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THE RELATIONSHIP BETWEEN CONCENTRATION
DEPENDENT DIFFUSION AND TRAPPING IN
THE HYDROGEN - IRON SYSTEM

by

Nathaniel R. Quick

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ABSTRACT

The influence of charging pressure on the diffusion of hydrogen through annealed iron was investigated. An ultra-high vacuum system, i.e., $\sim 10^{-9}$ torr), including a monopole residual gas analyzer (RGA) calibrated for an optimum resolution of 2.7×10^{12} atoms H/cm²-s was used to monitor the hydrogen flux over the temperature range 25-300°C. Hydrogen entry was affected by gas phase charging at .81, .46, .13, .016 and .0013 atm, respectively, for either a .0127, .0254 or .0381 cm thick specimen and a given temperature. The exponential pressure dependence of the steady state flux was determined in order to discern bulk controlled hydrogen transport from that which was surface controlled. The latter case was found to be prevalent over the temperature range 25-75°C.

Both the concentration and the membrane thickness dependence of diffusivity are explained on the basis of hydrogen trapping. Diffusivity was observed to decrease with both decreasing charging pressure and decreasing sample thickness at a constant temperature. The apparent activation energy for diffusivity was determined from isobaric measurements and found to range from $2.0 \pm .6$ to $9.6 \pm .6$ kcal/mole where the lower energies are associated with thicker samples. Hence the apparent activation energy for diffusion is observed to show an increase with decreasing sample thickness.

The permeability activation energy was found to be 8.2 ± 7 kcal/mole and is virtually insensitive to variation in both

charging pressure and sample thickness. In addition, the solubility activation energy is determined to be $6.1 \pm .7$ kcal/mole after determining the lattice diffusivity activation energy, $2.1 \pm .6$ kcal/mole, over the temperature range 400-500°C.

I. INTRODUCTION

A. General Remarks

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

Exposure of the higher strength alloys to low pressures of hydrogen gas is observed to instigate subcritical crack growth at very low stress intensities⁽⁴⁾. This phenomena is best categorized as external hydrogen brittleness since the crack is propagating in a bulk environment of molecular hydrogen gas. Electrochemical charging or prior exposure to hydrogen gas at high temperature and, perhaps pressure, where the hydrogen is distributed throughout the microstructure prior to the application of stress, results in what may be categorized as internal hydrogen brittleness⁽⁵⁾. The total bulk concentration of hydrogen is usually supersaturated with respect to the external hydrogen gas at low pressure, i.e., less than 1 atm.

Troiano⁽⁶⁾ suggests that during the embrittlement process, hydrogen diffuses preferentially to areas of maximum hydrostatic tension, i.e., lattice dilation, and subsequently, instigates cracking. 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 triaxiality.

Although the role of hydrogen in stress corrosion cracking is controversial, 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). Recently Johnson⁽⁵⁾ has put forth the fundamental concepts to allow the development of a diffusion controlled subcritical crack growth model which hinges upon a favorable agreement between the velocity of growth of subcritical cracks present in the metal lattice and that of hydrogen transport through the metal lattice. By allowing the physical interpretation of the "subcritical crack" to include pits, voids and other bulk stress concentrators, the theory can be used to elucidate the role of hydrogen not only in varieties of hydrogen assisted cracking but also in stress corrosion cracking.

B. Hydrogen-Iron System

Results from the numerous studies concerning the permeability, diffusivity and solubility of hydrogen in iron have yet to be synthesized into a clear and concise characterization of the system. Differences in experimental technique, specimen

preparation and material composition probably account for the majority of inconsistencies, observed mainly at low temperatures, in the compiled data. Nevertheless, several physical aspects characterizing this system are generally agreed upon.

Early solubility data based on gas-volume difference measurements show Sievert's law⁽¹⁰⁾, which is expressed below, to be obeyed at temperatures extending as low as 400°C and at pressures up to 100 atm.

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

where C = input subsurface concentration of hydrogen

k = proportionality parameter, which has an Arrhenius temperature dependence

p = hydrogen charging pressure

The $p^{1/2}$ dependence indicates that hydrogen enters the iron lattice in the atomic or dissociated form, rather than the molecular form and is distributed as a random solute.

Substantial evidence has been accumulated suggesting that hydrogen in solution occupies interstitial lattice sites. This concept is immediately suggested by consideration of the hydrogen and α -iron lattice parameters. Hydrogen with an atomic diameter of 1.06 Å⁽¹¹⁾ is smaller than the iron atom by a factor of 2.4 and should easily fit into tetrahedral and octahedral interstitial sites. In addition, lattice dilations

accompanying the diffusional jumps of hydrogen atoms from one interstitial site to another are anticipated to be small resulting in a low energy barrier to interstitial diffusion. With the assumption that interstitial diffusion is the operative mechanism of hydrogen transport through the α -iron lattice, McNeil⁽¹²⁾ has calculated the activation energy for lattice diffusivity to be 1.3 kcal/mole, while Wert and Zener⁽¹³⁾ have calculated the pre-exponential or diffusion frequency terms, approximately $1.6 \times 10^{-3} \text{ cm}^2/\text{s}$. Both values compare reasonably well with the high temperature experimental values shown in Fig. 1.

Snoek peaks have recently been observed by Gabala⁽¹⁴⁾ and Lord et.al.⁽¹⁵⁾, who used ultrasonic attenuation techniques, indicating the presence and rearranging of bcc interstitial atoms into preferential sites.

Finally, experiments on aged, hydrogen charged, electrolytic iron conducted by Mamontov and Toshkin⁽¹⁶⁾ substantiate not only the presence of hydrogen at interstitial lattice sites, but also reveal a steady change in the internal friction with large applied stress amplitudes, an effect they attribute to the accumulation of hydrogen in "traps".

C. Observed 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⁽¹⁷⁾ revealed a positive deviation from

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

Sievert's pressure dependence below 673°K as is shown in Fig. 2. In addition, an analysis of hydrogen solubility in α -iron by Hill and Johnson⁽¹⁸⁾ demonstrates in Fig. 3 that the solubility of hydrogen in α -iron is substantially greater at low temperatures, say 300°K. Nelson and Stein's⁽¹⁹⁾ solubility value determined by dividing their permeability expression by that for diffusivity is in agreement with this observed value.

Low temperature anomalies have also been prevalent in recent diffusivity studies resulting in substantial scatter of the data. However, refined experimental techniques, allowing the monitoring of minute fluxes and the consequent extension of diffusivity measurements to room temperature and below have revealed a discontinuity in the diffusivity versus the reciprocal of temperature curve.

A summary of these results for high purity iron, obtained with various vacuum techniques, appear in Fig. 1. Johnson and Hill⁽²⁶⁾ have extended their temperature range low enough to directly detect the 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 Fig. 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 ex-

Figure 2. Steady state Flux and its Charging Pressure Exponent as a Function of Reciprocal Temperature (17)

Figure 3. Solubility of Hydrogen in Iron⁽¹⁸⁾

perimentalists employing evolution rate methods (22,24, 26) than by those using permeability methods indicating that some barrier to hydrogen transport is operable in the iron at these low temperatures.

D. 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⁽²⁷⁾:

- 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⁽²⁷⁾ approach the problems by equating fluxes in the steady state and developing a series of equations applicable to most experimental conditions. Their conclusion is that the steady state flux may be expressed by

$$J = \frac{K(p_1, \theta, U_s)}{\left(\frac{L}{D} + \frac{1}{K_4}\right)} \quad (2)$$

where L = membrane thickness

D = diffusivity

K_4 = the transmission coefficient for the passage of a gas atom through the surface boundary

$K(p_1, \theta, U_s)$ = a parameter that is a function of charging pressure (p_1), surface coverage (θ), and saturation concentration (U_s).

The diffusion or bulk transport processes are flux controlling under the condition

$$\frac{L}{D} > \frac{1}{K_4} \quad \text{i.e.,}$$

$$J \approx K(p_1, \theta, U_s) \frac{D}{L} \quad (3)$$

while surface transport processes are flux limiting when

$$\frac{1}{K_4} > \frac{L}{D} \quad \text{i.e.,}$$

$$J \approx K(p_1, \theta, U_s) K_4 \quad (4)$$

However, certain limitations of this approach are immediately obvious when applying equation (3) to evaluate the presence of bulk transport control. A geometrical limitation must be necessarily placed on L , for if L is too large, surface limiting processes are not discernible; whereas if L is too small, bulk

processes cannot be resolved.

Chang and Bennett's⁽¹⁷⁾ simplification of Ash and Barrer's approaches elucidates the influence of surface flux impedance processes on the pressure dependence of the flux. Their mathematics yield

$$J\left\{1+\left(\frac{L\sqrt{J}\sqrt{K_2}}{D}\right)^2\right\} = K_1 p \quad (5)$$

where J = steady state flux

K_2 = rate of evaporation

K_1 = rate of solution

} surface transfer coefficients

and

$$\frac{LJ}{D} = C_1 - C_2 \approx C_1 \quad (6)$$

where C_1 = input subsurface concentration

C_2 = output subsurface concentration

(≈ 0 since p_1 is usually maintained $\gg p_2$)

The ratio $\frac{K_2}{J}$ expresses the relative magnitudes of the surface transfer rate to that of permeation. If at high temperatures it is assumed that K_2 is fast such that $K_2 > J$, then concentration equilibrium is maintained at both surface boundaries and equation (5) reduces to

$$J \approx \frac{D}{L} \sqrt{\frac{K_1}{K_2}} p_1^{1/2} \quad \text{for } \frac{L\sqrt{J}\sqrt{K_2}}{D} \gg 1 \quad (7)$$

Since Sievert's Law is obeyed under these conditions, equation

(6) is rewritten

$$J = \frac{DK}{L} \sqrt{p} \quad (8)$$

showing that $K \approx \sqrt{\frac{K_1}{K_2}}$. At low temperatures the surface processes are assumed slow; consequently $K_2 \ll J$ and non-equilibrium conditions exist at both surface boundaries, i.e.,

$$J = \frac{K_1}{2} p \text{ for } \frac{L\sqrt{J}\sqrt{K_2}}{D} \ll 1 \quad (9)$$

For intermediate cases, $J \propto p^x$ where $1/2 < x < 1$. In other words, if surface processes are operable, Sievert's pressure dependence is not obeyed! In addition, the influence of surface processes can be discerned by plotting the permeating flux as a function of pressure and computing the pressure exponent.

The effect of surface flux impedance processes on time lag diffusivity measurements should be mentioned. The mathematics developed by Jaeger⁽²⁸⁾ together with the model of permeation developed by Dodge and Phillips⁽²⁹⁾ imply that any time lag measurements taken when the surface flux limiting processes are relatively large compared to the bulk diffusion will yield a diffusivity calculable to within a factor of 3. This result substantiates Barrer's⁽³⁰⁾ earlier comment that the time lag and consequently the diffusivity is relatively insensitive to surface processes.

The obvious surface barrier on α -iron is the chemisorbed

iron oxide ($\alpha\text{-Fe}_2\text{O}_3$) film extending about $30\text{\AA}$ ⁽³¹⁾ above the metal surface. M. R. Piggot⁽³²⁾ has calculated the diffusivity of hydrogen in the film, at room temperature, to be $1.8\text{--}66 \times 10^{-17} \text{ cm}^2/\text{s}$ for films ranging from 90 to $1000\text{\AA}$, a factor of 10^{-12} slower than bulk diffusion.

E. Bulk Hydrogen Delay

A major shortcoming of the surface resistance concept is its inability to explain the high residual hydrogen concentrations in iron observed during evolution studies at low temperatures. This phenomenon, implying a trapping of hydrogen at preferential bulk sites, and the related theory have been well documented by Kumnick⁽³³⁾ and Hancock⁽³⁴⁾. Consequently, only a brief summary of recent developments dealing with the characterization of traps will ensue.

All structural irregularities including grain boundaries, dislocations, voids and internal surfaces can be operational trapping sites. By assuming local equilibrium between lattice (ordinary sites) and traps (extraordinary sites), Oriani⁽²¹⁾ has expressed the parameters employed by MacNabb and Foster⁽³⁵⁾ in terms of the kinetic trapping parameter, k_T , and the kinetic trap release parameter, p_T , as follows:

$$\alpha = N_x k_T / p_T = \text{trapping parameter} \quad (10)$$

where N_x = trap density

and

$$\beta = C_L k_T / p_T = n / 1 - n = \text{activity of hydrogen in traps} \quad (11)$$

where C_L = normal lattice solubility

n = fractional occupancy of traps.

For small values of fractional trap occupancy such that $\beta \ll 1$, the true lattice diffusivity can be related to the experimentally measured diffusivity in thin membranes in the following manner:

$$D = \frac{D_L}{1+\alpha} \quad (12)$$

A discussion on the two limiting conditions of equation 12, i.e., $\alpha \gg 1$ and $\alpha \ll 1$, is deferred to a later section.

For large n such that $\beta \gg 1$,

$$D = D_L \left(1 + \frac{3N_x}{C_L} \right)^{-1} \quad (13)$$

In the latter case, it follows that⁽²¹⁾

$$\frac{\partial \ln D}{\partial (1/T)} = \frac{E_L}{R} + \frac{3N_x}{C_L + 3N_x} \left(\frac{\Delta H^\circ}{R} \right) \quad (14)$$

where E_L is the activation energy of normal lattice diffusion and ΔH° represents the heat of solution (E_s) at fixed pressure for the reaction $1/2H_2(g) = H$. At high temperatures and/or low trap densities, i.e., $C_L \gg N_x$, the apparent activation energy, E_D , then approaches E_L . Conversely, at low temperatures and/or high trap densities, i.e., $N_x \gg C_L$, the apparent activation energy approaches the sum, $E_L + E_s$ equal to the permeation activation energy, E_ϕ . Consequently, the apparent

activation energy is predicted to show a variation with lattice solubility and/or trap density within the limits $E_L + E_S \geq E_D$ ($N_x, C_L \geq E_L$); an apparent activation energy transitional range is predicted. By interpreting the extraordinary sites as voids and utilizing the concept of localized equilibrium between voids and lattice sites, Chew⁽³⁶⁾ arrives at the same limitations on the apparent activation energy.

While C_L obeys the general form of Sievert's Law, i.e.,

$$C_L = K_O p^{1/2} e^{-E_S/kT} \quad (1a)$$

the influence, if any, of temperature and charging pressure on trap density has yet to be experimentally examined. In addition, both the inequalities $C_L \gg N_x$ and $C_L \ll N_x$ probably can be established for high and low charging pressures, respectively.

A particular kind of trap whose density is controlled by charging gas pressure and is not fixed by microstructure is the di-interstitial. The treatment of these di-interstitials, assumed to be immobile, in equilibrium with single interstitials is a major concept of the trapping theory proposed by Ono and Rosales⁽³⁷⁾. The total concentration of hydrogen in the iron lattice, C_T , in equilibrium with the hydrogen charging pressure, p_{ext} , is expressed for small values of C_r as:

$$3 \left(\frac{p_{exp}}{p_O} \right)^{1/2} \exp S_f^{(1)} / R \exp \left(-\frac{H_f^{(1)}}{RT} \right) + 2 \left(\frac{3Z}{2} \right) \left(\frac{p_{exp}}{p_O} \right) \exp \frac{S_f^{(2)}}{R} \exp \left(-\frac{H_f^{(2)}}{RT} \right) \quad (15)$$

where (1) = single interstitials

(2) = di-interstitials

P_o = standard external hydrogen pressure taken to be 1 atm

H_f = enthalpy of formation at $p_{exp}=P_o$

S_f = vibrational entropy of formation

Z = coordination number of the di-interstitials

R = gas constant

T = absolute temperature

A positive binding enthalpy is defined as $B = 2H_f^{(1)} - H_f^{(2)}$, the assumption is made that $2S_f^{(1)} = S_f^{(2)}$, then equation (2) is solved for C_1/C_T :

$$C_1/C_T = 2/1 + [1 + (4ZC/3) \exp(B/RT)]^{1/2} \quad (16)$$

This value is substituted into the equation for diffusivity,

$$D = \frac{C_1}{C_1 + 2C_2} D_L \quad (17)$$

derived under the condition $D_L \gg D_2$, resulting in the expression

$$D = 2D_o \exp(E_L/RT) / \{1 + [(1 + 4ZC_1/3) \exp B/RT]^{1/2}\} \quad (18)$$

A good agreement between calculated and experimental values are demonstrated when B is taken as 10-11 kcal; an anomalous apparent activation energy transitional range is evident.

Fig. 4 shows the large observable shifts in the diffusivity versus the reciprocal of temperature plot resulting from the variance in C_T . This observation indicates a concentration dependence of the effective diffusivity. The justification in assigning a relatively large value to B can only be borne out by future internal friction experiments.

In summary, the phenomenon of trapping is shown to be necessarily accompanied by a dependence of effective diffusivity upon lattice concentration. Darken and Smith⁽³⁸⁾ were first to consider this concept and to develop the general expression for diffusion as a function of concentration in the H - Fe system:

$$\frac{D_L t_{1/2}}{a^2} = K C_T / C_L \quad \text{or} \quad D = C_L / C_T D_L$$

where $t_{1/2}$ = half time for hydrogen evolution

a = specimen thickness

K = numerical constant

$$D = 1/K \frac{a^2}{t_{1/2}}$$

Recent work by Nanis⁽³⁹⁾ confirms the dependency of hydrogen diffusion in iron on concentration.

F. Purpose

The majority of gas-phase permeation studies conducted to determine the kinetics of hydrogen transport through iron

Figure 4 Effective Diffusivity as a Function of Reciprocal Temperature for Several Total Hydrogen Concentrations as Theorized by the Di-Interstitial Trapping Concept.

and iron base alloys have been limited to either high temperature ranges or high input concentrations. Because of the lack of system, material and material preparation specifications, much of this older data is unreliable. A system has been designed to accurately calculate the hydrogen transport parameters from gas-phase charging measurements at reasonable pressures and in the temperature range where hydrogen assisted cracking phenomena are most prevalent. Charging pressures below and near one atmosphere and temperatures in the range 300-600°K are used.

Anomalies in the values of these bulk transport parameters have been explained by the presence of traps in the material and the related concentration dependence of diffusivity. The applicability and validity of these theories can be examined. Since surface resistance to bulk adsorption can introduce large errors in the calculation of the bulk transport parameters, an investigation dealing with the surface preparation of the samples was also undertaken.

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 adjoining a high vacuum system.

II. EXPERIMENTAL

A. Material Composition

The ferritic iron chosen for this investigation is Ferrovac-E, supplied by Crucible Steel. This vacuum refined, high purity iron was received in 1/2 in. diameter rods having the following composition:

<u>Element</u>	<u>%</u>
Carbon	.016
Manganese	.002
Phosphorous	.004
Sulfur	.007
Silicon	.007
Nickel	.05
Chromium	.01
Vanadium	.004
Tungsten	.01
Molybdenum	.002
Cobalt	.003
Copper	.001
Aluminum	.01
Tin	.004
Lead	.0005
Nitrogen	.001
Oxygen	.001
Hydrogen	.0032

B. Specimen Preparation

The as-received iron rods were arc-cast under a 0.5 atm argon-gettered environment in order to produce 2.54 cm x 2.54 cm x .635 cm ingots. A succession of cold rolling reductions and anneals, as shown in Table I, were conducted until the desired thicknesses ranging from .0381 cm to .0127 cm were obtained.

Discs with a 1.205 cm diameter were then punched out of the rolled iron strips backed with .01 cm brass shim stock to prevent excessive deformation around the sample's circumference. Vacuum brazing of the discs onto especially machined copper gaskets (see Fig. 5) with a Nicro braze was accomplished at 950°C, after an additional anneal, under 5×10^{-6} torr. Following this operation, a leak check was performed on every assembly. The exposed sample area is approximately 1.5 cm².

The iron samples were chemically polished for approximately 90 seconds by placing a few drops of a solution comprised of 1 part H₂O₂: 2 parts H₃PO₄ on the surface; the copper gasket and braze region are suitably masked with etch-stop lacquer. After one side was etched, it was quickly rinsed and kept submerged in water, contained in a petrie dish, in order to impede reformation of the oxide film. During the rinsing, the lacquer is peeled off. The remaining side of the assembly was treated in the same manner. The samples were then palladium plated by placing the assembly in Pallamarse solution for approximately 30 seconds. This procedure yielded consistently

TABLE I.

Specimen Processing

Rolled Thickness (cm)	Anneal Temp. °C	Anneal Time hr.	Furnace Cooling
.635	850	2-4	unnecessary
.264	850	1	unnecessary
.0508-.0381	850	1-2	necessary to allow sufficient stress relieving
final thicknesses .0381, .0254, .0127	850	1	necessary to allow sufficient stress relieving

reproducible charging conditions.

C. Method

Utilization of an optimum system sensitivity of 2.7×10^{12} atoms $\text{H}/\text{cm}^2\text{s}$ allows the detection of those fluxes resulting from 10^{-3} to .85 atmospheres of charging pressure and the sample temperature range 25 to 550°C . The quantity of hydrogen passing through the iron membrane's exit surface into the monitoring chamber, initially maintained $\sim 10^{-9}$ torr, is recorded as a function of time. The evolved gas is ionized and then analyzed with a Veeco SPI-10 Monopole Residual Gas Analyzer (RGA) specifically calibrated for hydrogen identification. The ionization current is a direct measure of the amount of evolving hydrogen and is converted to the more convenient units of pressure by first calculating the RGA sensitivity to hydrogen. This value, given below, is determined by dividing the RGA hydrogen ionization current by the corresponding hydrogen pressure given by an adjoining ionization pressure guage:

$$\text{RGA sensitivity} = 2.4 \times 10^{-5} \text{ amp/torr.}$$

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

$$\text{Pressure} = \frac{(\text{RGA Meter deflection in amperes})}{\text{sensitivity in amp/torr}}$$

$$\text{Steady state pressure rise} = \frac{\Delta p}{\Delta t_{\infty}} = \frac{\Delta \text{RGA Meter deflection in amperes}}{\Delta (\text{corresponding time in seconds}) \times (\text{sensitivity in amp/torr})}$$

A companion Veeco SPR-12 (Yokogawa Type 3046) strip chart recorder plots the evolved hydrogen pressure in the monitoring chamber as a function of time.

Steady state flux is determined by the pressure rise technique⁽⁴⁰⁾ where the following relation is employed:

$$J_{\infty} = \frac{2}{A} \left. \frac{dN}{dt} \right|_{\infty} = \frac{2V}{KTA} \left. \frac{dp}{dt} \right|_{\infty} \quad (20)$$

J_{∞} = steady state flux ($\frac{\text{atoms H}}{\text{cm}^2\text{-s}}$)

$\left. \frac{dp}{dt} \right|_{\infty}$ = steady state pressure rise (torr/s)

N = atoms at hydrogen (necessitating use of the factor 2 since molecular hydrogen is measured)

V = monitoring subsystem volume (l)

K = Boltzmann's constant = 1.03×10^{-22} liter - torr/°K

T = temperature of the evolved gas equaling the temperature of the sample (°K)

In addition, J_{∞} is determinable by the following expression:

$$J_{\infty} = \frac{2}{A} \left. \frac{dN}{dt} \right|_{\infty} = \frac{2F(p-p_B)}{KTA} \quad (21)$$

where

F = pumping speed (= system conductance) (l/s)

p = evolved pressure (torr) at and beyond steady state

p_B = monitoring subsystem base pressure,

showing that the maximum system sensitivity, when under a dynamic vacuum, is dependent on the background hydrogen

pressure and the hydrogen pumping speed. Since the ultimate sensitivity of the RGA is 10^{-10} torr, by restricting the conductance of the monitoring chamber so that the effective pumping speed on the chamber is, say .01 l/s, an ultimate system sensitivity of 10^7 atoms H/cm²s can be obtained. However, the optimum conditions chosen in this experiment were $F=63.5$ l/s and $p_B = 10^{-9}$ torr giving a sensitivity of $2.7 \times 10^{12} \frac{\text{atoms H}}{\text{cm}^2\text{s}}$ at 300°K; at this pumping speed, evacuation of the system was relatively rapid.

All data, as mentioned above, was recorded under a dynamic vacuum at the above pumping speed, which is reasonably constant over the observed evolved pressure range, resulting in reduced magnitudes of flux. To compensate for this effect, a scaling factor b is derived as follows by first equating (20) and (21):

$$V \left. \frac{dp}{dt} \right|_{\text{actual}} = V \left(\left. \frac{dp}{dt} \right|_{\infty} b \right)_{\text{recorded}} = F (p - p_B)$$

$$\text{Therefore: } b = F(p - p_B) / V \left. \frac{dp}{dt} \right|_{\infty} \text{ recorded} \quad (22)$$

By using the data yielding the lowest detectable dp/dt_{∞} , b is calculated, i.e.,

$$b = 8.3 \times 10^3 \dots\dots\dots$$

Consequently, J_{∞} is expressed as follows:

$$J_{\infty} = \frac{2Vb}{KTA} \left. \frac{dp}{dt} \right|_{\infty} \text{ recorded} \quad (23)$$

A schematic of the stainless steel high vacuum system is shown in Figure 5. The entire system is initially roughed to $<10^{-3}$ torr by a mechanical pump in series with a liquid nitrogen cooled molecular sieve trap in order to limit contamination and, at higher temperatures, oil activated oxidation of the membrane surface. After the roughing pump is valved off, the system's base pressure is reduced to $<10^{-8}$ torr by two Veeco MagIon 20 l/s pumps. The system, which is insulated with asbestos cloth and aluminum foil, is baked with heating tape for at least 24 hrs. at 250-300°C. The pumps are allowed to cool down after the first 12 hrs. so as to boost their evacuation speed.

At the conclusion of the bakeout procedure, the entire system is cooled to room temperature and the monitoring subsystem is valved off from the charging subsystem. The RGA analyzer tube is then outgassed at 15 minute intervals, in order to prevent any extensive pressure rise, until the background pressure shows no noticeable increase with the RGA in operation; this particular procedure is repeated before each experimental run. Finally, the system is pumped out for an additional 24 hrs. to ensure minimal system degassing. Prior to the commencement of each set of experimental runs, the monitoring chamber is evacuated to a base pressure $\sim 10^{-8}$ torr.

Some hydrogen is prone to diffuse into the titanium coating covering the pump cathode without undergoing chemisorption. This residual hydrogen concentration is inevitably

VACUUM SYSTEM SCHEMATIC

Figure 5 Vacuum System, Electrical Circuitry and the Specimen-Gasket Assembly

regurgitated into the pump cavity and system, consequently, leading to a background pressure rise. In order to remove this unreacted hydrogen, the MagIon pumps are periodically baked for approximately 4 hrs. in the off position while under a rough vacuum.

Hydrogen is purified with an Englehart palladium diffusion purifier before flowing through a leak valve into the pressure adjustment chamber. The charging pressure is adjusted with an NRC type 501 thermocouple guage in conjunction with an Ashcroft absolute pressure guage. Application of the charging pressure to the specimen input surface is spontaneous upon the opening of the manual charging control valve.

Evacuation of the monitoring chamber and the charging chamber is allowed between the experimental runs of a set, characterized by a constant sample temperature and a sequence of charging pressures, until the initial background monitoring chamber background pressure is obtained thus ensuring sufficient degassing of the sample.

Regulation of the specimen's temperature is accomplished with a Leeds and Northrup Electromax controlling the current flow into the heating tape surrounding the flange which contains the specimen. It should be noted that the sample is heated indirectly by thermal conduction through the system's walls and the copper gasket. An alumel-chromel thermocouple, especially fabricated for high vacuum application by Temp-Pro Inc., is fed through a double sided conflat flange into the

system allowing direct contact of the thermocouple junction with the center of the iron disc. A Leeds and Northrup 8960 potentiometer displays the thermocouple readings. 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. Experimental Parameters

1. Bulk vs. Surface Control

It is imperative to demonstrate that surface boundary processes are not flux limiting in order to establish that hydrogen transport is bulk diffusion limited. If Sievert's Law is obeyed, which implies local equilibrium at the surfaces, the steady state flux is proportional to the charging pressure to the 1/2 power, i.e.,

$$J_{\infty} = \frac{KD\sqrt{p}}{L} \quad (8)$$

indicating the surface processes to be faster than bulk diffusion; the flux is volume controlled. Deviation of the pressure exponent within the limits $1/2 < n < 1$ signifies a gradual rise in the degree of flux impedance resulting from a decrease in the kinetics of the surface processes. Figures 6 - 9 illustrate that for the pd coated samples bulk diffusion flux control is prevalent at temperatures above 75°C; while below this temperature, surface impedance of the flux gradually increases with a continued reduction in temperature.

In addition, Chang and Bennett's data, shown in Fig. 2, reveal an anomalous break in the plot of permeability versus inverse temperature occurring with an increase of n above 0.6. This observation is substantiated by the results shown in

Figure 6 Steady state Flux as a Function of Charging Pressure for Several Isotherms

Figure 7 Steady State Flux as a Function of Charging Pressure for Several Isotherms

Figure 8 Steady State Flux as a Function of Charging Pressure for Several Isotherms

Figure 9 Steady State Flux as A Function of Charging Pressure for Several Isotherms

Fig. 10 where Q_s is the activation energy when surface impedance is observed for $T < 75^\circ\text{C}$. The corresponding anomalous break in the plot of diffusivity versus inverse temperature, shown in Fig. 11 for $T < 75^\circ\text{C}$, is associated with this surface impedance. When these diffusivities associated with surface impedance are multiplied by a factor of three or less, they fall near the volume controlled diffusivity values predicted by extrapolation of the curve for $T > 75^\circ\text{C}$. This observation substantiates the prediction of Dodge and Phillips⁽²⁹⁾ that surface impedance affects diffusivity by at most a factor of three.

The temperature dependence of surface activation suggests that the surface barrier is a hydrogen reducible oxide; i.e., PdO . A greenish film, characteristic of PdO ⁽⁴¹⁾ was observed on the input side of each removed sample. Since the charging chamber was repeatedly roughed out by the mechanical pump during the adjustment of charging pressure, the risk of surface oxidation is high if the cold trap and roughing line proves even slightly defective. The backstreaming of contaminations and the entrance of oxygen through leaks into the system is then possible.

This technique for determining the degree of surface impedance on hydrogen transport allows the evaluation of "good" data points; those points for which no surface influences are detectable. Occasionally, at the lower charging pressures, the residual background pressure produced by desorption of H_2

Figure 10 Steady State Flux as a Function of Reciprocal Temperature for Several Charging Isobars

Figure 11 Effective Diffusivity as a Function of Reciprocal Temperature for Several Charging Isobars

from the system's walls and by outgassing of the RGA filament obscure the actual steady state flux as shown in Fig. 6 ($T = 119^{\circ}\text{C}$).

The criterion for identifying volume flux control, i.e.,

$$J \propto 1/L \quad (3)$$

was examined to (a) determine its sensitivity to thin membranes, and (b) serve as a check on the above results; Figure 12 shows these results to be consistent. An interesting observation, seen also by Kumnick⁽³³⁾, is the existence of a threshold thickness above which no flux is detectable. This result is most plausibly explained as indicating the minimum flux detecting sensitivity of the experimental technique.

2. Palladium

It is important to show that the palladium, which is plated on both sides of each iron membrane, exerts no limitation on the hydrogen flux. Interferometer thickness measurements conducted on one of the .0127 cm specimens showed the film to be $<9 \times 10^{-6}$ cm and in some areas too thin to be detected by the instrument, i.e., $<2 \times 10^{-6}$ cm. In addition, the solubility of hydrogen in Pd is 3 orders of magnitude higher than that for iron.⁽⁴²⁾ The preceding information allows an order of magnitude comparison of the flux permeating the Pd films to that permeating the iron. The steady state flux is represented as follows:

$$J_{\infty} = \frac{DK\sqrt{p}}{L}$$

Figure 12 - Steady State Flux as a Function of Inverse Thickness

This computation is conducted for the thinnest membrane tested, i.e., .0127 cm, at 200°C.

	<u>Fe</u>	<u>Pd</u>
P	1	1
D	$\sim 10^{-4}$ (2)	$\sim 10^{-5}$ (3)
K	1	100 (1)
L	10^{-2}	10^{-5}

$$\frac{J_{\infty \text{Pd}}}{J_{\infty \text{Fe}}} = \left(\frac{100 \times 10^{-5}}{10^{-5}} \right) \left(\frac{10^{-2}}{1 \times 10^{-4}} \right) = 10^4$$

It should be remarked that this ratio slightly decreases with increasing temperature. Hence, the pd film is seen to have no limiting influence on the hydrogen flux.

The presence of palladium on both the entrance and exit surfaces of each specimen is necessary to render the data consistently reproducible. During the preparation of the specimen, the iron oxide film is removed by chemical polishing immediately prior to the pd plating operation. The presence of pd on the surface prevents any subsequent chemisorption of an oxide layer on the iron.

3. Recorded Data and Reproducibility

Two distinct regions are evident in the typical permeation curve, typical of those recorded in this experiment, shown in Figure 13. A transient region shows the increase of hydrogen flux, as indicated by the pressure rise, with time. The

Figure 13 Typical absorption transients for specimen temperatures above 75°C

curve then enters into a steady state region which is representative of a stationary concentration profile within the membrane. The various parameters affecting the magnitude of the steady state flux are given in equation (8).

In addition, a breakthrough time occurred for those experiments run below 75°C exhibiting flux impedance by the surface. Its length depends primarily on the system's sensitivity to low fluxes.

The diffusivities and permeability values for a given sample were easily duplicated over the various isobars. In addition, at least one check specimen for each thickness was tested and, as indicated in Figures 14 and 15, showed remarkable agreement with the diffusivities, permeability and activation energies of the original.

For curves yielding a lag time on the order of .1 second, as shown in Figure 13, a 20X microscope, equipped with a linear scale, was used. The chart speed for these cases was set at 1 second/cm.

4. Method of Data Analysis

Since it has been established that the hydrogen transport processes is diffusion controlled, Fick's law proves adequate in analyzing the absorption permeation curve. Application of Fick's second law under the boundary and initial conditions, which are presented below, characteristic of hydrogen diffusion relative to this experiment allows the evaluation of the diffusion coefficient by the time lag technique:

Figure 14 Representative Data Reproducibility for Effective Diffusivity as a Function Reciprocal Temperature.

Figure 15 Representative Data Reproducibility for Steady State Flux as a Function Reciprocal Temperature

$$\frac{\partial^2 C}{\partial x^2} - \frac{1}{D} \frac{\partial C}{\partial t} = 0 \quad 0 < x < L \quad (24)$$

$$C = C_1$$

$$\text{or } p = p_1 \quad \text{at } x = 0 \quad t \geq 0$$

$$C = C_2$$

$$p = p_2 \quad \text{at } x = \ell \quad t \geq 0$$

$$C = C_0 \quad \text{for } 0 < x < \ell \quad t = 0$$

Barrer⁽⁴³⁾ has solved this system using the method of Fourier analysis giving the series solution:

$$C = C_1 + (C_2 - C_1) \frac{x}{\ell} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{C_2 \cos n\pi - C_1}{n} \sin \frac{n\pi x}{\ell} \exp\left[-\frac{Dn^2 \pi^2 t}{\ell^2}\right] \\ + \frac{4C_0}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \sin \frac{(2m+1)\pi x}{\ell} \exp\left[-\frac{D(2m+1)^2 \pi^2 t}{\ell^2}\right] \quad (25)$$

The concentration of hydrogen, $C(t)$, permeating the membrane, of cross-sectional area A , evolves into a fixed volume, V , as a function of time. The flow of hydrogen is then expressed as

$$\frac{V \partial C(t)}{A \, dt} = D \left(\frac{\partial C}{\partial x} \right)_{x=0} \quad (26)$$

where $(\partial C / \partial x)_{x=0}$ is obtained from the differentiation of equation 25. Equation 26 is then integrated between the limits 0 and t , and as $t \rightarrow \infty$ is seen to approach the asymptote:

$$C(t) = AD/\ell V [(C_2 - C_1)t - \frac{C_2 \ell^2}{6D} - \frac{C_1 \ell^2}{3D} - \frac{C_0 \ell^2}{2D}] \quad (27)$$

Hypothetically, if there had been no time lag, $C(t)$ would equal the steady state concentration rise $C(t)_{\infty}$ expressed as:

$$C(t)_{\infty} = AD/\ell V(C_2 - C_1)t \quad (28)$$

Hence the intercept, t_L , on the time axis is assigned the value:

$$t_L = \frac{1}{(C_2 - C_1)} \left[\frac{C_2 \ell^2}{6D} + \frac{C_1 \ell^2}{3D} - \frac{C_0 \ell^2}{2D} \right] \quad (29)$$

If the initial hydrogen concentration in the membrane is $C_0 = 0$ at $t = 0$ and $C_2 \gg C_1$, then formula (29) reduces to the following:

$$t_L = \frac{\ell^2}{6D} \quad (30)$$

Since the membranes are vacuum annealed at approximately 900°C for two hours thereby allowing sufficient hydrogen degassing of the iron sample, the condition $C_0 = 0$ is obeyed. In addition, the monitoring chamber pressure is initially maintained at $<10^{-9}$ torr and never surpasses 10^{-5} torr during the experimental runs assuring compliance with the latter condition, i.e., $C_1 = K\sqrt{p_1} \gg C_2 = K\sqrt{p_2}$. Therefore, by extrapolating the steady state $dp/dt|_{\infty}$ curve, where $p(t) = \text{const } C(t)$, until it intercepts the time axis, the lag time value determined at the intercept, as illustrated in Figure 12, can be used to compute the diffusion coefficient;

$$D = \frac{\ell^2}{6t_L} \quad (31)$$

Later results will show that this diffusivity is not a true lattice diffusivity but rather an effective diffusivity dependent on concentration. This concentration dependence is analyzed by determining the diffusivity for a sequence of charging pressures, i.e., .81, .46, .13, .016, .0013 atm, at a fixed specimen temperature; the charging pressure sequence is then repeated at several other specimen temperatures. The resulting diffusivities for each isotherm are then graphed as a function of charging pressure. In addition, the diffusivities are plotted as a function of the reciprocal of temperature in order to derive the apparent diffusivity activation energy for each isobar. All graphical analysis is simulated by a least squares fit of the data.

The permeability is calculated by rearranging equation 8 as follows:

$$\phi = \frac{J_{\infty} L}{\sqrt{p}} \quad (32)$$

Since the factor $L/\sqrt{p}$ is temperature independent, a temperature variation in permeability is seen to be directly proportional to a temperature variation in steady state flux as shown, i.e.,

$$\phi = \phi_0 e^{-E_{\phi}/RT}, \text{ where } \phi_0 = D_0 K_0 \quad (33)$$

therefore,

$$J_{\infty} = J_{0\infty} e^{-E_{\phi}/RT}, \text{ where } J_{0\infty} = \frac{D_0 K_0 \sqrt{p}}{L} \quad (34)$$

The activation energy for hydrogen permeation can be calculated

directly from the steady state flux measurements taken at different temperatures.

B. Permeability

A least squares fit of the data plotted in Figure 16 gives a permeation activation energy of 8.2 ± 0.7 kcal/mole which agrees reasonably well with both Gonzalez's⁽⁴⁴⁾ literature summary value and the data of Nelson and Stein⁽¹⁹⁾ who used a similar experimental system. Figures 10, 17 and 18 illustrate the virtual insensitivity of this permeation activation energy to both thickness and charging pressure.

As will be discussed in the ensuing sections, diffusivity is a structure sensitive property, as shown by its thickness and concentration dependence which are related to the trapping phenomenon. In contrast, the permeability, which is computed after steady state flux conditions have been realized, is expected to be insensitive to structure. This concept is mathematically expressed by the following equation describing hydrogen transport in a lattice with trapping⁽³⁵⁾:

$$\frac{\partial C}{\partial t} + N \frac{\partial n}{\partial t} = \text{div} (D_L \text{ grad } C) \quad (35)$$

where C = concentration of the diffusing atoms at the instance considered

t = time

N = density of traps

Figure 16 Permeability as a Function of Reciprocal Temperature.

Figure 17 Steady State Flux as a Function of Reciprocal Temperature for Several Charging Isobars

Figure 18 Steady State Flux as A Function of Reciprocal Temperature for Several Charging Isobars

n = fraction of traps occupied

D_L = lattice diffusivity

When steady state conditions are obtained, the hydrogen trapping rate is in equilibrium with the rate of escape from the traps; consequently, the lattice transport mechanism, i.e., diffusion, is the dominating process. This insensitivity to traps implies an insensitivity to charging pressure and thickness as alledged earlier; therefore, agreement among permeation activation energies is not surprising.

The permeabilities are seen to be approximately a factor of eight greater than those observed by Nelson and Stein. A plausible explanation for this phenomenon is the flux amplification effect of the Pd film as was observed by Kumnick⁽³³⁾. Perhaps the presence of Pd prevents the recombination of the hydrogen atoms to gaseous hydrogen at the iron surface promoting more absorption of hydrogen into the material.

1. Concentration Dependence

The salient result of this investigation is the increase in diffusivity with charging pressure along various isotherms, as is observed in Figures 11, 19 and 20, indicating that diffusivity is a function of charging concentration. This dependence is further evaluated by plotting diffusivity vs. charging pressure on a log-log graph for decreasing isotherms. The derived pressure exponent n is seen in Fig. 21, to increase

Figure 19 Effective Diffusivity as a Function of Reciprocal Temperature for Several Charging Isobars

Figure 20 Effective Diffusivity as a Function of Reciprocal Temperature for Several Charging Isobars

Figure 21 Effective Diffusivity as a Function of Charging Pressure for Several Isotherms.

with decreasing temperature. A plot of n as a function of temperature, shown in Figure 22, suggests the bounding of n by asymptotes, i.e., $n \rightarrow .5$ for temperatures less than 60°C and $n \rightarrow 0$ for temperatures greater than approximately 400°C . Since as alluded to earlier, there is a possible association between an observed concentration dependence of diffusivity and the trapping phenomenon, the available trapping theories will be used to develop this relationship and, consequently, explain the results.

These results do not agree with the di-interstitial theory introduced by Ono and Rosales⁽³⁷⁾. The di-interstitial, which is assumed to be immobile, is a special kind of trap since its concentration is temperature and pressure dependent. As is implied by the equation $C_T = C_1 + 2C_2 =$

$$3\left(\frac{p_{\text{ext}}}{p_0}\right)^{1/2} \exp \frac{S_f(1)}{R} \exp \frac{-H_f(1)}{RT} + 2\left(\frac{3Z}{2}\right) \left(\frac{p_{\text{ext}}}{p_0}\right) \exp \frac{S_f(2)}{R} \exp \frac{-H_f(2)}{RT} \quad (15)$$

at a given isotherm, the lattice concentration, C_1 , can be taken proportional to $p^{1/2}$, i.e., $C_1 = \text{const } p^{1/2}$; while C_2 , the di-interstitial concentration can be taken proportional to p , i.e., $C_2 = \text{const } p$. Since the di-interstitials are assumed to be virtually immobile⁽³⁷⁾, then

$$D_T = \frac{C_1}{C_1 + 2C_2} D_L \quad (17)$$

For the condition $C_1 \gg C_2$, which holds at high temperatures,

Figure 22 Diffusivity Charging Exponent as a Function of Reciprocal Temperature

i.e., $T > 500^{\circ}\text{C}$,

$$D = D_L \quad (36)$$

However, at temperatures below 500°C where $C_2 \gg C_1$, equation 17 reduces to the form

$$D = \frac{\text{Const}_1}{\text{Const}_2} D_L p^{-1/2} \quad (37)$$

In other words, D is predicted to be inversely proportional to the charging pressure, a phenomenon not observed at the lower isotherms.

The experimental behavior is better explained by defining the trap concentration or density as a material property altered only by compositional additives, structural changes and deformational process⁽²¹⁾ and independent of temperature and pressure. Oriani⁽²¹⁾ using the criteria of MacNabb and Foster⁽³⁵⁾ has developed a relationship between the effective diffusivity and the normal lattice diffusivity (see equation 10), which is dependent on the relative magnitudes of the lattice concentration and the trap site density, i.e.,

$$D = D_L \frac{C_L}{C_L + 3N_x} \quad (38)$$

This relation only holds for heavily occupied traps; a discussion on the compliance of the observed results with this criterion is deferred to the next section. Variance of the lattice concentration above and below this fixed trap density,

by adjusting the sample temperature and the hydrogen charging pressure, is seen to directly affect the ratio D/D_L .

Since compliance of the data ($T > 75^\circ$) with Sievert's Law has previously been established, lattice concentration is represented by the equation

$$C_L = K_O \sqrt{p} e^{-E_s/KT} \quad (1a)$$

Along an isotherm

$$C_L = K \sqrt{p} \quad (1)$$

where $K = K_O e^{-E_s/KT}$ = constant is the Sievert's proportionality parameter. Along low isotherms, such that the condition $3N_x \gg C_L$ is maintained over a given pressure range, equation 34 reduces to the expression:

$$D = \frac{D_L C_L}{3N_x} \quad (38)$$

Substituting equation 1 into the above expression and using the definition $D_L K = \phi$, the effective diffusivity can be expressed as:

$$D = \frac{\phi \sqrt{p}}{3N_x} \quad (39)$$

On the contrary, along high temperature isotherms such that the condition $C_L \gg 3N_x$ is maintained throughout a given pressure range, equation 38 reduces to

$$D = D_L \quad (36)$$

and no concentration dependence is apparent. Thus the

limitations

$$0 < n < .5 \quad (40)$$

can be imposed on the pressure exponent.

In accord with the experimental observations made in this investigation, the exponent is predicted to decrease with increasing temperature until $D = D_L$ at which point the concentration dependence of diffusivity is abolished; for steadily increasing isotherms, the concentration dependence of diffusivity decreases.

2. Apparent Activation Energy

The variation in activation energy with charging pressure shown in Figures 11, 19 and 20 is consistent with the observed concentration dependence of diffusivity. The apparent diffusivity activation energies, as determined by least squares analysis, range from 2.0 kcal to 9.6 kcal and cover the majority of the low temperature values reported in the literature⁽¹⁹⁻²⁶⁾. This variance in the apparent diffusivity activation with charging pressure is then associated with the trapping phenomenon.

By continuing with the Oriani trap theory, the observed concentration dependence of the apparent activation energy can be plausibly explained. However, two approaches are possible depending on the limiting cases of trap occupancy. If the traps are sparingly occupied, β , as defined by equation 11, is $\ll 1$; whereupon the equation,

$$D = \frac{D_L}{1+\alpha} \quad (41)$$

is applicable.

When $\beta \ll 1$, the two limiting cases of α , as defined by equation 10, are of interest:

i) When $\alpha \gg 1$, then

$$D = \frac{D_L}{\alpha} \quad (42)$$

As is shown by Oriani⁽¹¹⁾, α is proportional to $e^{E_t/RT}$ where E_t , a positive quantity, is the trap potential. Partial differentiation of the natural logarithm of equation (42) with respect to temperature yields

$$E_D = E_L + E_t \quad (43)$$

ii) When $\alpha \ll 1$, $(1+\alpha)^{-1}$ can be expanded. Thus

$$D = D_L (1+\alpha) \quad (44)$$

After taking the natural logarithm of equation (44) and then the partial derivation with respect to temperature, the following relation results:

$$E_D = E_L - \frac{E_t \text{ const. } e^{E_t/RT}}{1 + \text{const. } e^{E_t/RT}} \quad (45)$$

As temperature increases, E_D approaches E_L ; but as temperature decreases, $E_D < E_L$ contrary to the observed results.

When the trap occupancy is taken to be heavily occupied,

i.e., $\beta \gg 1$, the relation

$$E_D = E_L + \frac{3N_x}{C_L + 3N_x} E_s \quad (45)$$

as derived from equation 14, is applicable. Hence the value of E_D depends on the relative magnitudes of the lattice concentration and that of the trap density. Drawing upon the conditions established in the previous section, it is evident that when $3N_x \gg C_L$,

$$E_D = E_L + E_s = E_\phi \quad (46)$$

where E_ϕ is the permeability activation energy and that when $C_L \gg 3N_x$,

$$E_D = E_L \quad (47)$$

Thus the following limits can be ascribed to the value of the apparent activation energy:

$$E_s + E_L = E_\phi \geq E_D \geq E_L \quad (48)$$

The apparent activation energy is seen to approach that for the lattice diffusivity as charging pressure, and hence the equilibrium lattice concentration, increases.

The highest apparent activation energy recorded was 9.6 kcal/mole for the .0381 cm sample charged at 1.32×10^{-3} atm. This value is within 17% of the recorded activation energy for permeation, 8.2 kcal/mole, substantiating the imposition of

the lower limit. In addition, the lowest apparent activation energy of 2.0 kcal/mole, recorded for the .0381 cm sample charged at .81 atm, is within 3% of the experimentally determined lattice diffusivity activation energy, 2.1 kcal/mole, discussed in the ensuing section, thus substantiating the upper limit.

D. Lattice Diffusivity and the Anomalous Break

In compliance with the conditions outlined in the previous section, lattice diffusivity is evaluated over the temperature range 400-550°C. The thickest sample, .0381 cm is used to assure the obtainment of an easily readable lag time, i.e., $D = \frac{L^2}{6t_L}$ where t_L increases with L for a given diffusivity. The results are presented in Figure 23.

For all thicknesses, the apparent activation energies at each isobar tend to merge together in the temperature range between 350-450°C as is shown in Figures 11, 19 and 20. This range includes the temperature at which the pressure exponent, n , was computed to be near zero signifying the inactivation of any trapping mechanism; i.e., $D \approx D_L$. By the general fan appearance of these activation curves, it is apparent that for the lower charging pressures, a substantial decrease in the apparent activation energy must occur over a limited temperature range if the lattice activation energy is to be approached. On the other hand, at the higher charging pressures, it is apparent that only a minor slope transition would be necessary.

The anomalous break temperature for each family of

Figure 23 Lattice Diffusivity as a Function of Reciprocal Temperature

isobaric diffusivities can be found by equating each D with D_L . For example, $D = 2.6 \times 10^{-1} e^{-6.6 \text{ kcal/RT}}$ for the .0381 cm sample charged at 1.8×10^{-2} atm. By equating this expression with $D_L = 7.0 \times 10^{-3} e^{-2.1 \text{ kcal/RT}}$, the anomalous break temperature is computed as 354°C . Proceeding in this manner, the anomalous break temperature range, for all diffusivity results, is $344 - 564^\circ\text{C}$. This value concurs with the original observations.

Therefore, the observance of an anomalous break in the diffusivity versus the reciprocal of temperature plot can be attributed to the concentration dependence of diffusivity, which is in turn caused by trapping.

Attempting to explain the possible disappearance of the anomalous break by the di-interstitial theory⁽³⁷⁾ yields a prediction contradictory to the observed results. After establishing the upper limit $C_1 \leq C_1 + 2C_2 = C_T$ the equation

$$C_1/C_T = 2 / \{1 + [1 + (4ZC/3) \exp(B/RT)]^{1/2}\} \quad (16)$$

shows the ratio C_1/C_T to decrease from unity with increasing C_T , where C_T is a function of charging pressure. Consequently, the effective diffusivity becomes increasingly smaller than the lattice diffusivity as demonstrated by equation 18. It is observed experimentally that the effective diffusivity approaches the lattice diffusivity with increasing C_T in agreement with the predictions of the Oriani trap theory.

E. Thickness Anomaly

A pronounced decrease in the apparent activation energy with increasing thickness, at a given isobar, is inferred from Figures 11, 19 and 20; the effective diffusivities show an increase with increasing thickness. As is shown in Figures 24 and 25, the occurrence of this anomaly is relatively insensitive to both specimen temperature and charging concentration. In addition, the steady state flux is seen to obey Sievert's Law and vary linearly with inverse sample thickness indicating that surface controls are not responsible for the anomaly; the results are representative of volume control. The possibility of any internal structural damage is doubtful because the results are reproducible since care was taken to use low charging pressures, i.e., less than 1 atm. Therefore, the earlier theories expounded by Heath⁽⁴⁵⁾ and Wach et. al.⁽⁴⁶⁾ to explain this anomaly are inapplicable.

The anomaly has been recently observed with the electrochemical permeation technique and analyzed by Kumnick⁽³³⁾. Here, the thickness anomaly is attributed to a higher density of traps in the thinner specimens. These residual traps originate when the material is subjected to cold working during processing and are not removed by subsequent annealing. This concept is consistent with the data and observations of this investigation where all samples undergo identical heat treatments.

An interesting application of the results in Section C is

Figure 24 Effective Diffusivity as a Function of Membrane Thickness for Several Isotherms.

Figure 25 Effective diffusivity as a Function of Membrane Thickness for Several Isobars.

the use of this criteria for estimating the Ferro-Vac-E's trap density. Equation

$$D = \frac{\phi}{3N_x} \sqrt{p} \quad (39)$$

is useful in this capacity within the proper temperature range. Figure 22 indicates this equation to be applicable at room temperature. By plotting diffusivity at room temperature as a function of $\sqrt{p}$, as simulated by a least squares analysis, the trap density can be computed from the slope of the curve after the permeability is determined at room temperature. The trap densities shown in Table II substantiate the concept of an increasing trap density with decreasing thickness used to explain the thickness anomaly. However, the validity of these absolute values of trap density is questionable since there exists no similar data on Ferro-Vac-E in the literature to use for comparison.

F. Total Concentration

Since the steady state flux was shown to be in agreement with Sievert's Law, for $T > 75^\circ\text{C}$ it is initially assumed that the total equilibrium bulk hydrogen concentration can be expressed by the formula,

$$C_L = K_O \sqrt{p} e^{-E_s/KT} \quad (1a)$$

However, at low isotherms, where trapping becomes operational, this formula is no longer representative of the total hydrogen concentration in solution. By rearranging equation 38, the

TABLE II.

Trap Density for Various Thicknesses

Thickness	Trap Density $\frac{\text{number traps}}{\text{cc}}$
.0127	2.5×10^{14}
.0254	5.3×10^{13}
.0381	4.8×10^{12}

following expression is derived:

$$D_L C_L = D(C_L + 3N_x) = D_L K_O \sqrt{p} e^{-E_s/RT} \quad (49)$$

Since the traps have been shown to be heavily occupied, the term $3N_x$ is equivalent to the concentration of trapped hydrogen, C_x . The total equilibrium bulk hydrogen concentration is then defined as follows:

$$C_T = C_L + C_x \quad (50)$$

Consequently,

$$DC_T = D_L K_O \sqrt{p} e^{-E_s/KT} \quad (51)$$

As discussed earlier, when $3N_x \gg C_L$, equation 49 reduces to the following:

$$D3N_x = D_L K \sqrt{p} \quad (52)$$

Since N_x is defined as a constant, D is ascribed the dependence on pressure. Contrastingly, when $C_L \gg 3N_x$

$$DC_L = D_L K \sqrt{p} \quad (49)$$

Since under this condition $D = D_L$, Sievert's concentration expression is extractable from the equation.

This rationalization is reinforced by the dependency of the steady state flux on pressure to the $1/2$ power for those isotherms discussed. If C_T were always dependent on $p^{1/2}$, the flux pressure dependence would be bounded by the limits⁽¹⁸⁾

$$.5 < p < 1 \quad (54)$$

Such a pressure dependence was observed only at very low isotherms but was coincidental with an anomalous break in both the permeability and diffusivities versus the inverse of temperature plots indicating surface limited flux transport processes to be responsible.

Hence the total bulk concentration is evaluated by the expression:

$$C_T = \frac{\phi\sqrt{p}}{D} \quad (55)$$

for each isotherm at the pressures designated in Tables II, III, IV and V.

The lattice solubility as determined by the expression $K = \phi/D_L$ is computed to be $1.2 \pm 1.1 \times 10^{20} e^{-\frac{6.1 \pm 1.3 \text{ kcal}}{RT} \frac{\text{atoms H}}{\text{cc(atm)}^{1/2}}}$. Therefore, the lattice concentration is expressed by the following:

$$C_L = 1.2 \pm 1.1 \times 10^{20} \sqrt{p} e^{-\frac{6.1 \pm 1.3 \text{ kcal}}{RT} \frac{\text{atoms H}}{\text{cc}}} \quad (52)$$

This value agrees reasonable well with that determined by both Nelson and Stein⁽¹⁹⁾ and Hill and Johnson⁽¹⁸⁾.

Subtracting C_L from the corresponding C_T values allows an estimate of the trapped concentration, C_x , for each set of experimental parameters as shown in Tables III-VI. As expected from the previous observations and results, the ratio C_x/C_L is seen to increase with decreasing thickness, temperature and charging pressure.

A more detailed examination of Tables II-V shows that for

TABLE III.

Hydrogen Concentration Data:

Thickness = .0127cm, Temperature = 162°C

	Charging Pressure			Atm
	.79	.45	.13	1.6×10^{-2}
$C_T(\text{atom}\%)$	3.26×10^{-6}	3.20×10^{-6}	3.42×10^{-6}	1.9×10^{-6}
C_L	6.55×10^{-7}	4.84×10^{-7}	2.66×10^{-7}	$.932 \times 10^{-7}$
C_x	2.61×10^{-6}	2.71×10^{-6}	3.15×10^{-6}	1.82×10^{-6}
C_x/C_L	3.98	5.49	11.84	18.92

TABLE IV.

Hydrogen Concentration Data:

Thickness = .0254cm, Temperature = 161°C

	Charging Pressure			Atm
	.82	.46	.13	1.6×10^{-2}
$C_T(\text{atom}\%)$	8.93×10^{-7}	7.23×10^{-7}	7.28×10^{-7}	3.9×10^{-7}
C_L	3.59×10^{-7}	2.69×10^{-7}	1.43×10^{-7}	$.501 \times 10^{-7}$
C_x	5.34×10^{-7}	4.54×10^{-7}	5.85×10^{-7}	3.41×10^{-7}
C_x/C_L	1.49	1.69	4.09	6.81

TABLE V.

Hydrogen Concentration Data:

Thickness = .0381cm, Temperature = 157°C

	Charging Pressure			Atm
	.81	.46	.13	1.8×10^{-2}
C_T (atom%)	1.64×10^{-7}	2.00×10^{-7}	2.03×10^{-7}	1.52×10^{-7}
C_L	2.01×10^{-7}	1.51×10^{-7}	$.804 \times 10^{-7}$	$.299 \times 10^{-7}$
C_x	0	$.49 \times 10^{-7}$	1.23×10^{-7}	1.22×10^{-7}
C_x/C_L	0	.325	1.53	4.08

TABLE VI

Hydrogen Concentration Data:

Thickness = .0381cm, Temperature = 283°C

	Charging Pressure			Atm
	.81	.46	.13	1.8×10^{-2}
C_T (atom%)	1.69×10^{-6}	1.37×10^{-6}	$.925 \times 10^{-6}$	$.468 \times 10^{-6}$
C_L	2.03×10^{-6}	1.55×10^{-6}	$.815 \times 10^{-6}$	$.303 \times 10^{-6}$
C_x	0	0	$.11 \times 10^{-6}$	$.165 \times 10^{-6}$
C_x/C_L	0	0	.135	.545

$C_x > C_L$, the value C_x is relatively constant for each thickness. In contrast, when $C_L \approx C_T$, i.e., $C_L \gg C_x$, $C_x \approx 0$, indicating the trapping mechanism to be inactivated. This latter result occurring for the .0381 cm thick sample is consistent with its diffusivity expression (Figure 22) which is within the error margin of the lattice diffusivity expression, Figure 25, indicating $D \approx D_L$.

G. Trap Characterization and Its Relation to $D = D(c)$.

In summary, the trap density is characterized as a material property dependent only on thickness, structure and compositional changes. The equilibrium lattice concentration, not the trap density, is the parameter that is sensitive to a variance in both temperature and pressure. In addition, these traps are heavily occupied resulting in the equality, $3N_x = C_x$, between trap density and trapped concentration. When $C_x > C_L$, the concentration of trapped hydrogen is relatively constant for a given thickness. However, when $C_L \approx C_T$, the trapped concentration drops abruptly to zero, i.e., $C_x = 0$, indicating the inactivation of the traps.

The apparent magnitude of the ratio C_L/N_x is manifested by the observed concentration dependence of diffusivity exhibiting the following limiting cases.

i) When $N_x \gg C_L$,

$$D = \frac{\phi}{3N_x} p^{1/2} \quad (39)$$

ii) On the contrary, when $C_L \gg N_x$,

$$D = D_L p^0$$

or

$$D = D_L \quad (36)$$

Within these limits, the apparent diffusivity activation energy is bounded as follows:

$$E_L \leq E_D \leq E_\phi \quad (48)$$

CONCLUSIONS

1. In gas phase charging permeation studies, bulk controlled hydrogen transport can be discerned from surface controlled transport by determining the exponential pressure dependence of the steady state flux.
2. The diffusivity of hydrogen in annealed Ferro-Vac-E iron is a function of concentration over the charging pressure range .0013-.82 atm and temperature range 75°C-300°C.
3. The diffusivity of hydrogen in annealed iron is also a function of membrane thickness over the range .0127cm-.0381cm.
4. The apparent diffusivity activation energy varies with isobaric pressure and membrane thickness spanning the majority of the low temperature values given in the literature.
5. Both the concentration and membrane thickness dependence of the diffusivity can be explained on the basis of hydrogen trapping.
6. The permeability, within the accuracy of this experiment, is virtually insensitive to variation in both charging pressure and membrane thickness.

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