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GAS PHASE HYDROGEN PERMEATION
THROUGH FERRITIC IRON, AUSTENITIC STAINLESS STEEL
AND NEUTRON IRRADIATED AUSTENITIC STAINLESS STEEL
FROM NEAR 300°K TO 873°K

by

Nathaniel Richard Quick

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Ph.D. Thesis
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ABSTRACT

Hydrogen permeation through iron was studied over the temperature range 300-873°K by an ultra high vacuum, monopole gas analyzer technique. Hydrogen gas input pressures were varied from 0.0043 to 0.62atm and membrane thicknesses from 0.0165 to 0.243cm. Volume diffusion control of the permeation process was demonstrated by the pressure and membrane thickness dependence of the steady state flux. The permeation coefficient, with an activation enthalpy found to be $8.1 \pm .4$ kcal/mole, was independent of both gas pressure and membrane thickness. At temperatures below approximately 600°K, the effective diffusivity increased with both increasing hydrogen gas pressure and increasing membrane thickness. The transition temperature from classical to anomalous behavior decreases with increasing thickness. Apparent activation enthalpies for diffusion were found

to range from 1.6 to 8.2 kcal/mole with the lower values associated with thicker membranes. The results are explicable in terms of volume trapping. A positron annihilation study showed dislocations to be the most probable, dominant trap species.

In contrast, hydrogen permeation through type 310 austenitic stainless steel, studied over the temperature range 425-873°K, showed no volume trapping effects. However, the membranes, ranging in thickness from 0.0051 cm to 0.013 cm, did show an increase in both effective diffusivity and permeation coefficient with increasing hydrogen gas pressure when surface processes were flux limiting. Once volume diffusion control of the permeation process was established, the dependence of permeation and diffusivity on hydrogen gas pressure was eliminated. The permeation coefficient activation enthalpy was found to be $13.1 \pm .4$ kcal/mole while that for diffusivity was found to be $11.2 \pm .45$ kcal/mole. However, samples neutron irradiated at a fluence of 10^{17} n/cm² showed anomalous effects in that both effective diffusivity and permeation were reduced in value. These results are explicable in terms of volume processes.

Finally, the hydrogen-deuterium isotopic effect was shown to be non-classical in iron while classical in stainless steel. In the case for iron, the non-classical behavior is confined to the pre-exponential diffusion constant since the activation enthalpy for diffusion is identical within experimental error for both isotopes.

I. INTRODUCTION

A. General Remarks

The relatively high permeability rate of hydrogen through ferritic iron and iron alloys is thought to be associated with the brittleness induced in these materials by hydrogen⁽¹⁻³⁾. An accurate determination of the hydrogen solubility and diffusivity in these metals is, therefore, essential before a thorough understanding of this phenomenon can be obtained.

Electrochemical charging or prior exposure to hydrogen gas at high temperature or pressure, where the hydrogen is distributed throughout the microstructure prior to the application of stress, results in what may be described as internal hydrogen brittleness⁽⁴⁾. Troiano⁽⁵⁾ suggests that during the embrittlement process, hydrogen diffuses preferentially to areas of maximum hydrostatic tension (i.e., lattice dilation) and, subsequently, instigates cracking most plausibly by lattice decohesion. Graville et al.⁽⁶⁾ give evidence that the strain rate sensitivity of hydrogen embrittlement is connected to the interaction of diffusing hydrogen with mobile dislocations. Hydrogen embrittlement is most pronounced at room temperature⁽⁷⁾ but vanishes at lower temperatures since the diffusivity is too low to supply the critical hydrogen concentration. At higher temperatures, diffusivity is high allowing the hydrogen to pass completely through the material resulting in a smaller hydrogen concentration at trapping sites and positions of maximum tri-axiality.

Although the role of hydrogen in stress corrosion cracking is controversial, particularly for the austenitic stainless steels, an increasing number of investigators suggest that hydrogen assisted cracking, as opposed to anodic path dissolution, is prevalent under many environmental testing conditions (8,9). Hydrogen evolution from the tips of propagating stress corrosion cracks has been reported. Martensitic surface phase transformations also have been reported in austenitic stainless steel under relatively severe hydrogen charging conditions (10,11). This surface phase is much more brittle or stress sensitive than the underlying austenitic structure. However, brittleness has been observed in the absence of phase transformations.

The first wall and structural materials within the blanket and shield region components of the proposed controlled thermonuclear fusion reactor interface the plasma, comprised of various concentrations of deuterium and tritium, (12) and are irradiated with neutron and gamma doses produced by the fusion reaction. Permeation, diffusion and solubility of hydrogen and its isotopes in those materials under consideration for this application, i.e. stainless steels, Nb, V, Mo, require characterization especially after the generation of radiation damage. Resultant microstructural sites including vacancies, voids, and dislocation configurations, can trap concentrations of hydrogen or deuterium larger than that of the normal lattice. Adding to this condition the chemical formation of hydrides and the mechanical considerations of fatigue and stress cycling of the

structural components, it is evident that internal hydrogen embrittlement, possibly even at high temperatures, is a potential major concern in fusion reactor materials specifications. The problem is even more enhanced by the temperature cycling incurred during system debugging and repair where the stressed components containing substantial hydrogen concentration will see room temperature, the temperature range where catastrophic mechanical failure resulting from hydrogen embrittlement is most severe.

B. Hydrogen-Iron System

1. Classical Behavior at Elevated Temperatures

Early solubility data based on gas-volume difference measurements show Sieverts' law (13), equation 1, to be obeyed at temperatures above 900°C and at pressures up to 100 atm.

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

$$C = K_o \sqrt{p} \exp^{-\Delta H_s / RT} \quad (1a)$$

where C = input subsurface equilibrium concentration of hydrogen

K_o = pre-exponential solubility constant

ΔH_s = heat of solution

The solubility is endothermic and has the typical value(14)

$$C = 3.63 \times 10^{18} \sqrt{p} \exp\left(-\frac{6500}{RT} \frac{\text{cal}}{\text{mole}}\right) \frac{\text{atoms H}}{\text{cc Fe}} \quad (2)$$

Extrapolation to room temperature, at 1 atm, shows a solubility of hydrogen in iron to be low, on the order of 10^{14} atoms H/ccFe.

Hydrogen is believed to occupy interstitial lattice sites, as is suggested by the small size of the hydrogen atom and the observation of Snoek internal fraction peaks (15), (16). Interstitial occupancy is also compatible with the reported partial atomic volume of $2\text{cm}^3/\text{mol}$ (17).. With the assumption of interstitial diffusion, McNeil (18) has calculated the activation energy for lattice diffusivity of hydrogen in iron to be 1.3 kcal/mole, while Wert and Zener (19) have calculated the pre-exponential diffusion to be approximately $1.6 \times 10^{-3} \text{cm}^2/\text{s}$. These values compare reasonably well with the experimental values shown in Figure 1 for temperatures greater than 300°C .

The assumptions underlying the classical diffusion model have been questioned because of the non-classical nature of the isotope effect. Gonzalez (20), Heumann and Primas (21) and Heller (22) have shown the inverse mass dependence relationship of the diffusion coefficient between protium and deuterium isotopes to be different from the ratio 1.4. Quantum mechanical models, including hydrogen tunnelling and coupling with lattice phonons, have been used to explain this phenomenon in Nb, V and Ta (23), (24).

2. Low Temperature Anomalies

Conflicting data on both the diffusivity and the solubility of hydrogen in iron have been reported in the low temperature range. Chang and Bennett (25) revealed a positive deviation from Sieverts' pressure dependence below 673°K as is shown in Figure 2. In addition, an analysis of hydrogen solubility in α -iron by Hill and Johnson (26) demonstrates in Figure 3 that the solubility of hydrogen in α -iron is substantially greater at low temperatures, say 300°K.

A summary of diffusivity results for high purity iron, obtained with various vacuum techniques, appears in Figure 1. Johnson and Hill (33) have extended their temperature range low enough to directly detect a discontinuity. The occurrence of this diffusion anomaly, near the temperature where the solubility anomaly was observed, indicates that they are undoubtedly connected.

As is evident in Figure 1, the anomalous break is more prevalent than would be anticipated if experimental errors were responsible, while compositional variance among the tested materials is unlikely to account for such a predominant anomaly. In addition, lower diffusivities are recorded by experimentalists employing evolution rate methods (29,31,33) than by those using permeability methods indicating that some barrier to hydrogen transport is operable in iron at these low temperatures. Quick (35) has developed an explanation for these observations using as-received Ferrovac-E iron which has yet to be tested

for other ferrous metals.

a. Surface Boundary Processes

The mass transport of a gas through a metal involves several processes, any one of which may be rate controlling.

These are:

- a) collision of a gas molecule with the metal surface; the molecule then dissociates and is adsorbed as atoms;
- b) transfer of the adsorbed gas atoms into solution with the metal;
- c) diffusion of the gas atom through the metal to the exit surface;
- d) desorption of the gas from solution with the metal to an adsorbed layer on the exit surface; and
- e) recombination of a gas atom with another adsorbed gas atom and evaporation as a molecule.

For most permeation studies, the competing rate controlling processes are steps b) and c); it must be determined whether mass transport of the gas is surface or bulk controlled.

Ash and Barrer (36) approach the problem by equating steady state fluxes and developing a series of equations applicable to most experimental conditions. Their conclusion is that the steady state flux may be expressed by

$$J = \frac{K(p, \theta, U_s)}{\left(\frac{L}{D} + \frac{1}{k_1}\right)} \quad (3)$$

where L = membrane thickness

D = diffusivity

k_1 = the transmission coefficient for the passage of a gas atom through the surface boundary

$K(p, \theta, U_s)$ = a parameter that is a function of charging pressure (p), surface coverage (θ), and saturation concentration (U_s).

The diffusion or bulk transport processes are flux controlling under the condition $\frac{L}{D} > \frac{1}{k_1}$,

In this case

$$J \approx K(p, \theta, U_s) \frac{D}{L}; \quad (4)$$

there is an inverse dependence upon thickness.

Surface transport processes are flux limiting when $\frac{1}{k_1} > \frac{L}{D}$,

In this case

$$J \approx K(p, \theta, U_s) k_1; \quad (5)$$

there is no dependence upon thickness.

The steady state flux pressure dependence determined through this analysis varies from p^0 to p^1 . Chang and Bennett's (25) data, Figure 2, shows a pressure dependence of $p^{1/2}$ at temperature above 500°C which increases to p^1 at lower temperatures. The $p^{1/2}$ dependence shows compliance with Sieverts' law. Here $k_1 \gg D/L$ and the mass transport of hydrogen is bulk limited;

Figure 1 Diffusion Data for Iron Obtained by Various Vacuum Techniques.

Figure 2 Steady State Flux and the Input Pressure Exponent as a Function of Reciprocal Temperature.

Figure 3 Solubility of Hydrogen in Iron.

equilibrium is maintained at both surfaces. The p^1 dependence is associated with surface flux limiting processes; consequently, $k_1 \ll D/L$ and non-equilibrium conditions exist at both surfaces. For intermediate cases $J \propto p^x$ where $\frac{1}{2} < x < 1$. In addition, the dominance of surface processes leads to an anomalous negative curvature in both the steady state flux and diffusivity Arrhenius plots.

The influence of surface processes, therefore, can be discerned by plotting steady state flux as a function of inverse thickness, where linearity is examined; pressure, where the pressure exponent is examined and reciprocal temperature, where linearity is examined.

b. Bulk Hydrogen Delay

All structural irregularities including dislocations, dislocation cell walls, micro-voids and internal surfaces are candidates for trapping sites. By ignoring the structural identification of the trap and assuming all traps to behave physically as potential wells, McNabb and Foster⁽³⁷⁾ have developed a general trapping model. These traps are uniformly distributed with varying capacities for capturing and delaying hydrogen atoms. Those traps which are too shallow to significantly delay hydrogen or those that permanently remove hydrogen from the diffusion process are not considered. The remaining density of traps, N (number/cc), is only fractionally occupied (i.e., n is the fraction occupied). This trap population exhibits both reversibility and saturability.

This model predicts that steady state flux should be in-

dependent of any trapping effects. Fick's second law can now be written as

$$\frac{\partial C_L}{\partial t} + N \frac{\partial n}{\partial t} = \text{div} (D \text{ grad } C_L), \quad (6)$$

where C_L = lattice concentration of diffusing atoms at the instant considered.

At steady state flux conditions, these traps are considered to be in equilibrium with the ordinary lattice sites. Therefore, $\text{div} (D \text{ grad } C_L) = 0$ as in the classical case.

The number of atoms captured per second per unit volume is $k_T C_L N(1-n)$ while the number being released is $(p_T n N)$ where

k_T = kinetic trapping parameter

p_T = kinetic trap release parameter.

The rate of interchange of hydrogen atoms between the trapped and diffusing populations now is:

$$\frac{\partial n}{\partial t} = k_T C_L (1-n) - p_T n \quad (7)$$

Then at steady state flux conditions,

$$\beta = \frac{n}{1-n} = C_L \frac{k_T}{p_T} \quad (8)$$

where $\frac{n}{1-n} = \beta$ = fractional trap occupancy.

Using the descriptive potential energy diagram given in Figure 4., coupled with equation 8, important information on the trapping kinetics can be realized.

First, the following approximations are made:

$$k \sim e^{-\Delta H_m / RT} \quad (9)$$

$$p \sim e^{-(\Delta H_b + \Delta H_m) / RT} \quad (10)$$

$$C_L \sim \sqrt{p} e^{-\Delta H_s / RT} \quad (11)$$

where

R = universal gas constant

p = input pressure

T = temperature

and all activation enthalpies assume a positive value.

Therefore

$$\beta = \frac{n}{1-n} \sim \frac{-(\Delta H_s - \Delta H_b)}{RT} \quad (12)$$

Immediately, β is seen to increase with input concentration.

The temperature dependence must be analyzed under the following extremes:

case (i) $\Delta H_b < \Delta H_s$ $\beta \ll 1$ at 25°C.

case (ii) $\Delta H_b > \Delta H_s$ $\beta \gg 1$ at 25°C.

case (iii) $\Delta H_b = \Delta H_s$ $\beta = 1$ β at 25°C and is independent of temperature.

It should be remarked that the parameter β , the fractional trap occupancy, has no bearing on the individual hydrogen capacity of each trap species.

Oriani (28) has extended this model to describe the effect of trapping on effective diffusivity. N , the trap density, is assumed to be fixed with the microstructure of the membrane.

The McNabb and Foster expression for lag time:

$$t_i = \frac{a^2}{D} \frac{1}{6} + \frac{\alpha}{2\beta} + \frac{\alpha}{\beta^2} - \frac{\alpha}{\beta^3} (1 + \beta) \log (1 + \beta) \quad (13)$$

, where the trapping parameter $\alpha = \frac{Nk_T}{p_T}$, (14)

is analyzed for the particular extremes of β and α of interest.

Case 1) $\beta \gg 1$ $\alpha \gg 1$: Heavily occupied traps where $\Delta H_b > \Delta H_s$.

The lag time condenses to the following equation,

$$t_L = \frac{L^2}{6D_L} \left\{ 1 + \frac{3\alpha}{\beta} \right\} \quad (15)$$

Substituting equation 8 for β and equation 14 for α then defining effective diffusivity as $\frac{1L^2}{6t_L}$, equation 15 is rewritten

as:

$$D = \frac{D_L C_L}{(3N + C_L)} \quad (16)$$

After differentiation of the natural logarithm of equation 16 with respect to the reciprocal of temperature, the activation enthalpy for effective diffusivity is expressed as

$$\Delta H_D = \Delta H_L + \Delta H_S \frac{3N}{C_L + 3N} \quad (17)$$

where ΔH_L = activation enthalpy for lattice diffusivity

ΔH_S = heat of solution.

The limiting conditions on expressions 16 and 17 are as follows:

a) when $C_L \gg 3N$,

$$D = D_L \quad (18)$$

$$\text{and } \Delta H_D = \Delta H_L \quad (19)$$

b) when $3N \gg C_L$,

$$D = \frac{D_L C_L}{3N} \quad (20)$$

$$\text{and } \Delta H_D = \Delta H_L + \Delta H_S \quad (21)$$

Between these limits, a concentration and thermal dependence of effective diffusivity is predicted.

case (ii) $\beta = 1, \alpha \gg 1$: 50% of the traps occupied

where $\Delta H_b = \Delta H_s$.

These results show the same trends as those for case (i), except that the numerical constant is different. The following equations are developed;

$$D = D_L \left(1 + .114 \frac{N}{C_L} \right)^{-1} \quad (22)$$

$$\Delta H_D + \Delta H_L + \Delta H_s \left(\frac{.114N}{C_L + .114N} \right) \quad (23)$$

case (iii) $\beta \ll 1, \alpha \gg 1$: Lightly occupied traps

where $\Delta H_b < \Delta H_s$.

Equation 13 reduces to the following:

$$D = \frac{D_L}{1+\alpha} \quad (24)$$

, while the activation enthalpy for diffusivity is expressed as follows:

$$\Delta H_D = \Delta H_L + \frac{\alpha}{1+\alpha} \Delta H_b \quad (25)$$

The trap binding enthalpy ΔH_b is related to the trapping para-

meter α by the Arrhenius relationship⁽¹⁷⁾.

$$\alpha = \text{constant} \exp \frac{\Delta H_b}{RT} \quad (26)$$

The limiting conditions to these expressions are determined by the magnitude of temperature:

a) For high temperature (i.e., $T \geq 300^\circ\text{C}$),

$$D = D_L \quad (18)$$

$$\text{and } \Delta H_D = \Delta H_L \quad (19)$$

b) For low temperatures (i.e., $T < 300^\circ\text{C}$),

$$D = D_L / (1 + \alpha) \quad (27)$$

$$\text{and } \Delta H_D = \Delta H_L + \Delta H_b \quad (28)$$

In contrast to cases (i) and (ii), a concentration dependence on effective diffusivity is not predicted. The behavior of saturable traps including dislocations, dislocation substructures and impurity atoms (38) is best described by one of these cases.

Finally, for those cases where $\alpha \ll 1$, no trapping behavior

is predicted.

The McNabb and Foster analytical trapping model recently has been fitted to particular trapping species. Microvoids have received extensive treatment by several investigators (39), (40), (41), (42), (43). The expression developed by Kass (42), as analyzed by Johnson (43), best summarizes the salient trend of these results:

$$D = \frac{D_L}{1 + \eta \frac{C_L}{2}} \quad (29)$$

Hydrogen is assumed to be trapped in its diatomic state by recombination of atomic hydrogen on the void surface. Hence, the void can be considered a nonsaturable trap.

The variable (η) is defined as follows:

$$\eta = \frac{\rho}{RT K^2} \quad (30)$$

where ρ = the number of voids per cubic centimeter.

and K = Seivert's constant.

The limits of the effective diffusivity are again analyzed:

$$\text{case (i) when } \eta C_L / 2 \ll 1, D = D_L \quad (18)$$

$$\text{case (ii) when } \eta C_L / 2 \gg 1, D = \frac{2D_L}{\eta C_L}$$

$$\text{or } D = \frac{2D_L}{\eta K \sqrt{p}} \quad (31)$$

Figure 4 Iron-Hydrogen Potential Energy Diagram.

For the theoretical trapping of hydrogen by microvoids near room temperature, where case (ii) is applicable, effective diffusivity is seen to be inversely proportional to input pressure in contrast to the general expectations of the McNabb Foster model. Therefore, when microvoids predominate as the trapping species, effective diffusivity is predicted to decrease with increasing input pressure. This concentration behavior of effective diffusivity is also predicted by the disinterstitial trapping model proposed by Ono and Rosales (44) as evaluated by Quick (35).

C. HYDROGEN - 310SS SYSTEM

The permeability, diffusivity and solubility data of the austenitic stainless steels have been treated with little regard given to compositional variation. Differences in composition along with surface problems may account for the data spread.

Hydrogen is believed to enter the lattice in the atomic form as indicated by the Seiverts' law dependence of solubility and migrates through the octahedral interstitial sites of the face centered cubic lattice. However, few internal friction experiments and theoretical modelling of the diffusion process have been attempted because of complications arising from the lattice distribution of alloying elements.

A summary of the results for austenitic stainless steel, obtained with various vacuum techniques, appears in Table I.

TABLE I.

Summary of Hydrogen Mass Transport Parameters
in Austenitic Stainless Steels

Reference	Year	Material	Temp Range (°C)	$\phi_o \frac{\text{atomsH}}{\text{cms atm}^{1/2}}$
Collins & (45) Turnbull	1961	304	130-400	
Eschbach et al. (46)	1963	304	250-600	
Phillips & Dodge (47)	1968	321	300-800	1.27×10^{19}
Chaney & (48) Powell (37)	1970	304	100-300	
Kass & (49) Andrzejewski	1972	309S	150-600	2.31×10^{16}
Nelson & (27) Stein	1972	304	100-600	4.00×10^{18}
Austin & (30) Oleminen	1972	304 316	25-222	
Louthan & Derrick (57)	1973	304N 304L 310 309S 21-6-9 A-216	112-440	3.23×10^{17}
Louthan & (52) Derrick	1974	304L	112-440	

† Gas phase charging

‡ Deuterium gas phase charging

TABLE I. (con't)

Reference	H_{ϕ} cal/mole	$D_O \frac{cm^2}{s}$	H_D cal/mole
Collins &(45) Turnbull	13000		
Eschbach et al. (46)	17800		15600
Phillips & Dodge(47)	15500	7.33×10^{-3}	12500
Chaney &(48) Powell(37)		1.24×10^{-2}	136000
Kass &(49) Andrzejewski	14100	1.2×10^{-2}	13100
Nelson &(27) Stein	15300	2.72×10^{-2}	13000
Austin &(30) Olemenan		1.8×10^{-2}	14000
Louthan & Derrick(57)	14300	4.71×10^{-3}	12900
Louthan &(52) Derrick		6.6×10^{-2}	12900

TABLE I. (con't)

Reference	$K_O \frac{\text{atomsH}_2}{\text{cc ptm}^2}$	$H_K \frac{\text{cal}}{\text{mole}}$	Method
Collins &(45) Turnbull			Permeation (G.P) †
Eschbach et al. (46)		2200	Permeation (G.P)
Phillips & Dodge(47)	1.73×10^{21}	3000	Permeation (G.P)
Chaney &(48) Powell(37)			Permeation (T.I.) ‡
Kass &(49) Andrzejewski	1.93×10^{18}	1000	Permeation (G.P)
Nelson &(27) Stein	1.47×10^{20}	2300	Permeation (G.P)
Austin &(30) Olemenan			Permeation (T.I.)
Louthan & Derrick(57)	6.86×10^{19}	1400	Permeation (GPD) ‡
Louthan &(52) Derrick			Permeation (T.I.)

† Gas phase charging.

‡ Deuterium gas phase charging.

‡ Tritium injected through the ${}^6\text{Li}(\eta, \alpha){}^3\text{H}$ reaction.

In the results of Nelson and Stein (27), Phillips and Dodge (47); Kass and Andrzejewski (49) and Louthan and Derrick (51), where the surface treatment was characterized, it is evident that surface boundary processes, unless eliminated, are flux controlling. Since surface processes have been observed to cause greater than an order of magnitude discrepancy in both diffusion and consequently, permeation data (49), it is probable that in those literature results exhibiting unusually high activation enthalpies for both diffusion and permeability that surface processes are responsible. In addition, Phillips and Dodge⁽⁴⁷⁾ observed a pseudo-concentration dependence of diffusivity resulting from surface impedance to the mass transport of hydrogen through 321 stainless steel.

Austin and Elleman's (50) data for tritium mass transport through 304SS, Figure 5, are lower than the hydrogen data by approximately the classical isotopic mass relationship. Tritium charging was accomplished by the transmutation of a surface layer of enriched ^6LiF by the reaction $^6\text{Li}(n,\alpha)^3\text{H}$; concentration profiles were analyzed. In Figure 5 what termed the "surface trapping effect" is observed to only reduce the pre-exponential diffusion constant. First this surface trapping was thought to be caused by helium filled voids produced through (n,α) reactions penetrating only a 10^{-3} cm thick input surface layer. More recent examination of these results show surface trapping to be exhibited on both input and output surfaces leading to the conclusion that surface, not subsurface processes, are responsible for the effect.⁽⁵³⁾

Louthan et al. (52) have shown evidence for "short circuit" diffusion paths and a grain size effect on tritium to be present in 304SS for exposures at less than 383°K. Prior cold worked samples also exhibit enhanced tritium transport, but this effect is believed to be caused by preferential diffusion through strain-induced martensite.

D. Purpose

The majority of gas-phase permeation studies conducted to examine hydrogen transport through iron and austenitic stainless steel have been limited to either high temperature ranges or high input concentrations. Because of the lack of system, material and material preparation specifications, the reliability of this older data is questionable. A system has been designed to accurately calculate permeability, diffusivity and, hence, solubility from gas-phase charging measurements at reasonable pressures in the temperature range where hydrogen assisted cracking phenomena are most prevalent. Charging pressures below and near one atmosphere and temperatures in the range of 300-873°K for iron and 425-873°K for stainless steel are used.

Quick (35) has explained the anomalies in the values of the iron bulk transport parameter by the presence of traps and the related concentration dependence of diffusivity. The validity of these results, determined for as received Ferrovac-E, are tested for four pass zone refined Ferrovac-E having a much lower impurity content. In addition, more detail is given to

Figure 5 Surface Trapping in 304SS.

the physical interpretation of the trapping mechanism and physical identity of the dominant trapping species with the aid of the positron annihilation technique.

Anomalies in the values of the austenitic stainless steel bulk transport parameters have been explained by the dominance of surface processes. The applicability and validity of these theories are examined with detail given to the kinetics and chemical identity of the surface barrier. Once the surface processes are understood, the bulk transport parameters can be examined and any bulk delay behavior analyzed. In order to examine the effect of radiation damage on the mass transport of hydrogen in austenitic stainless steel, a possible candidate for components in the controlled thermonuclear fusion reactor, experiments are conducted on fast neutron irradiated membranes. Here the traps are intentionally implanted within the sample. Theories then can be analyzed for applicability to any observed bulk phenomena with detail given to the mechanism of this behavior and physical identity of the trap sites.

Deuterium permeation through both Ferrovac-E and 310SS, when compared to that for hydrogen, is used to analyze the nature of the isotope effect. These results can be used to analyze the validity of classical diffusion assumptions.

As is indicated by the low range of charging pressure, small fluxes are evolved during permeation which minimize the possibility of surface structural transformation and bulk void formation. The sensitivity required to monitor these low hydrogen fluxes is achieved using a residual gas analyzer ad-

joining a high vacuum system.

II. EXPERIMENTAL

A. Material Composition

The principle ferritic iron chosen for the investigation is Ferrovac-E, supplied by Crucible Steel. The as-received rod had the composition cited by Quick.⁽³⁵⁾ These rods were then zone refined in an electron beam melting vacuum unit undergoing 4 passes. This high purity iron had the resultant composition:

<u>Element</u>	<u>%</u>
Aluminum	0.01
Chromium	0.001
Cobalt	0.001
Copper	0.0003
Lead	*0.002
Manganese	0.003
Molybdenum	0.002
Nickel	0.05
Silicon	0.007
Tin	0.005
Tungsten	0.005
Vanadium	0.004
Carbon	0.026
Sulfur	0.002
Nitrogen	0.0005
Hydrogen	0.0001
Oxygen	0.0013

* ----- less than value shown

The austenitic ferrous alloy studied in this investigation was 310 stainless steel supplied by Rodney Metals. This stainless steel was received in 0.013, 0.011 and 0.0051 cm thick annealed sheets having the following composition:

<u>Element</u>	<u>%</u>
Aluminum	0.02
Chromium	25.14
Cobalt	0.13
Copper	0.15
Lead	<0.003
Manganese	1.66
Molybdenum	0.07
Nickel	19.32
Silicon	0.48
Tin	<0.003
Tungsten	<0.05
Vanadium	0.04
Titanium	0.03
Sulfur	0.010
Nitrogen	0.076
Hydrogen	0.0004
Oxygen	0.010
Carbon	0.035

This type stainless steel was particularly chosen because of its resistance to the surface martensite phase transformation common to 304SS and 316SS upon exposure to moderate pressures of hydrogen.

B. Specimen Preparation

1. Zone Refined Ferrovac-E

A succession of cold rolling reductions and vacuum anneals were conducted until the desired thicknesses, ranging from 0.0165 cm to 0.254 cm, were obtained. Single crystals grown by the strain anneal technique were chemically thinned with the polishing solution discussed below. Discs with a 0.625 cm diameter were then punched out of the rolled iron strips backed with 0.015 cm brass shim stock in order to prevent excessive deformation around the sample's circumference. Vacuum brazing the discs onto copper gaskets, at pressures less than 5×10^{-6} torr, with Nicro braze was accomplished at 950°C after an additional two hour vacuum anneal at 850°C. A leak check was performed on every assembly which has an iron cross-sectional area of 1.98 cm².

The iron samples were chemically polished for approximately 90 seconds in a solution comprised of 1 part H₂O₂: 2 parts H₃PO₄; the copper gasket and braze region are suitably masked with etch-stop lacquer. After polishing, the samples were quickly rinsed in cold water then chemically palladium plated by submerging the assembly in Pallamarse solution for approximately 45 seconds. This procedure yielded consistently reproducible charging conditions. After the etch stop lacquer was removed, all samples were rinsed in tri-chloroethylene then nitrogen dried prior to mounting in the vacuum system.

2. 310 Stainless Steel

Discs punched from the as received stainless steel sheets were mounted onto copper gaskets in the manner described for iron. The surface oxide film, intrinsic to stainless steel, was removed by chemical reduction with ultra high purity hydrogen after the sample was mounted into the vacuum system.

The thermodynamic parameters shown in Figure 6 were more than satisfied when the system was adjusted to a hydrogen partial pressure of 10^{-6} torr, relative to a background pressure of 4×10^{-10} torr, and a sample temperature of 300°C . In calculating the minimum hydrogen concentration necessary to favor oxide reduction, the water vapor partial pressure is conservatively estimated to be equal to the initial background pressure. Successive surface reductions at these or higher partial hydrogen pressures and temperatures yielded consistently reproducible charging conditions.

Alternatively, palladium was vapor-deposited on both surfaces of the 310SS-gasket assemblies in a bell jar system capable of maintaining vacuums of 7×10^{-7} torr. The sample was heated by an RF induction heating unit where the coil was formed to allow evaporation on both surfaces. Unlike the process used by Kass (49) and Makrides (54), chemical reduction of the oxide film in an atmosphere of 10^{-5} torr hydrogen at 900°C preceded the evaporation of palladium, having the composition shown in Table II., at the reduced sample temperature of 700°C .

Figure 6 Thermodynamic Diagram for the Reduction of Fe_3O_4 with Hydrogen.

Table II.
Sponge Palladium Composition

<u>Element</u>	<u>ppm</u>
Al	<10
Cu	<5
Fe	<10
Mg	<5
Si	<50
Ag	<5

C. Method

Utilization of an optimum system sensitivity of 7×10^{10} atoms $\text{H}/\text{cm}^2\text{-s}$ allows the detection of fluxes resulting from 0.0043 to 0.43 atm input pressures and 300 to 873°K sample temperatures. The quantity of hydrogen passing through the membrane's exit surface into the monitoring chamber, initially evacuated to $<10^{-9}$ torr, was recorded as a function of time. The evolved gas was ionized and analyzed with a Veeco SPI-10 Monopole Residual Gas Analyzer (RGA) specifically calibrated for either hydrogen or deuterium identification. This ionization current is a direct measure of the amount of evolving gas and is converted to the more convenient units of pressure by first calculating the RGA's sensitivity to both hydrogen and deuterium.

The sensitivities are determined by a modification of the known flow technique⁽⁵⁵⁾ where, at fixed temperature and flow rate, the flux is first monitored by a Mag Ion $20^1/\text{s}$ pump whose output is plotted by a SPR-12 strip chart recorder. Since the pump is essentially a larger version of the Penning cold cathode pressure gauge, its amperage output is easily converted to pressure readings by pressure amperage graphs supplied by Veeco; pumping speed is constant over the pressure range 10^{-8} to 10^{-5} torr. The flux measurement is then repeated under the specified conditions with the RGA where $\Delta(\text{amperage})/\Delta t$ is recorded under a partial dynamic vacuum. These RGA readings assume the same gas ionization factor, for a given gas, as that for the Magion pump.

Since the flux determined by each procedure is equal, the following expression for RGA sensitivity is developed:

$$S = \frac{\Delta I}{\Delta t} \bigg|_{\infty} \frac{V}{F(p_{\infty} - p_B)} \quad (32)$$

where

F = pumping speed (liters/s)

p_{∞} = pump steady state pressure (torr)

p_B = monitoring chamber base pressure (torr)

V = monitoring chamber volume (liters)

I = RGA amperage reading (amps).

Several readings were taken and averaged to give the following results:

$$S_{H_2} = \text{Hydrogen sensitivity} = 1.78 \times 10^{-7} \text{ amp/torr}$$

$$\text{and } S_{D_2} = \text{Deuterium sensitivity} = 1.55 \times 10^{-7} \text{ amp/torr}.$$

Steady state pressure rise and pressure may then be determined by the following relationships:

$$i) \quad \left. \frac{\Delta p}{\Delta t} \right|_{\infty} = \frac{\left. \frac{\Delta I}{\Delta t} \right|_{\infty}}{S} \text{ torr/s}$$

$$ii) \quad p = \frac{I}{S} \text{ torr}$$

Steady state flux is determined by the pressure rise technique (58) through the following relationship:

$$J_{\infty} = \frac{2V}{k_B T A} \left. \frac{\Delta p}{\Delta t} \right|_{\infty} \frac{\text{atoms H}}{\text{cm}^2 \text{ s}} \quad (33)$$

where k_B = Boltzman's constant = 1.03×10^{-22} (liter-torr/°K)

T = sample temperature (°K)

A = sample cross-sectional area (cm^2)

Since all measurements are obtained under dynamic vacuum conditions, the fraction of the evolved gas exhausted by the pump is maintained at least 2 orders of magnitude less than the flux sampled by the RGA by adjusting an isolation valve separating the monitoring chamber from the pump:

$$F = F_o \frac{\Delta h}{h_o} \quad (34)$$

F_o = unstricted pumping speed (20 l/s)

h_o = maximum orifice height (3.5 cm)

Δh = adjusted orifice height. (the valve throughput is assumed to be cylindrical).

The fraction of the flux exhausted by the pump is then calculated by the expression:

$$J_{\infty}|_{\text{pump}} = \frac{2F(p-p_B)}{k_B T A} \quad (35)$$

The pumping speed is fixed at 1.14 l/s assuring that the condition $J|_{\infty} \text{ RGA} > 100 J|_{\infty} \text{ pump}$ holds over all experimental temperatures and input pressures. At this pumping speed, evacuation of the monitoring chamber between runs is relatively rapid. It is clear that the optimum flux sensitivity of the system can be improved by further decreasing the pumping speed.

A schematic of the stainless steel ultra high vacuum system is shown in Figure 7. The entire system is initially roughed to $<10^{-3}$ torr by a mechanical pump in series with a molecular seive trap in order to limit contamination and, at higher temperatures, oil activated oxidation of the membrane's surface. After the roughing pump is valved off, the base pressure is reduced to $<10^{-8}$ torr in the monitoring chamber by a Veeco Magion 20 l/s pump. This operation is accomplished in the charging chamber by a Veeco Magion 30 l/s pump. The monitoring chamber, including the pump, is baked with heating tape for at least 12 hours at 250°C while the charging chamber is baked at a 100°C in order to protect the Viton seal in the pneumatic charging valve. The sample is simultaneously outgassed by a kanthal wound resistance furnace.

Prior to terminating the bakeout procedure, the RGA analyzer tube is outgassed for 15 minutes. By this time the background pressure shows no noticeable increase with the RGA in operation; this particular procedure is repeated for a few minutes prior to each experimental run. Finally, the system is allowed to cool to room temperature by which time the monitoring chamber is evacuated to a base pressure $<10^{-9}$ torr.

Some hydrogen is prone to diffuse into the sputtered titanium layers covering the pump cathode without undergoing chemisorption. This residual hydrogen concentration is inevitably regurgitated into the pump cavity and system consequently leading to a background pressure rise. In order to remove this unreacted hydrogen, the Mag Ion pumps are periodically removed(e.g., every four months)and soaked at 250°C in a vacuum furnace.

The hydrogen and deuterium gases are passed through a Matheson palladium purifier before flowing through a Veeco leak valve into the charging pressure chamber where the input pressure is adjusted with an alphasatron pressure gauge. Application of the input pressure to the sample's input surface is spontaneous upon the opening of the pneumatically operated charging control valve. Time is allowed for the evacuation of both the monitoring and charging chambers before each experimental run until the initial background pressures are obtained thus assuring sufficient degassing of the sample. Selection and regulation of the sample's temperature is accomplished

Figure 7 Schematic of the Vacuum System.

with a Leeds and Northrup Electromax IV current adjusting unit in parallel with a kanthal wound resistance furnace. It should be noted that the sample is heated by thermal conduction through the flange containing it and its copper gasket. An iron-constantan thermocouple is fed through two glass to metal transition seals mounted on a double sided conflat flange into the system allowing direct contact of the thermocouple junction with the center of the membrane. Variance of the temperature over a maximum range of 25°C-800°C is controlled to within $\pm 1^\circ\text{C}$ after allowing the sample to reach a steady state temperature.

III. RESULTS AND DISCUSSION

A. Recorded Data and Reproducibility

Three distinct regions: breakthrough, transient and steady state, are displayed in a typical recorded output, Figure 8. The breakthrough time depends on the sensitivity of the measuring system and membrane thickness. A transient region follows which may be characterized by a diffusivity. The steady state region represents a stationary concentration profile within the membrane; the slope is proportional to the steady state flux.

Successive absorption transients recorded for both iron and stainless steel on the same specimen show excellent reproducibility as shown in Figure 9. This suggests that trap density remains unchanged and hydrogen is not irreversibly trapped during gas phase charging, in contrast to most electrochemical charging techniques (56, (57)).

Figure 8 Typical Monitored Absorption Transient.

Figure 9 Reproducibility of the Monitored Absorption Transient.

Since sufficient time is given between runs for thorough membrane degassing, data reproducibility is independent of whether the input pressure sequence proceeds from low to high values or the reverse. This indicates that reversible trapping is observed.

B. Method of Data Analysis

Once it is established that the hydrogen transport processes are diffusion controlled, the standard time lag technique may be used to analyze permeation data in the classical region. Barrer (58) showed that the concentration profile under the experimental boundary conditions is

$$C = C_2 + (C_1 - C_2) \frac{x}{L} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_1 \cos n\pi - C_2}{n} \sin \frac{n\pi x}{L} \exp\left[-Dn^2 \frac{\pi^2 t}{L^2}\right]$$

$$+ \frac{4C_o}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \sin \frac{(2m+1)\pi x}{L} \exp[-D(2m+1)^2 \pi^2 t], \quad (36)$$

and the steady state concentration profile is

$$C(t) = AD/LV [(C_1 - C_2)t - \frac{C_1 L^2}{6D} - \frac{C_2 L^2}{3D} - \frac{C L^2}{2D}] \quad (37)$$

The corresponding time lag is

$$t_L = \frac{1}{C_1 - C_2} \left[\frac{C_1 L^2}{6D} + \frac{C_2 L^2}{3D} - \frac{C_0 L^2}{2D} \right] , \quad (38)$$

and for the current boundary conditions this becomes

$$t_L = \frac{L^2}{6D} \quad (39)$$

which relates the measured time lag to the lattice diffusivity.

The condition $C_0 = 0$ is satisfied since the membranes are vacuum annealed at approximately 900°C for a minimum of two hours. In addition, the monitoring chamber base pressure is initially maintained at $<10^{-9}$ torr, and the evolved pressure never surpasses 10^{-5} torr during the experimental runs assuring compliance with the latter condition, i.e., $C_1 \propto p_1 \gg C_2 \propto p_2$. Therefore, on the evolved pressure versus time plot output of the recorder, where $p(t)$ is related to concentrations as follows:

$$p(t) = k_B T C(t) , \quad (40)$$

the steady state portion of the curve can be extrapolated until it intercepts the time axis. The lag time value determined at this intercept, as illustrated in Figure 8, can be used to compute the diffusion coefficient from equation 39.

Later results will show that this diffusivity is not,

under all experimental conditions, a lattice diffusivity; it is more accurate to describe this value as an effective diffusivity.

The steady state fluxes are directly calculable from the steady state portion of the $p(t)$ vs t plots by equation 33. Permeability, defined as the product DK , is calculated through the expression:

$$\phi = \frac{J_{\infty} L}{\sqrt{p}} \left(\frac{\text{atoms H}}{\text{cm s atm}^{1/2}} \right) . \quad (41)$$

Once diffusivity and steady state flux are known for a particular experimental run, solubility can be calculated as follows:

$$C = \frac{\phi}{D \sqrt{p}} . \quad (42)$$

C. Palladium

It is important to show that the palladium coating does not influence the permeation curves. Interferometer thickness measurements conducted on an iron membrane showed the film to be $<9 \times 10^{-6}$ cm. Similar measurements conducted on a stainless steel membrane showed the vapor deposited palladium film to be $<10^{-5}$ cm.

The permeability and thickness data are tabulated for palladium, iron and stainless steel in Table III. First, a comparison of the flux permeating the palladium film relative

to that of the iron or stainless steel substrate can be computed from this data. The thinnest membrane of each metal is analyzed at 300°K and 800°K for an input pressure of 1 atm. The steady state flux is calculated as follows:

$$J_{\infty} = \frac{\phi}{L} \sqrt{p} \quad (43)$$

The results for each metal shown in Table IV substantiate that palladium has no influence on the hydrogen flux.

Second, the effect of the palladium film on the diffusivity of both iron and stainless steel can be analyzed through the mathematical expression developed by Barrie et al. (59):

$$t_{p-s-p} = \frac{\frac{L_p^2}{D_p} \frac{4L_p}{3D_p K_p} + \frac{L_s}{D_s K_s} + \frac{L_s^2}{D_s} \frac{L_p}{D_p K_p} + \frac{L_s}{6D_s K_s} + \frac{L_s L_p^2 K_s}{D_p K_p^2}}{\frac{2L_p}{D_p K_p} + \frac{L_s}{D_s K_s}} \quad (44)$$

where (s) denotes the substrate and (p) denotes the palladium film.

Table III.

Typical Literature Permeation Data

Metal Thickness (cm)		Temperature (°K)
Pd †	10^{-5}	300
Pd	10^{-5}	800
α -Fe ‡	.0075	300
α -Fe	.0075	800
γ -SS §	.0051	300
γ -SS	.0051	800

† Koffer et al. (60)

‡ Nelson and Stein (No palladium surface treatment) (27)

§ 304 stainless steel (27)

Table III. (con't)

Typical Literature Permeation Data

$\phi \frac{\text{atoms H}}{\text{cm s atm}^{1/2}}$	$D \text{ cm}^2/\text{s}$	$K \frac{\text{atoms H}}{\text{cc atm}^{1/2}}$
1.83×10^{14}	3.27×10^{-7}	5.60×10^{20}
9.20×10^{15}	1.34×10^{-4}	6.87×10^{19}
1.48×10^{11}	1.58×10^{-4}	9.37×10^{14}
7.94×10^{14}	8.42×10^{-4}	9.43×10^{17}
2.96×10^7	9.50×10^{-12}	3.12×10^{18}
2.68×10^{14}	7.73×10^{-6}	3.47×10^{19}

Table IV.

Steady State Flux Comparisons

Temperature (°K)

J_{Pd}/J_{Fe}

$J_{Pd}/J_{\gamma-SS}$

300

9.3×10^5

3.2×10^9

800

8.7×10^3

1.75×10^4

Utilization of the data presented in Table III. shows that for both temperature extremes equation 44 reduces to the lag time expression through the substrate, equation 39. Hence, the palladium film has no limiting influence on diffusivity. In addition, the presence of palladium on both surfaces improves data reproducibility since it prevents subsequent chemisorption of an oxide layer on the substrate.

D. Iron

1. Surface Processes

It is imperative to demonstrate that surface boundary processes are not flux limiting in order to examine bulk hydrogen transport processes. If Sieverts' law is obeyed, the steady state flux is proportional to the square root of input pressure (i.e., $J_{\infty} = \frac{KD\sqrt{P}}{L}$ indicating the surface processes to be in equilibrium with or faster than bulk diffusion; hence, the flux is volume controlled. Figure 10 shows the data for the palladium coated sample to obey this expression over the entire temperature range investigated (i.e., 300°K - 873°K). In addition, Figure 11 shows that the steady state flux is linear with respect to inverse thickness as predicted.

The obvious surface barrier on the untreated surface of α -iron is the chemisorbed iron oxide film about 20 Å (61) in thickness; several experiments were designed to better characterize the oxide's effect on permeation. A 0.243cm thick sample, whose surface is untreated with Pd, was run yielding diffusivity and permeability Arrhenius plots identical to those

of a duplicate sample that was palladium coated (see Figures 12 and 13). Since the sample was exposed to pure environments, of hydrogen during testing, it is suggested that any possible surface barrier, particularly the oxide, was chemically reduced by hydrogen.

Next the input surface was pre-oxidized prior to hydrogen charging. After the run, the surface was re-oxidized and charged with a 48% O_2 + 52% H_2 gas mixture. The results shown in Figure 14 demonstrate the suppression of diffusivity (increase of the lag time) caused by the presence of surface oxide. A more severe suppression is observed when oxygen is contained in the input gas mixture. The latter diffusivity is approximately 0.4 times the diffusivity of the control unoxidized sample.

Likewise, the steady state flux (the slope of the steady state curve) is suppressed where the value calculated from the gas mixture charge is also approximately 0.4 times that of the control unoxidized sample. Therefore the solubility, determined by equation 42, is not significantly effected.

Figure 10 Steady State Flux as a Function of Input Hydrogen Pressure for Ferrovac-E.

Figure 11 Steady State Flux as a Function of Inverse Thickness for Ferrovac-E.

Figure 12 Effective Diffusivity as a Function of Reciprocal Temperature for Ferrovac-E with and without the Palladium Surface treatment.

Figure 13 Permeability Coefficient as a function of Reciprocal Temperature for Ferrovac-E with and without the Palladium Surface Treatment.

Figure 14 Oxidation Effect on the Absorption Transient of Ferrovac-E.

2. Permeability

A least squares fit of the data plotted in Figure 15 gives the following expression for the permeability coefficient:

$$\phi = 1.02 \pm .54 \times 10^{17} \exp\left(\frac{-8106 \pm 247 \text{ cal}}{RT} \frac{\text{atoms H}}{\text{mole}}\right) \frac{1}{\text{cm s atm}^{1/2}} .$$

All Arrhenius expressions are within 95% confidence limits. Although the pressure range 0.0043 to 0.43 atm was studied, only data for input pressures of 0.43 atm are shown for the sake of clarity. The measured permeability coefficients fall within the error bands derived by Gonzalez⁽⁶²⁾ represented by the upper and lower lines where the analyzed data extends to only 126°C and is necessarily extrapolated to 25°C. Good agreement is also shown with the results of Nelson and Stein⁽²⁷⁾ who using a similar system were only able to extend their data to 60°C. This good agreement with past work indicates that the thin palladium coating has no impedance effect on hydrogen permeation through iron while allowing lower temperature permeation studies, in the vicinity of 25°C, with the vacuum technique.

The permeability coefficient, which describes steady state conditions, is expected to be insensitive to structure. This concept is mathematically expressed by the following equation describing hydrogen transport in a lattice with trapping⁽³⁷⁾:

$$\frac{\partial C_L}{\partial t} + N \frac{\partial n}{\partial t} = \text{div} (D_L \text{ grad } C_L) \quad (6)$$

Figure 15 Ferrovac-E Permeability Coefficient as a Function of Reciprocal Temperature.

where C_L = lattice concentration of the diffusing atoms at the instant considered

t = time

n = fraction of traps occupied

D_L = lattice diffusivity

In the steady state the trapping and de-trapping rates are of necessity equal since the time dependent terms in equation 6 are zero. The steady state flux then depends only on lattice quantities and is insensitive to charging pressure and membrane thickness (e.g. trap density). Therefore, agreement among permeation activation energies is not surprising.

3. Bulk Diffusion Observations

The Arrhenius plot shown in Figure 16 demonstrates the non-classical behavior is extended for thin samples (i.e., 0.0165cm) to fairly high temperatures before classical behavior dominates. For a given isotherm within the anomalous region, effective diffusivity increases with increase in input hydrogen gas pressure. Hence, the apparent activation energy for diffusion, discerned by forcing a straight line through the data, is seen to decrease with increasing input pressure. In Figures 17 through 18 the transition temperature range from classical to anomalous behavior is shown to decrease with increasing thickness. For a 0.0165cm thick sample, this transition temperature is in the vicinity of 310°C, while for the 0.125cm thick sample, this transition temperature is reduced to 60°C. In addition, for the same input pressure and tempera-

ture, effective diffusivity increases with increasing thickness.

An expression for lattice diffusivity is determined by a least squares fit of the 0.124, 0.183 and 0.243cm thick membranes above 60°C where no concentration nor thickness anomalies exist. The derived expression:

$$D_L = 2.23 \pm .17 \times 10^{-3} \exp \frac{-1640 \pm 87 \text{ cal}}{RT} \frac{\text{cm}^2}{\text{mole s}}$$

is in excellent agreement with the results of Nelson and Stein⁽²⁷⁾. In addition, this result further indicates that palladium has no effect on the transient behavior of hydrogen in iron.

An upper bound, where effective diffusivity is equal to lattice diffusivity, is apparent in Figure 19 which shows that as the transition temperature is gradually approached, the pressure dependence of the effective diffusivity diminishes. This observation suggests the gradual inactivation of the trapping mechanism; hydrogen is thermalized from these trapping sites. At and beyond the transition temperature, $D \neq D(p)$ (i.e., $D = D_L$ since the traps are completely inactivated).

The thickness effect, Figure 20, is attributed to an increasing trap density with decreasing membrane thickness. This thickness dependence of effective diffusivity gradually dampens out with increasing temperature again suggesting the thermalization of hydrogen from traps; when $D = D_L$, the thickness effect disappears.

16 Ferrovac-B Effective Diffusivity as a Function of Reciprocal Temperature for Several Input Pressures for a Thin Membrane.

Figure 17 Ferrrovac-E Effective Diffusivity as a Function of Reciprocal Temperature for Several Input Pressures for a Membrane of Intermediate Thickness.

Figure 18 Perovvac-E Effective Diffusivity as a function of Reciprocal Temperature for Thick Membranes.

Figure 19 Ferrovac-E Effective Diffusivity as a Function of Input Pressure.

Figure 20 Ferrovac-E Effective Diffusivity as a Function of Membrane Thickness.

Figure 21 Ferrovac-E Effective Diffusivity as a Function of Input Pressure for Several Isotherms.

A possible lower bound for the value of effective diffusivity is suggested in Figure 16 where for the 0.0165cm membrane at 0.0043atm input pressure, the activation enthalpy for diffusivity equals 8.2 kcal/mole. This limit is further evaluated by plotting diffusivity versus input pressure on a log-log graph for decreasing isotherms. The derived pressure exponent, n , is seen in Figure 21 to increase from 0 to 0.5 with decreasing temperature. This lower bound is firmly established by the results for the 0.0075cm thick sample in Figures 22 and 23.

where

1) the activation enthalpy for diffusivity is invariant with input concentration.

and

2) the effective diffusivity is dependent on pressure to the $\frac{1}{2}$ power near 26°C.

4. Iron Solubility

Since the steady state flux was shown to be in agreement with Seiverts' law, the total lattice hydrogen concentration, over the range where classical diffusivity is observed, can be expressed by the formula

$$C_L = K_O \sqrt{p} e^{-\Delta H_s / RT} \quad (1a)$$

Since

$$C = \frac{\Phi}{D} \sqrt{p} \quad (42)$$

Figure 22 Ferrovac-E Effective Diffusivity as a Function of Reciprocal Temperature for an Extremely Thin Membrane.

Figure 23 Ferrovac-E Effective Diffusivity as a Function of Input Pressure for an Extremely Thin Membrane.

Figure 24 Ferrovac-E Total Solubility as a Function of Reciprocal Temperature.

Figure 25 Ferrovac-B Fraction of Trapped Hydrogen as a Function of Reciprocal Temperature.

the values of the heat of solution, ΔH_s , and the pre-exponential solubility term, K_o , are determined by dividing the expression for permeability (i.e., equation 41) by that for lattice diffusivity (i.e., equation 39). The expression for lattice concentration derived from these results yield

$$C_L = 4.57 \pm .37 \times 10^{19} \sqrt{p} \exp \frac{-6466 \pm 247}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{atoms H}}{\text{cc Fe}},$$

which is in excellent agreement with the results of Geller and Sun (14) and Gonzalez (62).

At low temperature where trapping becomes operative, this lattice concentration is no longer the total hydrogen concentration in solution. Figure (24) shows the total concentration calculated from equation 42 as a function of reciprocal temperature for a .0075 cm thick membrane. In this range the independence of total solubility with temperature implies that the traps are saturable.

Since

$$C_T = C_L + C_x, \quad (45)$$

equation 42 can be written in the Arrhenus form giving

$$C_T = \frac{\phi_o}{D_o} \sqrt{p} e^{-\frac{(\Delta H_\phi - \Delta H_D)}{RT}}. \quad (46)$$

It will be shown in the ensuing section that the trapped con-

centration, C , equals the trap density $3N$. Dividing C_x by C_T allows an estimate of the fraction of trapped hydrogen, and these results can be plotted as a function of reciprocal temperature governed by the expression,

$$\frac{C_x}{C_T} = 1 - \frac{D_o}{D_L} \exp \frac{\Delta H_\phi - \Delta H_s + \Delta H_D}{RT} , \quad (47)$$

where C_x is represented as $C_T - C_L$.

Results appear in Figure 25 for a 0.0165 cm thick membrane. The ratio C_x/C_L is zero throughout the classical region but approaches one near room temperature.

Throughout the classical region, the hydrogen is easily and completely thermalized from the trapping sites. As the temperature is decreased through the anomalous region, the thermalization process is slowed, and consequently, an increasing population of hydrogen is delayed at the trapping sites.

5. Trapping Model

The anomalous break in the diffusivity versus the reciprocal temperature plots indicate that the trapping behavior is precipitated with decreasing temperature giving evidence that the condition $\alpha \gg 1$ is obeyed at low temperatures. The solubility plot shown in Figure 24 demonstrate that at room temperature total solubility is over two orders of magnitude

larger than the ordinary lattice solubility. In addition, the fractional trapped concentration shown in Figure 25 has a strong dependence on decreasing temperature. These observations suggest that the fractional trap occupancy is temperature dependent and is much greater than one at room temperature, (i.e., $\beta \gg 1$).

The satisfying of these conditions, $\alpha \gg 1$ and $\beta \gg 1$, allows the use of the trapping model.

where the effective diffusivity is expressed as

$$D = \frac{D_L C_L}{(3N + C_L)} \quad (16)$$

while that for the activation enthalpy of diffusivity is expressed as

$$\Delta H_D = \Delta H_L + \Delta H_S \left(\frac{3N}{C_L + 3N} \right) \quad (17)$$

The consistency of this model now will be examined.

Since the trap occupancy is very large at room temperature the trapped concentration C_X is taken equivalent to the trap density $3N$ where the constant 3 is assumed to have only geometrical significance.

Figure 25 shows that at temperatures above the anomalous break, the fraction of trapped hydrogen is much less than 1, therefore $C_L \gg C_X$. For this upper bound, it was predicted

that

$$D = D_L \quad (18)$$

$$\text{and} \quad \Delta H_D = \Delta H_L \quad (19)$$

This prediction is apparently obeyed in Figures 16 through 18.

At temperatures below the anomalous break, particularly near room temperature, Figure 25 shows $C_X \gg C_L$. Here the model predicts that

$$D = \frac{D_L C_L}{3N} \quad (20)$$

$$\text{and} \quad \Delta H_D = \Delta H_L + \Delta H_S \quad (21)$$

$$\text{Since } C_L = K\sqrt{p}, \quad \Phi = D_L K \text{ and } \Delta H_\Phi = \Delta H_L + \Delta H_S,$$

these expressions can be modified to read

$$D = \frac{\Phi \sqrt{p}}{3N} \quad (48)$$

$$\text{and} \quad \Delta H_D = \Delta H_\Phi \quad (49)$$

Figures 22 and 23 show the lower bound prediction of the trapping model to be apparently obeyed.

The dependence of effective diffusivity on the square root of input pressure is shown in Figure 23, while Figure 22 shows the activation enthalpy for effective diffusivity to be equal to that for permeation regardless of input pressure.

Besides showing applicability to the 4 pass zone refined Ferrovac-E iron, this model has previously been used to describe the trapping behavior in as-received Ferrovac-E⁽³⁵⁾ and Armco Iron⁽⁵⁶⁾ indicating its general applicability to irons.

6. Grain Boundary Effect

Diffusion data for the zone-refined Ferrovac-E single crystal specimen shown in Figure 26 has virtually an identical Arrhenius plot as the polycrystal specimen having the same thickness. Both samples show nonclassical behavior below 150°C. Optical microscopic examination verified that the single crystal prepared by the strain annealing technique was structurally unaltered during the niobium vacuum brazing cycle after prior chemical thinning. The single crystal also exhibits an effective diffusivity that is dependent on input pressure. These observations substantiate the conclusion reached by McBreen⁽⁶⁵⁾ that the presence of grain boundaries in iron has no effect on diffusivity. Consequently, the trap species is limited to microstructural defects.

7. Positron Lifetime Defect Study

The measurement of positron lifetimes has been used extensively to probe the structure of condensed materials for the past 20 years.^(66,67) Recently, this work has been extended to include metals and the detection of their lattice

Figure 26 Ferrovac-E Effective Diffusivity as a Function of Reciprocal Temperature for a Single Crystal Compared to a Polycrystal Membrane.

defects, particularly vacancies and dislocations. The positron, the antiparticle of the electron, is sensitive to variations in electron density throughout the lattice. Rapid annihilation of positrons is observed in the ordinary lattice where lifetimes are on the order of 10^{-10} sec. Defects, which have a lower electron density, appear to "trap" the positron, relative to the ordinary lattice, increasing its lifetime prior to annihilation.

Detailed descriptions of techniques for measuring positron lifetimes are dealt with elsewhere. (68) , (69) In these studies, a 20μ Ci Na^{22} positron source is deposited on, then sandwiched between, two annealed iron membranes of identical thickness. The time difference between the 1.28 MeV gamma ray, emitted simultaneously with the emission of a positron, and the 0.51 MeV gamma ray, emitted simultaneously with the annihilation of a positron, was measured by the "start-stop" technique. The resolution time of our system, as given by the full width at half maximum for a Co^{60} "prompt spectrum" was 310 psec. approximately 10^5 events were collected per decay curve over a 24-hour period. These positron decay spectra were then computer analyzed by a modified non-linear regression technique to give the reported decay rates. A typical spectrum is shown in Figure 27 with the background subtracted out. In all cases, the regression coefficient of the computer fit was greater than 0.995.

Table VI displays the experimental results which can be used to calculate the defect concentration. The data is in

Figure 27 Typical Positron Lifetime Spectrum.

need of refinement but is adequate for describing the analytical technique.

Table V . Positron Annihilation

L(cm)	$\bar{\tau}_1$ (nsec)	Positron	Lifetime	Parameters
		f_1	τ_2	f_2
0.194	.174±.05	0.98±.01	1.18±.12	0.02±.01
0.052	.141±.04	0.97±.01	1.01±.10	0.03±.01

The lifetime τ_2 is caused by positron interaction with the source; therefore, f_2 is the fraction of positrons annihilating in the source. The primary lifetime $\bar{\tau}_1$ for the 0.052cm membrane is much lower than the lattice value, τ_c , of 0.160 determined by Weisberg and Beckos (70) indicating the sample to be too thin for significant positron interaction with the lattice. Samples are usually at least 1mm thick or larger. Therefore the positron lifetime system employed proves to be inadequate for determining defect concentrations in those membranes less than 1mm in thickness.

The lifetime of positron interaction with the lattice⁽⁷¹⁾
(72) (73) and that with defects are close in value for metals, and consequently, are not clearly resolvable. The primary lifetime $\bar{\tau}_1$ is then an average of these two components. In order to calculate the defect positron trapping rate, K , the following expression is employed:⁽⁶⁶⁾

$$K = \frac{1}{\tau_c} \frac{\bar{\tau}_1 - \tau_c}{\tau_d - \bar{\tau}} \quad (57)$$

where τ_c = the positron lifetime in the lattice

τ_d = the positron lifetime in the defect.

Cotterill et al. (74) have shown the positron lifetime in a dislocation and that in a vacancy to be virtually identical for aluminum (i.e., 250 psec and 246 psec respectively). This observation is considered to hold true for all metals, i.e.

$\tau_{\text{disl}} \approx \tau_{\text{vac}} \approx \tau_{\text{vac}} \approx \tau_d$. For iron, $\tau_d = .217$ nsec.⁽⁷⁵⁾ The positron trapping rate is then calculated to be $0.00203 \text{ nsec}^{-1}$.

As with the resistivity technique, the identity of the defect is not directly determinable. Consequently, the trapping rate is used to calculate the density of first dislocations then voids followed by an evaluation of these results.

If voids are the dominant defect species then

$$K = 4\pi r N_p D_t \quad (58)$$

where r = void radius (cm)

N_p = void number density (cm^{-3})

D_t = the diffusion constant of thermalized positrons

$(10^{-2} \frac{\text{cm}^2}{\text{s}} \text{ for Fe(75)})$.

The volume fraction of voids, i.e., $v = N_p (4/3 \pi r^3)$, now can be solved as a function of void radius and positron trapping rate:

$$v = \frac{1}{3} K r^2 \quad (59)$$

For the 0.184cm thick membrane, this expression reduces to

$$v = 6.78 \times 10^{-7} r^2 \quad (60)$$

Volume fractions on the order of 10^{-3} cc/cc are easily achieved in cold rolled steels⁽⁷⁶⁾ which through equation (60) yields an average void radius of 380Å in iron. Kass's⁽⁴¹⁾ calculations predict this void volume to show a significant trapping below 100°C as shown in Figure 28. In the thinner membranes examined here, trapping behavior is observed at temperatures near 300°C. Through Kass's analysis, a void volume of approximately 10^{-1} cc/cc is necessary to cause the phenomenon! Assuming that the void number density in the thinner membranes is at most two orders of magnitude greater than for the 0.184cm membrane, the void radius would range between 380-3800Å. Voids of this prominent size have yet to be reported in high purity annealed iron (77).

Pure iron has no significant inclusion concentration to nucleate voids during cold working, and after an anneal is expected to have a much lower void volume fraction than that of cold rolled steel. The void volume in annealed iron has been shown to be at least less than 10^{-4} cc/cc by Evans and Rollason

Figure 28 Total Solubility as a Function of Temperature for an Input Pressure of 1 atm.

(78). According to Figure 28, void volumes of this magnitude would result in trapping behavior only significant below 25°C, contrary to the results observed here.

If dislocations are the dominant trap species then

$$K = \frac{4 N_p D_t}{\ln \frac{1}{\pi N r^2}} \quad (61)$$

where

N_p = dislocation density
(cm/cm³)

r = dislocation core radius (Å)

From electron microscopy results⁽⁷⁷⁾ it is evident that r is on the order of 10Å. The density calculated for the 0.184cm membrane by an iterative technique is 2×10^9 cm/cm³. This value compares excellently with that determined by Keh (79) (i.e., $10^8 - 10^9$ cm/cm³) using electron microscopy.

This density corresponds to approximately 4×10^{15} atomic planes perpendicular to the dislocation line per unit volume of material. The trap density, 1.9×10^{14} ; c_c , estimated from the permeation data at 25°C through equation 48, does not exceed this value indicating that accommodation of trapped hydrogen by dislocations is possible. In the thinnest sample, $L = 0.0075$ cm, where the calculated trap density is 1.5×10^{16} , the dislocation density is predicted to be on the order of $10^9 - 10^{10}$ cm/cm³ if the core interaction is dominate.

The dislocation evaluation, in contrast to that for voids,

yields a more realistic defect density. Hall (73) has shown through positron analysis that dislocations are the dominant defect at room temperature in aluminum. Here the positron analysis on annealed iron is performed at 25°C, the vicinity where the dislocation contribution is anticipated to be dominant.

8. Determination of the Trap Binding Enthalpy

The Oriani⁽²⁸⁾ physical treatment of McNabb and Foster's⁽³⁷⁾ trapping mathematics offers an expression for the calculation of the trap binding enthalpy, ΔH_b (i.e., the hydrogen atom bond energy to the dominant trap species). However, this approach is only applicable to cases of low trap occupancy where effective diffusivity is virtually independent of input concentration.

A more unrestricted expression applicable to the determination of ΔH_b can be developed by first considering the general equation for the total hydrogen concentration in solution within the membrane,

$$C_T = C_x + C_L, \quad (45)$$

The variables C_x and C_L can be replaced with the following Oriani expressions;

$$C_x = N n_x, \quad (50)$$

$$C_L = N_L n_L, \quad (51)$$

and

$$K = 1/n_L \frac{n_x}{1-n_x} \quad (52)$$

$$= e^{-\Delta H_b/RT} \quad (52a)$$

where

n_L = the fraction of ordinary lattice sites occupied.

N_L = ordinary lattice site density (#/cc).

The proper algebraic manipulation as given in Appendix I yields the following result:

$$K = \frac{N_L (C_T/C_L - 1)}{C_L + N - C_T} \quad (53)$$

The general expression for effective diffusivity as a function of concentration,

$$D = \frac{D_L C_L}{C_T} \quad (54)$$

first developed by Darken and Smith⁽⁶³⁾, can be rearranged to the ratio C_L/C_T terms $\frac{D}{D_L}$. Use of equation 54 is shown by

Oriani to be only appropriate in cases where trap occupancy is heavy. As discussed in section (IIIe) this condition has been

clearly satisfied by the data. In addition, $\frac{C_L D_L}{D}$ can be substituted for C_T .

Therefore,

$$K = \frac{N_L \left(\frac{D_L}{D} - 1 \right)}{C_L + N - \frac{C_L D_L}{D}} \quad (53)$$

Finally, substitution of equation (52a) for K in the expression $\Delta H_x = -RT \ln(K)$ yields the result

$$\Delta H_b = - RT \ln \frac{N_L \left(\frac{D_L}{D} - 1 \right)}{C_L + N - \frac{C_L D_L}{D}} \quad (56)$$

Both lattice diffusivity (D_L) and lattice solubility $\left(C_L = \frac{\phi \sqrt{p}}{D_L} \right)$ are calculable from the data collected at high temperatures where classical behavior of the mass transport parameters is observed. A maximal trapping effect is evident when

$$D = \frac{\phi \sqrt{p}}{3N} \quad (48)$$

This condition was shown to be obeyed for the data sets $L = 0.0165$ cm, $p = 0.0043$ cm and $L = 0.009$ cm, $p = 0.0043$. Consequently, trap densities for these respective sets of data can be legitimately calculated. The calculation ΔH_b will be

referenced to 25°C where the release of trapped hydrogen has a kinetically low probability. The ordinary lattice site concentration, N_L , is taken to be equivalent to the number of octahedral and tetragonal interstitial sites per/cm³;

$N_L = 3.825 \times 10^{23} \frac{\text{sites}}{\text{cm}^3}$. The results for each data set are shown in Table V.

Table VI. Trap Binding Enthalpy Data

L (cm)	p (atm)	N_x (traps/cc)	ΔH_b (kcal/mole)
.0165	.0043	8.09×10^{15}	10.1
10075	.0043	1.53×10^{16}	10.0

The trap binding enthalpy is seen to be virtually constant for both data sets having an average value of = 10.1 kcal/mole. Error amounting to as much as 200% for any of the parameters constituting K has an insignificant effect on ΔH_b since it is proportional to the natural logarithm of K . For example, assuming N_L to be halve of its calculated value, $\Delta H_b = 9.7$ kcal/mole for $L = 0.0165$ cm.

This value of ΔH_x compares well to the value of 9600 cal/mole theoretically calculated by Oriani⁽²⁸⁾ where binding enthalpy is taken to be equivalent to the interaction free energy $\bar{V}_H \sigma_h$ where V_H is the partial molal volume of hydrogen in α -Fe and σ_h is the hydrostatic component of the stress system two Burgers vectors from the dislocation core⁽⁶⁴⁾. Gabala⁽¹⁵⁾ has measured the interaction energy of a dislocation

with its hydrogen atmosphere to be 6400 kcal, approximately 35% lower than the value derived here. However, these results show large errors (i.e., ± 1.4 kcal/mole). The trap binding enthalpy derived here tends to indicate that a dislocation core-hydrogen interstitial interaction, rather than a dislocation - hydrogen atmosphere interaction, predominates. In addition, the fact that $\Delta H_b > \Delta H_s$ is consistent with the previously established condition $\beta \gg 1$.

E. 310SS

1.a. Surface Boundary Processes

An accurate examination of the bulk hydrogen transport in 310SS requires the elimination of surface impedances. Several experiments were conducted to investigate the effects of oxide films, hydrogen reduction treatments, and palladium coatings.

Samples either Pd coated or prepared by a sufficient number of hydrogen surface reductions obeyed the general criteria used to establish a bulk controlled transport process as previously discussed. Figures 29, and, 30 shows $J \propto p^{.5}$ behavior as predicted by Sieverts' law while Figure 31 shows $J_{\infty} \propto 1/L$. Scatter results from the inaccuracies in measuring the thickness of these extremely thin samples with a metric micrometer.

In contrast, surface processes are indicated by Figures 32 and 33 to be in effect for those samples undergoing only one surface reduction with hydrogen. Steady state flux

Figure 29 310SS Steady State Flux as a Function of Input Pressure.

Figure 30 310SS Steady State Flux as a Function of Input Pressure.

Figure 31 310SS Steady State Flux as a Function of Inverse Thickness.

Figure 32 Steady State Flux as a Function of Input Pressure for 310SS Exhibiting Surface Impedance.

Figure 33 Steady State Flux as a Function of Inverse Thickness for 3105S Exhibiting Surface Impedance.

is no longer linear with the square root of pressure or the reciprocal of thickness. Diffusivity is dependent on concentration as shown in Figure 34. Reproducibility in these runs was poor. Figures 35 and 36 show that after approximately 5 successive reduction with 0.43atm of hydrogen, at a fixed temperature of 268°C or above, both the steady state flux and diffusivity approach reproducible behavior. On the other hand, samples whose surfaces were reduced below 268°C showed no permeation no matter how many successive surface reductions were performed. The effect of this surface treatment, in comparison to an untreated sample, is to elevate both the diffusivity and permeability as shown in the Arrhenius plots, Figures 37 and 38. The results for the untreated sample are as follows:

$$\phi = 1.26 \pm 2.22 \times 10^{-18} \exp - \frac{17542 \pm 1399}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{atoms H}}{\text{cm s atm}^{\frac{1}{2}}}$$

$$D_E = 8.85 \pm .89 \times 10^{-3} \exp - \frac{11676 \pm 559}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{cm}^2}{\text{s}}$$

Results given for treated samples, discussed in the following two sections, show that the surface impedance has no effect on the apparent activation enthalpy for diffusion, while the frequency term is elevated by approximately a factor of two. In contrast, the surface impedance reduces the activation enthalpy for permeation by 26%.

Figure 34 Effective Diffusivity as a Function of Input pressure for 310SS Exhibiting Surface Impedance.

Figure 35 310SS Permeability Coefficient Diffusivity as a Function of the Number of Successive Hydrogen Reductions.

Figure 36 310SS Permeability and Effective Diffusivity as a Function of the Number of Successive Hydrogen Reductions.

Figure 37 310SS Effective Diffusivity as a Function of Reciprocal Temperature for Different Surface Treatments.

Figure 38 310SS Permeability Coefficient as a Function of Reciprocal Temperature for Different Surface Treatments.

The expression

$$J_{\text{eff}} = k_1 C_{\text{eff}} \quad (62)$$

as developed by Ash and Barrer, (36) can be used to ascribe a temperative dependence to an empirical surface kinetic transfer parameter. After normalizing equation 62 to classical parameters (i.e., $\frac{J_{\text{eff}}}{J} = \frac{k_1}{D/L} \frac{C_{\text{eff}}}{C}$), the following expression for the surface kinetic transfer parameter can be derived:

$$k_1 = \frac{J_{\text{eff}}}{J} \frac{C}{C_{\text{eff}}} \frac{D}{L} = \frac{D_{\text{eff}}}{L} \cdot \frac{L}{D} \frac{D}{L}$$

$$k_1 = \frac{D_{\text{eff}}}{L} \quad (63)$$

Figure 39 shows k_1 plotted as a function of reciprocal temperature. Values for the diffusivity of hydrogen in magnetite, a major constituent of the γ -SS oxide film, Table VII, yield on activation enthalpy of 15 kcal/mole.

Table VII. Data for Hydrogen Diffusion in Fe_3O_4 (80)

$T^\circ\text{K}$	$D(\text{cm}^2/\text{s})$
1084	0.028
1184	0.04
1284	0.087

Figure 39 310SS Surface Transfer Kinetic Parameter as a Function of Reciprocal Temperature.

This value is 20% higher than the observed activation enthalpy for surface transfer indicating that a Fe_3O_4 continuous film is not the probable flux limiting surface barrier.

The surface transfer activation enthalpy is nearly equivalent to that for classical diffusion. Therefore, the major effect on permeability is attributed to the solubility component which in turn is influenced by surface impedance. This surface impedance is removed chemically by reaction with hydrogen, above 268°C; below 268°C, no permeation is achieved. Fujii (81) has suggested that the upper layers of the oxide film form a spinel structure which is impermeable to hydrogen. Above 268°C it is removed by reduction with hydrogen exposing the more permeable sublayers. Electron microscopy and X-ray diffraction studies (82), (83) show the 50 Å intrinsic oxide film (i.e., the sublayers) to exist in a finely crystalline state, one approaching an amorphous nature.

Of interest is the virtual independence of the activation enthalpy of diffusion on surface treatment. This phenomena perhaps can be attributed to selective reduction of the stainless oxide sublayers. Areas rich in iron oxide are more easily reduced than those areas rich in chromium oxide. Therefore, during the initial reduction runs, islands of chromium oxide are still present on the surface, and consequently, reduce the effective cross sectional area of the specimen that actually permeates a measurable quantity of hydrogen. Recent atom-probe FIM analysis of 410SS by Krishnaswamy et al. (84) gives support to this concept. Chromium depletion from the surface oxide

with increase in annealing temperature, over the range 200-1000°C, was observed. Grain boundary diffusion of Cr was assumed operative and therefore it is plausible that the most significant areas of depletion are in the vicinity of surface grain boundaries. Park et al.⁽⁸⁵⁾ earlier showed similar results for 304SS by soft X-ray appearance spectroscopy. In addition, a slight manganese enrichment was observed. Therefore, an oxide layer inhomogeneous in composition is expected for stainless steel since the experiments are run within the temperature range where chromium depletion has been observed.

Selective oxidation also requires that the inter-molecular bonding between each oxide species must be much weaker than the primary oxide bonding. Secondary ion mass spectroscopy (SIMS)⁽⁸⁶⁾ for both positive and negative ion analysis indicate FeO, CrO, FeO₂, CrO₂ and small quantities of SiO and NiO to be present on the surface; no bimetallic oxides were observed indicating bi-metallic oxide structures to be weakly bonded.

2. Permeability

Once surface flux controlling processes are shown to be eliminated, an expression for the permeability coefficient is calculated by a least squares fit through the combined permeability data of all thickness, Figure 40, since no thickness dependence is observable. This expression for those samples whose surfaces were treated with hydrogen under the cited thermodynamic conditions is as follows:

Figure 40 310SS Permeability Coefficient as a Function of Reciprocal Temperature.

$$\phi = 5.55 \pm 1.56 \times 10^{17} \exp - \frac{13024 \pm 930}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{atoms H}}{\text{cm s atm}^{1/2}}$$

This activation energy is 26% lower than for the untreated sample, Figure 38.

This permeability coefficient is in excellent agreement with those samples undergoing the palladium surface treatment as is shown in Figure 41. This expression for permeation given below,

$$\phi = 5.43 \pm 1.45 \times 10^{17} \exp - \frac{13538 \pm 830}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{atoms H}}{\text{cm s atm}^{1/2}}$$

is lower than that observed by Kass (49) who also employed a palladium coating on 309S-SS without the prior surface reduction with hydrogen used here.

The literature survey showed values for the activation enthalpy for permeation ranging from 13000 to 17800 cal/mole. The value observed here lies in the lower percentile of permeability values suggesting other studies yielding higher values may have been influenced by surface impedance. In addition, the hydrogen surface treatment process shows excellent agreement with the more established palladium treatment technique.

3. Diffusivity

Effective diffusivity is independent of input gas pressure once surface flux limiting processes are eliminated,

Figure 41 310SS Permeability Coefficient as a Function of Reciprocal Temperature.

Figure 42. In addition, the diffusivity data for the hydrogen reduced membranes compiled in Figure 43 show no thickness variations in diffusivity implying this data to be representative of true lattice diffusion. An expression for diffusivity, given below, is calculated by a least squares fit through this data:

$$D = 9.56 \pm .40 \times 10^{-3} \exp - \frac{10788 \pm 474}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{cm}^2}{\text{s}}$$

Figure 44 shows this value for diffusivity to be in reasonable agreement with those membranes undergoing the palladium surface treatment. Here the expression for lattice diffusivity is given as:

$$D = 5.15 \pm .48 \times 10^{-3} \exp - \frac{11679 \pm 277}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{cm}^2}{\text{s}} ;$$

this activation enthalpy is lower than that observed by Kass (49).

The literature surveyed showed values for the activation enthalpy for diffusivity in austenitic stainless steel ranging from 11034 to 15600 cal/mole. The values determined here fall near the lower end of these bounds.

A plausible explanation for this low activation enthalpy for diffusion is the operation of grain boundary diffusion in austenitic stainless steels at temperatures less than 100°C, well below the lower temperature limit (i.e., 152°C) of this study. In addition, an anomalous break is anticipated in the

Figure 42 310SS Effective Diffusivity as a Function of Input Pressure.

Figure 43 310SS Effective Diffusivity as a Function of Reciprocal Temperature.

Figure 44 310SS Effective Diffusivity as a Function of Reciprocal Temperature.

diffusivity as a function of reciprocal thickness plot, where at lower temperatures the activation enthalpy for diffusivity shows a reduction in value. This phenomenon is not observed here. Since the grain size of 6 μ m is independent of thickness for the membranes tested, no grain size effect can be discerned.

Because low hydrogen input pressures (i.e. less than one atmosphere) are employed, the conditions for inducing a surface martensitic transformation in 310 SS, where fugacities are of the order of 10^3 atm are necessary, (10) are not satisfied. The X-ray diffractometer analysis, Figure 45 and Table VIII, verifies the sole existence of the fcc structure.

This lower activation enthalpy is attributed to neither grain boundary diffusion nor a hydrogen induced phase transformation but is only indicative of 1) an extremely clean surface and 2) perhaps a slight compositional effect on diffusivity among the different austenitic stainless steels.

4. Solubility

Once surface processes are eliminated, an expression for lattice solubility is derived from the permeability and lattice diffusivity data through equation 42.

The resulting expression for lattice solubility is

$$C_L = 5.81 \pm 1.16 \times 10^{19} \sqrt{P} \exp - \frac{2416 \pm 930}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{atoms H}}{\text{cc Fe}} .$$

The corresponding expression for the Pd coated samples shows

Figure 45 X-ray Diffractometer Data for 310SS.

Table VIII Diffractometer Data

<u>Sample</u>	<u>Bragg Angle (θ)</u>	<u>Resolved Planes</u>	<u>Lattice Parameter ($\text{\AA}$)</u>
NON-IRRADIATED 310SS	27.95°	(111)	3.5826 $\text{\AA}$
L = 0.011cm	32.75°	(200)	
	49.8°	(200)	

C

reasonable agreement with the above value:

$$C_L = 1.06 \pm .97 \times 10^{20} \sqrt{p} \exp - \frac{1859 \pm 830}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{atoms H}}{\text{cc Fe}} .$$

Examination of the literature data^{(27) (47) (49) (51)} shows that the heat of solution for hydrogen in austenitic stainless steel is always approximately 2 kcal/mole, regardless of variations in diffusivity and permeability among these studies. This consistency among values for the heat of solution supports the contention that the lower values of diffusivity and permeability observed in this study result from extremely clean membrane surface conditions.

For membranes undergoing no surface treatment, solubility is reduced and has the expression:

$$C = 1.42 \pm 1.33 \times 10^{20} p^n \exp - \frac{5866 \pm 1399}{RT} \frac{\text{cal}}{\text{mole}} \frac{\text{atoms H}}{\text{cc Fe}}$$

where $0.5 < n \leq 1$. This solubility no longer represents the true lattice solubility but describes the depletion effect that an oxide surface barrier has on the bulk solubility.

5. The Absence of Trapping in 310 SS

The independence of effective diffusivity from both input pressure and membrane thickness suggests that reversible trapping is not diffusion limiting in the hydrogen-310 SS system. Table IX shows that trapping in α -Fe enhances total solubility by 2 orders of magnitude at room temperature. When extrapo-

Table IX. Comparative Solubility Data

	L(cm)	P _c (atm)	T(°K)	C _L $\frac{\text{atomsH}}{\text{cc}}$
α -Fe	0.0165	0.43	300°K	5.93×10^{14}
γ -SS	0.013	0.43	300°K	3.09×10^{18}

Table IX. Comparative Solubility Data (con't)

	$C_T \frac{\text{atomsH}}{\text{cc}}$	$C_X \frac{\text{atomsH}}{\text{cc}}$
$\alpha\text{-Fe}$	1.72×10^{16}	1.66×10^{16}
$\gamma\text{-SS}$	-	-

lated to room temperature, the γ -SS lattice solubility is 4 orders of magnitude greater than the total solubility for α -Fe. Evidence has been given that dislocations are the dominant trap species in annealed iron where densities of 10^8 - 10^9 disl./cm² have been observed. Oriani (28) sites the same dislocation density for annealed steels in general. Therefore, the trap density and, consequently capacity(C_x) are on the same order of magnitude in both γ -SS and α -Fe. In this case, the trap contribution to the total solubility in γ -SS is negligible when compared to the larger lattice solubility.

6. Neutron Irradiation

a. Irradiation Conditions and their Influence on Radiation-Damage

In addition to the normal sample preparation procedure, membranes of the cited three thicknesses were neutron irradiated in a General Dynamics Triga-Mark II thermonuclear reactor in order to examine the influence of radiation damage, particularly microvoids, on hydrogen permeation. Fast and thermal neutrons are produced at flux levels of 1×10^{12} n/cm²s with a corresponding energy between 0.3-1 MeV. Gamma radiation at the reduced flux level of 6×10^{16} photons/cm²s is produced with low energies of approximately 0.3 MeV. Alpha radiation is also prominent. Sample temperature during irradiation is approximately 100°C.

The samples were wrapped with cadmium in order to minimize thermo neutron irradiation assuring less severe nuclear reactions, and consequently, a shorter decay period to safe radia-

tion levels, (e.g., 2 milliroentgens). Only 30 hours exposure was permitted due to the time-table of this study followed by a two month decay period. Under these conditions, the samples were exposed to a total fluence of 10^{17} n/cm².

Neutrons have a very high recoil energy and these recoils are distributed uniformly in energy. In addition, the track length of neutrons is over 100cm.⁽⁸⁷⁾ These features allow uniform irradiation of large volumes enabling surface and damage gradient effects to be avoided. Neutrons with energies between 100eV-2MeV undergo direct collisions with metal atoms which resemble, theoretically, those between elastic hard spheres. The basic effect of these collisions in metals is the displacement of atoms from lattice sites with the resultant interstitials and vacancies producing various configurations, the species depending on sample temperature and dosage. The elastic distortions produced by these defects can be treated by continuum mechanics resulting in a relative isotropic volume change $\frac{\Delta V}{V}$; therefore, an elastic strain is predicted to be present in these irradiated membranes.

Brager and Straalsund⁽⁸⁸⁾ have investigated the dependence of various defect types in 316 SS on sample temperature, ranging from 300 - 850°C, and neutron fluence, ranging from $0.75-5.1 \times 10^{22}$ n/cm² (E>0.1MeV), and observed the following tendencies:

- 1) The void number density decreases while the void diameter increases with increasing irradiation temperature.

- 2) The total faulted loop line length per unit volume and dislocation density increases with increasing fluence and decreases with increasing temperature.
- 3) The Frank loop diameter increases and number density decreases with increasing temperature.

However, the irradiation conditions (i.e., sample temperature of 100°C and fluence of 1×10^{17} n/cm²) of this study are well below those of Brager and Straalsund. Here the vacancy and interstitial concentrations are expected to be extremely high, in the neighborhood of 9×10^{-3} vacancies or interstitials /cc as determined by the following equation (87)

$$C_d = \frac{t \phi \sigma \Lambda E_1}{V_1 4 E_a} \quad (64)$$

where C_d = atomic concentration of displaced atoms/cc
 E_a = the critical displacement energy for Fe = 24eV
 σ = atomic scattering cross-sectional area for
Fe = 2.56×10^{-24} cm²
 Λ = $\Lambda(M(\text{neutron}), M(\text{Fe})) = 0.086$
 E_1 = energy of the neutron before collision = 10^6 eV
 V_1 = sample volume

This value is reduced by only a factor of 2.6 for the thinnest membrane.

Vacancy migration to voids or vacancy coalescence into voids and interstitial migration to sinks are considered to be

slow because of the low sample temperature (i.e., $\sim 100^\circ\text{C}$) during irradiation. Fast fluence (n, α) reactions can also produce helium concentrations uniformly distributed within the stainless steel on the order of 10^{12} atoms of He/gm γ -SS as extrapolated from Figure 46. This helium concentration would tend to stabilize the microvoids or vacancies against collapse, migration to sinks or contribute to their nucleation and growth.

Gamma radiation is not of great practical importance since neutrons generate recoils with much more energy thus causing orders of magnitude more damage. The principle means by which gamma rays produce damage are indirect processes in which fast electrons are generated: The possibility of M_{23}C_6 precipitates generated in sensitized stainless steels is negligible in this study since irradiation temperature never exceeds 100°C well below the sensitizing range.

In summary, under the irradiation conditions employed in this study large vacancy and interstitial concentrations on the order of $10^{-2}/\text{cc}$ are expected. These vacancies are probably stabilized by helium generated through (n, α) reactions. Approximately 10^{12} atoms $^{\text{He}}$ /gm S.S. exists in each sample and is uniformly distributed throughout the bulk.

b. Experimental Observations

The steady state flux plotted as a function of input pressure for the three thickness tested is shown in Figure 47 where

$$J \propto p^{.5 \pm .02}$$

Figure 46 Helium Content in Stainless Steel Irradiated in EBR-II.

Figure 47 Steady State Flux as a Function of Input Pressure for Irradiated 310SS.

indicates Sieverts' law to be obeyed; consequently, hydrogen transport is volume controlled. This result again demonstrates the utility of the successive surface reduction technique for the removal of surface oxides.

The induction period observed when nickel oxide is reduced by hydrogen is significantly shortened by irradiation of the nickel oxide with 260 MeV protons (90). Enhanced diffusion of nickel ions away from the surface is believed responsible; radiation induced vacancies increase ion mobility through the oxide. Similar effects are anticipated in iron oxide and chromium oxide, the other primary constituents of the austenitic stainless oxide. Therefore, neutron irradiation is expected to improve the efficiency of the oxide chemical reduction with hydrogen.

Effective diffusivity as a function of reciprocal temperature is shown in Figure 48. These results are about a factor of 3 below the values for non-irradiated samples, although the activation enthalpies for diffusion are comparable, indicating that some type of microstructural bulk delay mechanism is in operation which influences only the pre-exponential constant. However, Figure 49 and 48 show neither a concentration nor thickness effect on effective diffusivity, in contrast to those results for trapping in iron. Therefore, these delay sites are not of the "reversible" variety analyzed by McNabb and Foster (37). The suppression of the permeability coefficient and consequently, the solubility, Figure 50, appears to be confined to the pre-exponential constant.

Figure 48 Effective Diffusivity as a Function of Reciprocal Temperature for Irradiated 310SS.

Figure 49 Effective Diffusivity as a Function of Input Pressure for Irradiated 310SS.

Figure 50 Permeability Coefficient as a Function of Reciprocal Temperature for Irradiated 310SS.

Solubility plotted as a function of reciprocal temperature is shown in Figure 51. These results are about two orders of magnitude below the values in non-irradiated samples and are even an order of magnitude below the non-irradiated values where surface processes were evident.

Trapping of atomic hydrogen by vacancies is expected to increase solubility, not to decrease it as observed here. In those theoretical trapping models recently developed, trapping sites are generally assumed to be in local equilibrium with lattice sites, and hence, no effect on the steady state flux would be anticipated. In addition, diffusivity is predicted to be dependent on input pressure. Neither of these predictions are borne out here.

Whether or not the presence of helium within vacancies has any effect on the potential trapping effect is questionable. A chemical driving force for hydrogen migration to these helium filled vacancies should exist but this may be countered by mechanical energy considerations resulting from helium occupancy and vacancy surface stresses. Since helium is inert, no chemical reaction with hydrogen is anticipated. Consideration of these points lead to a helium effect that when maximized would only cancel the vacancy trapping capability thus rendering results comparable to those for non-irradiated samples. Vacancies, then, are not probable candidates for explaining the observed bulk behavior.

Traps that remove hydrogen from the lattice permanently tend to saturate with increase in input pressure and repeated

Figure 51 Solubility as a function of Reciprocal Temperature for 310SS.

exposure to hydrogen. Here, the bulk effect is independent of input pressure and is repeatedly reproducible. The traps may be saturated at fairly low input pressures (i.e., 0.0043 atm) but for a trap species capable of reducing solubility by two orders of magnitude, this is very unlikely.

The observed bulk behavior can be plausibly explained by considering the antithesis of trapping, a denuding operation, which phenomenologically parallels the observed results. The interaction energy between a pair of point defects derived by Eshelby⁽⁹¹⁾ is expressed as follows:

$$E_{int} = - \frac{15}{32\pi\gamma^2} \frac{\Delta V_1}{\Omega} \frac{\Delta V_2}{\Omega} \Omega d \frac{a_o^3}{r} \Gamma \quad (65)$$

where γ = Poisson's term

a_o = lattice constant

r = atomic volume

ΔV = volume change resulting from the interstitial atom species (1 or 2).

Γ = directional cosine term

d = elasticity constant term

$$= C_{11} - C_{12} - 2C_{44} .$$

For iron, the major elemental constituent of 310SS, d is negative. The volume change of hydrogen in tetrahedral interstitial sites is positive as is the volume change for interstitial iron. Therefore, E_{int} is positive, increasing as the migrating hydrogen interstitial atoms approach the iron inter-

stitial atoms. This localized interaction tends to increase the overall lattice energy and is therefore repulsive. The effective compressive stress field of each iron interstitial is expected to be denuded of atomic hydrogen thus decreasing the overall hydrogen lattice solubility.

In Eshelby's⁽⁹¹⁾ development of the point defect-point defect interaction, the stress field is assumed to have a non vanishing hydrostatic component, σ , while the lattice is elastically isotropic; the point defect expands the lattice equally in all directions. The complete equation for chemical equilibrium is, therefore, simplified to⁽⁶⁴⁾

$$RT \ln \frac{C}{C_{\infty}} = \bar{V}_H \sigma_h \quad (66)$$

where C_{σ} is the hydrogen concentration at the stress σ_h and C_{∞} is the hydrogen concentration under conditions of $\sigma_h = 0$.

Since no data is available for the partial molar volume of hydrogen, $\bar{V}_H$, in γ -SS, it is taken as that for ferritic iron, $2 \text{ cm}^3/\text{mole}$. After referencing the calculation to the temperature of the lowest data point, 461°K , C_{σ} and C_{∞} are determined from the irradiated and non irradiated results of Figure 51.

The hydrostatic stress under these conditions is

$-5.22 \times 10^{10} \text{ dyne/cm}^2$, the minus sign denoting compression.

Since the elastic modulus for steels is approximately

$210 \times 10^{10} \text{ ergs/cm}^2$, the corresponding isotropic strain is 0.02

well within the elastic strain of γ -SS. This compares reasonably well to neutron irradiation induced strains, on the order

of 10^{-1} (92) (93) which have been calculated for fcc metals with interstitial concentrations on the order of 10^{-2} . In addition, this compressive stress field accounts for the reduced lattice diffusivity as is theoretically expected by the analysis of Johnson⁽⁹⁴⁾.

Figure 52 and 53 show that after a 12 hr. anneal of 400°C of a membrane previously run at low temperatures, permeability is increased significantly while diffusivity show a relatively minor increase. Hence, recombination of these interstitials with vacancies or their migration to sinks reduces their effective concentration resulting in a larger hydrogen solubility.

In summary, surface processes and the traditional "reversible" trapping sites, such as vacancies, and permanent traps are not believed to be responsible for the bulk behavior observed in hydrogen mass transport through neutron irradiated 310 SS. The bulk behavior can be plausibly described by the repulsion of atomic hydrogen in solution form compressive Fe, Cr, Ni, etc. interstitial centers resulting in hydrogen denuded zones throughout the lattice.

F. The Isotope Effect

1. Procedure

The mass transport of deuterium through both zone refined Ferrovac-E iron and annealed 310 SS was compared to that of hydrogen. For each material, permeation was con-

Figure 52 Permeability Coefficient as a Function of Reciprocal Temperature for Irradiated 310SS.

Figure 53 Effective Diffusivity as a Function of Reciprocal Temperature for Irradiated 310SS.

ducted on the same membrane at identical input gas pressures and temperatures in order to minimize systematic errors in the diffusivity and permeability isotope ratios. All samples were palladium coated, by chemical plating on iron and vacuum evaporation on stainless steel to eliminate any flux limiting surface processes. Between deuterium and hydrogen runs, the purifier was evacuated to pressures of approximately 10^{-5} torr and then purged with the particular test gas to be used next. During the purifier preparation, the input chamber of the vacuum system was evacuated to base pressure (e.g., $\sim 10^{-9}$ torr) and then also purged with the particular test gas of interest. These precautions were necessary to prevent contamination between the test gases since the purifier palladium membrane is permeable to both gas species.

2. Ferrovac-E Iron

The Arrhenius plots for both permeability and diffusivity shown in Figures 54 and 55 parallel one another in that curves for hydrogen are higher than those for deuterium, and the respective hydrogen and deuterium activation enthalpies are identical within experimental error as shown in Table X. The low value of the pre-exponential constant ratios given in Table X reflect their sensitivity to small variations in activation enthalpy; this effect is further shown in Table XI by the data point comparison, for a 0.43 atm input pressure, where the ratio for both permeability and diffusivity vary from 1.25 at

Figure 54 Ferrovac-E Permeability Coefficient as a Function of Reciprocal Temperature for Different Hydrogen Isotopes.

Figure 55 Ferrovac-E Effective Diffusivity as a Function of Reciprocal Temperature for Different Hydrogen Isotopes.

Table X. Ferrovac-E Isotope Data

	$D_O \text{ (cm}^2/\text{s)}$	$\Delta H_D \frac{\text{kcal}}{\text{mole}}$	$\phi_O \frac{\text{atomsH}}{\text{cm s atm}^{1/2}}$
HYDROGEN	$1.61 \pm .23 \times 10^{-3}$	1688 ± 426	$2.53 \pm .71 \times 10^{17}$
DEUTERIUM	$1.52 \pm .22 \times 10^{-3}$	1934 ± 475	$2.25 \pm .68 \times 10^{17}$

Table X. Ferrovac-E Isotope Data (con't)

	$\Delta H_{\phi} \frac{\text{atomsH}}{\text{cm s atm}^{1/2}}$	$\frac{D_{\text{OH}}}{D_{\text{OD}}}$	$\frac{\phi_{\text{OH}}}{\phi_{\text{OD}}}$
HYDROGEN	8525±670	$1.06^{+.36}_{-.27}$	$1.13^{+.91}_{-.51}$
DEUTERIUM	8784±653		

TABLE XI

A Comparison of permeability and Diffusivity between Hydrogen
and Deuterium through Ferrovac-E Iron.

$T(^{\circ}\text{K})$	$\phi_{\text{H}}/\phi_{\text{D}}$	$D_{\text{H}}/D_{\text{O}}$
402	1.25	1.27
358	1.31	1.29
326	1.45	1.17
294	1.59	1.30
263	1.63	1.37
235	1.45	1.33
209	1.25	1.38
196	1.27	1.37
150	1.90	1.43
120	1.36	1.60
115	1.84	1.49
100	1.82	1.61
49	1.75	1.75

402°C to 1.75 at 49°C.

The ratios for diffusivity compare well to those for permeability within experimental error indicating the isotope effect to have no influence on solubility. The expressions for solubility of each gas species:

$$C_{H_2} = 1.57 \pm .94 \times 10^{-20} \sqrt{p} \exp - \frac{6837 \pm 670}{RT} \frac{\text{kcal}}{\text{mole}} \frac{\text{atomsH}}{\text{cc}}$$

$$C_{D_2} = 1.48 \pm .90 \times 10^{-20} \sqrt{p} \exp - \frac{6850 \pm 653}{RT} \frac{\text{kcal}}{\text{mole}} \frac{\text{atomsH}}{\text{cc}}$$

are virtually identical.

Flux is plotted as a function of input gas pressure for both hydrogen and deuterium in Figure 56. These plots not only show the absence of surface impedances (i.e., $J_{\infty} \propto \sqrt{p}$) but show the hydrogen/deuterium flux ratio to be independent of input pressure, effectively lattice concentration, at a given temperature.

In a classical model, the hydrogen/deuterium diffusivity ratio should be the square root of the effective mass ratio of $\sqrt{2}$. However, nonclassical behavior has been reported, Table XII, by Gonzalez⁽²⁰⁾ and Heumann and Primas⁽²¹⁾, who both employed permeation techniques at temperatures above 300°C, and by Heller⁽²²⁾ who employed the internal friction technique. Here the diffusivity and permeability ratios are 1.75 for the lowest temperature, 49°C, which compares well to the results of Heller, while

Figure 56 Ferrovac-E Steady State Flux as a Function of Input Pressure for Different Hydrogen Isotopes.

Table XII Literature Isotope Data

$\frac{D_H}{D_D}$	$\frac{D_{OH}}{D_{OD}}$	$\frac{J_{\infty OH}}{J_{\infty OD}}$	T (°K)	Reference
		$1.2^{+.15}_{-.29}$		Gonzalez (20)
	1.2			Heumann and Primes (21)
1.7			48°K	Heller (22)

the pre-exponential constant ratios compare reasonably well to the literature results.

3. 310 Stainless Steel

In contrast to iron, the permeability and diffusivity ratios, for an input pressure of 0.43 atm, at several temperatures show, Table XIII, 310 SS to exhibit the classical mass ratio, $\sqrt{2}$, within experimental error. The pre-exponential constants and activation enthalpies for this data plotted in Figures 57 and 58 are given in Table XIV.

Solubility again shows no isotope effect:

$$C_{H_2} = 1.05 \pm 1.54 \times 10^{20} \sqrt{p} \exp - \frac{1859 \pm 665}{RT} \frac{\text{kcal}}{\text{mole}} \frac{\text{atomsH}}{\text{cc}}$$

$$C_{D_2} = 1.48 \pm 1.60 \times 10^{20} \sqrt{p} \exp - \frac{2350 \pm 787}{RT} \frac{\text{kcal}}{\text{mole}} \frac{\text{atomsH}}{\text{cc}}$$

Steady state flux is plotted as a function of input pressure in Figure 59 demonstrating the pressure independence of the isotope effect and the absence of surface impedances.

Louthan and Derrick⁽⁵¹⁾ have fitted their data for deuterium in 304 SS to the classical mass law in comparing their data to the tritium data of Chaney and Powell⁽⁴⁸⁾, Figure 60. The authors consider the agreement to be excellent although some scatter is evident. Kass and Andrzejewski⁽⁴⁹⁾, using 309S-SS palladium coated by the

Table XIII.

A Comparison of Permeability and Diffusivity
between Hydrogen and Deuterium through
310-SS

$T(^{\circ}\text{K})$	$\phi_{\text{H}}/\phi_{\text{D}}$	$T(^{\circ}\text{K})$	$D_{\text{H}}/D_{\text{D}}$
779	1.51	717	1.39
745	1.31	679	1.37
714	1.43	647	1.34
672	1.58	616	1.35
646	1.43	587	1.37
613	1.40	556	1.50
584	1.40	525	1.49
560	1.51	499	1.33
492	1.41	472	1.29

Figure 57 310SS Permeability Coefficient as a Function of Reciprocal Temperature for Different Hydrogen Isotopes.

Figure 58 310SS Effective Diffusivity as a Function of Reciprocal Temperature for Different Hydrogen Isotopes.

Table XIV 310SS ISOTOPE DATA

	$D_O \text{ (cm}^2/\text{s)}$	$\Delta H_D \frac{\text{kcal}}{\text{mole}}$
HYDROGEN	$5.15 \pm .48 \times 10^{-3}$	11679 ± 277
DEUTERIUM	$3.20 \pm .37 \times 10^{-3}$	11499 ± 210

Table XIV 310SS ISOTOPE DATA (con't)

	$\phi \frac{\text{atomsH}}{\text{cm s atm}^{1/2}}$	$\Delta H_{\phi} \frac{\text{kcal}}{\text{mole}}$
HYDROGEN	$5.43 \pm 1.45 \times 10^{17}$	13533 ± 830
DEUTERIUM	$4.76 \pm 1.67 \times 10^{17}$	13357 ± 1001

Figure 59 310SS Steady State Flux as a Function of Input Pressure for Different Hydrogen Isotopes.

Figure 60 Tritium and Deuterium Diffusivity in Type 304L SS.

vacuum evaporation technique, obtained an average isotope effect:

$$\frac{\phi_{H_2}}{\phi_{D_2}} = 1.27 \pm 0.3$$

and

$$\frac{D_{H_2}}{D_{D_2}} = 1.23 \pm 0.08$$

, over the temperature range 150-550°C, indicating a possible deviation from classical behavior. This is in contrast to the values observed here:

$$\frac{\phi_{H_2}}{\phi_{D_2}} = 1.44 \pm 0.14$$

$$\frac{D_{H_2}}{D_{D_2}} = 1.38 \pm 0.12$$

over the temperature range 219-506°C.

It is evident that greater experimental accuracy is necessary in examining the deviation of the isotope effect from classical behavior.

4. Theoretical Modelling

The inability of the classical rate theory developed

By Wert and Zener⁽¹⁹⁾ to account for the iron results is thought to lie in its fundamental difficulty in defining the metastable energy when the diffusion process is arrested at the saddlepoint plane between points of stable equilibrium. Recently, quantum mechanics has been employed to describe the diffusion process for the case of strong coupling between lattice phonons and the migrating interstitial. This approach is based on the development of a band structure for hydrogen in metals⁽⁹⁵⁾ where the migrating hydrogen particle, a proton, is excited from a localized ground state to time dependent Wannier states, in several accessible bands, then descends into neighboring sites. The jump probability is now defined as

$$W = v_0 \exp^{-E/kT} \quad (67)$$

where E is the excitation energy of the band and v_0 is related to the width of the band. This approach can explain the Nb, Ta and V anomalies by defining the band by which hydrogen or deuterium migrate.

In iron although a band width difference is evident, no difference between the hydrogen and deuterium bands is observed. All quantum mechanical models including direct hopping transitions, lattice activated transitions and tunnelling treatments predict different energies for hydrogen versus deuterium lattice interactions and, like the classical rate theory, are presently inapplicable to

the case of iron.

CONCLUSIONS

Hydrogen-Iron System

1. The formation of a surface oxide film suppresses both the effective diffusivity and, consequently, the steady state flux, but have little effect on solubility indicating the oxide to be removable by chemical reduction with hydrogen.
2. At temperatures below approximately 600°K, the effective diffusivity increases with both increasing hydrogen gas pressure and increasing membrane thickness, while permeability is independent of these variables.
3. This transition temperature from classical to anomalous behavior decreases with increasing thickness.
4. Apparent activation enthalpies for diffusion range from 1.6 to 8.2 kcal/mole within the nonclassical region.
5. The fraction of trapped hydrogen approaches one near room temperature for the thinner samples.
6. The trapping behavior is explicable in terms of the McNabb and Foster model.
7. The trap binding enthalpy is calculated to be 10.1 kcal/mole, independent of trap density.

CONCLUSIONS (con't)

8. The presence of grain boundaries in iron has no effect on diffusion behavior.
9. Measurement of the defect density by the positron annihilation technique shows dislocations to be the most probable, dominant trap species.
10. The nonclassical protium-deuterium isotope effect is confined to the pre-exponential constant of the diffusivity expression.

Hydrogen-Austenitic Stainless Steel System

1. Effective diffusivity is dependent on input pressure while solubility is reduced by an order of magnitude when surface processes are flux limiting.
2. The activation enthalpy of diffusion is not influenced by surface processes although the pre-exponential constant is decreased by a factor of two.
3. A hydrogen reduction surface treatment, alternatively followed by deposition of a palladium film, establishes volume flux control.
4. The surface impedance behavior is explained by selective chemical reduction of surface oxide components.
5. Once surface processes are eliminated, effective diffusivity is independent of both input pressure and thickness and, therefore, is a true lattice diffusivity.
6. Samples neutron irradiated to a fluence of 10^{17} n/cm^2 show only a slight decrease in diffusivity while the solubility is decreased by over two orders of magnitude.
7. This solubility depletion is explained by the repulsion of hydrogen from the compressive stress field of the lattice interstitial atoms created during irradiation.

Hydrogen-Austenitic Stainless Steel System(con't)

8. The protium-deuterium isotope effect is classical within experimental error.

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Appendix I. Derivation Of An Expression For The Trapping
Equilibrium Constant, K.

$$1. \quad C_T = C_x + C_L \quad (45)$$

$$2. \quad C_T = 1 + \frac{C_x}{C_L} \cdot \frac{\frac{1}{1-n_x}}{\frac{1}{1-n_x}} \quad (68)$$

3. The following definitions are given by the Oriani analysis:

$$C_x = N n_x \quad (50) \quad C_L = N_L n_L \quad (51) \quad K = \frac{1}{n_L} \left(\frac{n_x}{1-n_x} \right)$$

4. Therefore,

$$\frac{C_T}{C_L} = 1 + \frac{C_x}{C_L} \cdot \frac{\left(\frac{1}{1-n_x} \right)}{\left(1 + \frac{n_x}{1-n_x} \right)} \quad (69)$$

$$\frac{C_T}{C_L} = 1 + \frac{C_x \left(\frac{K n_L}{n_x} \right)}{C_L \left(1 + K n_L \right)} \quad (70)$$

$$\frac{C_T}{C_L} = 1 + \frac{KN}{N_L + C_L K} \quad (71)$$

5. Expression (71) is now solved for K yielding the following result:

$$K = \frac{N_L \left(\frac{C_T}{C_L} - 1 \right)}{(C_L + N - C_T)} \quad (53)$$