenw., 21, 423 (1950).
9. T. M. Stross and F. C. Tompkins, J. Chem. Soc., 230 (1956).
10. W. Eichenauer, H. Kunzig and A. Pebler, Z. Metallk., 49, 220 (1958).
11. E. W. Johnson and M. L. Hill, Trans. Met. Soc. AIME, 218, 1104 (1960).
12. W. L. Bryan and B. F. Dodge, A.I.Ch. E. Journal, 9, 223 (1963).
13. M.A.V. Devanathan, Z. Stachurski, and W. Beck, J. Electrochem. Soc., 110, 886 (1963).
14. R. Wagner and R. Sizmann, Z. Angew. Phy., 18, 193 (1964).
15. J. McBreen, Ph.D. Thesis, University of Pennsylvania, 1965.
16. S. Wach, A. P. Miodownik, and J. Mackowiak, Corrosion Science, 6, 271 (1966).

17. Th. Heumann and D. Primas, Z. Naturforsch, 21A, 260 (1966).
18. P. K. Subramanvan, Ph.D. Thesis, University of Pennsylvania, 1970.
19. W. R. Heller, Acta. Met., 9, 600 (1961).
20. R. Gibala, "Internal Friction in Hydrogen-Charged Iron", Report from Case Institute of Technology, Cleveland (1967).
21. E. W. Johnson and M. L. Hill, Trans. Met. Soc. AIME, 221, 622 (1961).
22. L. S. Darken and R. P. Smith, Corrosion, 5, 1 (1949).
23. J. H. Keeler and H. M. Davis, Journal of Metals, 5, 44 (1953).
24. M. L. Hill and E. W. Johnson, Trans. Met. Soc. AIME, 215, 717 (1959).
25. J. O'M. Bockris and P. K. Subramanyan, J. Electrochem. Soc., 1114 (1971).
26. G. G. Hancock, Ph.D. Thesis, Cornell University, 1968.
27. A. McNabb and P. K. Foster, Trans. Met. Soc. AIME, 227, 618 (1963).
28. R. A. Oriani, Acta Met., 18, 147 (1970).
29. H. G. Ellerbrock, G. Vibrans, and H. P. Stuive, Acta Met., 20, 53 (1972).
30. F. A. Lewis, The Palladium Hydrogen System, Academic Press, New York, 1967, p. 7.
31. M.A.V. Devanathan and Z. Stachurski, Proc. Roy. Soc., A270, 90 (1962).
32. V. C. Ewing and A. R. Ubbelohde, Proc. Roy. Soc., A230, 301 (1955).
33. T. P. Radhakrishnan and L. L. Shreir, Electrochimica Acta, 11, 1007 (1966).
34. R. D. McCright, personal communication.
35. S. Wach, Br. Corros. J., 6, 114 (1971).
36. H. S. Carslaw and J. C. Jaeger, Conduction of Heat in Solids, Oxford University Press, Ely House, London, 1959.

37. J. McBreen, L. Nanis, and W. Beck, J. Electrochem. Soc., 113, 1219 (1966).
38. O. D. Gonzalez, Trans. Met. Soc. AIME, 245, 607 (1969).
39. W. Raczynski, Arch. Hutnictiva, 3, 59 (1958).
40. T. P. Radhakrishnan and L. L. Shreir, Electrochimica Acta, 12, 889 (1967).
41. H. R. Heath, Brit. J. Appl. Phys., 3, 13 (1952).
42. A. Krupkowski and M. Smialowski, Arch. Hutnictiva, 1, 101 (1956).
43. A. S. Keh, Direct Observation of Imperfections in Crystals, J. B. Newkirk and J. H. Wernick, Eds., Interscience, New York, 1962, p. 213.
44. L. J. Cuddy, Acta Met., 16, 23 (1968).
45. W. E. Parkins, G. J. Dienes, and F. W. Brown, J. Appl. Phys., 22, 1012 (1951).
46. J. T. Michalsk and H. W. Paxton, Trans. Met. Soc. AIME, 221, 850 (1961).