

THE DIFFUSION AND TRAPPING OF HYDROGEN IN STEEL*

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The mobility of dissolved hydrogen in an iron lattice having a population of extraordinary, or trapping, sites for hydrogen is analyzed under the assumption of local equilibrium between the mobile and the trapped populations. It is shown that at low coverage of the trapping sites the usual solutions of the diffusion equations can be used to analyze the experimental results and that the effective diffusivity is a function of trap density and of the magnitude of the trap depth. In the domain of coverage in which the activity of trapped hydrogen is not linear in the fractional occupation of the trap population, the concept of phenomenological diffusivity becomes non-operational and the diffusion equation must be solved with terms for sources and sinks, as done by McNabb and Foster.

Values for trap number and depth are obtained by applying the relevant equations to selected data on a variety of steels with and without cold work. The results lead to the suggestion that in the absence of cold work the solid-solid interfaces are as or more important than dislocations as loci of trapping sites, and that in cold-worked steels, microcrack surfaces are more important than dislocations for hydrogen trapping.

DIFFUSION ET PIEGEAGE DE L'HYDROGENE DANS L'ACIER

La mobilité de l'hydrogène dissout dans un réseau de fer possédant une population de sites susceptibles de piéger l'hydrogène est étudiée dans l'hypothèse d'un équilibre local entre les populations mobile et piégée. L'auteur montre que, pour une faible occupation des pièges, les solutions courantes des équations de diffusion peuvent être utilisées pour analyser les résultats expérimentaux, et que la diffusivité effective est une fonction de la densité et de la profondeur des pièges. Pour les systèmes pour lesquels l'activité de l'hydrogène piégé n'est pas linéaire en fonction de la proportion d'occupation de la population piégée, le concept de diffusivité phénoménologique ne peut plus être utilisé et des termes relatifs aux sources et aux puits doivent entrer dans l'équation de diffusion, comme l'ont fait McNabb et Foster.

Les valeurs pour le nombre de pièges et leur profondeur ont été obtenues en appliquant l'équation correcte aux résultats sélectionnés pour une variété d'aciers écrouis à froid ou non. Les résultats conduisent à suggérer l'idée que, en l'absence d'écrouissage à froid, les interfaces solide-solide sont des lieux de sites de piégeage aussi importants ou même plus importants que les dislocations, et que, dans les aciers écrouis à froid, les surfaces portant des microfissures jouent un rôle plus important que les dislocations pour le piégeage de l'hydrogène.

DIFFUSION UND EINFANGEN DES WASSERSTOFFS DURCH HAFTSTELLEN IN STAHL

Die Beweglichkeit gelösten Wasserstoffs in einem Eisengitter mit Haftstellen für Wasserstoff wird unter der Annahme eines lokalen Gleichgewichts zwischen dem beweglichen und dem an Haftstellen gebundenen Wasserstoff analysiert. Es wird gezeigt, daß bei kleiner Besetzung der Haftstellen die gewöhnlichen Lösungen der Diffusionsgleichungen zur Analyse der experimentellen Ergebnisse herangezogen werden können und daß die effektiven Diffusionskonstanten eine Funktion der Haftstellendichte und der Tiefe der Haftstellen sind. In dem Bereich, in dem die Aktivität des an Haftstellen gebundenen Wasserstoffs nicht linear zur prozentualen Besetzung des gebundenen Anteils ist, funktioniert das Konzept der phänomenologischen Diffusion nicht mehr und die Diffusionsgleichung muß mit Quell- und Senkentermen gelöst werden, wie es McNabb und Foster durchgeführt haben.

1. INTRODUCTION

The anomalous behavior of hydrogen both as to its solubility and its diffusivity in cold-worked steels is well known and has been the subject of repeated investigations.⁽¹⁻⁴⁾ At the present time there seems to be fair agreement that these phenomena are due to attractive interactions between the dissolved hydrogen atoms and structural imperfections developed by the deformation. Less attention has been given to similar anomalous behavior of hydrogen in steels not subjected to cold work.

Darken and Smith⁽¹⁾ were the first to suggest that dissolved hydrogen is impeded in its diffusion by imperfections in the lattice of a cold-worked steel and applied the theory of subscale kinetics, as modified by the assumption of local equilibrium, to the problem. A similar point of view has since been adopted by other workers.^(2,3,5) McNabb and Foster⁽⁵⁾ have developed a more general modelistic formulation for the phenomenon of diffusion with accompanying trapping at one kind of trap. The present writer⁽⁶⁾ has reformulated their work in the context of the assumption of local equilibrium for a restricted domain of degree of trap coverage.

The object of the present paper is to make more

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specific the treatment based on the local equilibrium hypothesis, to show how the relevant parameters may be evaluated from experiment, and to apply the theory to existing experimental data. The results of this application serve as the basis for suggestions concerning the nature of the trapping sites in cold-worked and in non-cold-worked steels. In the light of the point of view developed, recommendations are made for more definitive experiments.

2. THEORETICAL DEVELOPMENT

We consider a lattice consisting of two kinds of sites for occupancy by hydrogen. The vast majority of sites are the ordinary or normal sites characterized by the normal enthalpy of solution, ΔH° , with respect to an atmosphere of gaseous hydrogen with which the lattice may be brought into contact. The minor fraction of the sites, to be called the extraordinary or trapping sites, provides an energetically favored environment for occupancy by the hydrogen, so that the equation

$$H = H_x, \Delta E_x \quad (1)$$

represents the transfer of hydrogen from a normal to an extraordinary site with the change of energy, ΔE_x , a negative quantity.

Because we consider only the case in which the ratio of extraordinary to normal sites is small we can assume that the trap population does not appreciably reduce the cross-section for diffusion in the normal lattice. Hence we can write Fick's first law for the flux J in terms of the occupied normal sites only, as

$$J = -D_L \frac{dc_L}{dx} \quad (2)$$

where c_L is the hydrogen concentration upon normal lattice sites and D_L is the normal diffusivity, that is, that which would obtain in a homogeneous lattice. However, in the majority of experiments one is concerned with the relation between the observed flux and the gradient of total concentration c_T , which is the sum of c_L and c_x , the latter being the concentration upon the extraordinary sites:

$$J = -D \frac{dc_T}{dx} \quad (3)$$

The relation between the apparent or phenomenological diffusivity, as defined by equation (3), and D_L may be easily derived by assuming that the trapped population is in equilibrium with the population upon normal lattice sites not only in the static ($J = 0$) situation but also during diffusion.⁽¹⁾ (Hill and Johnson⁽²⁾ have also made this assumption for the static

case.) The domain of validity of this assumption for the finite flux case will be discussed subsequently. The equilibrium between the two atomic populations, each one occupying a fraction θ_i , of the available sites, can be described by the equilibrium constant, $K = a_x/a_L$, where a_x and a_L are the activities of the hydrogen upon the trapping sites and upon the normal lattice sites, respectively. Remembering that both types of sites constitute finite populations and assuming no interaction between occupied sites, each of the two activities can be expressed in terms of fractional occupancies as $a_i = \theta_i/(1 - \theta_i)$, where the reference state is $a_i = \theta_i$ when $\theta_i \rightarrow 0$. Furthermore, since we are considering only very low c_L , $\theta_L \ll 1$, so that the equilibrium constant for reaction (1) may be written as

$$K = \frac{1}{\theta_L} \left(\frac{\theta_x}{1 - \theta_x} \right). \quad (4)$$

If N_L and N_x represent, respectively, the number of normal and of extraordinary sites per unit volume, then the volume concentrations of hydrogen in the two states of binding can be written as $c_L = N_L \theta_L$ and $c_x = N_x \theta_x$. Remembering that $c_T = c_L + c_x$ and using equation (4) and the foregoing definitions, one finds that the relation between the apparent diffusivity of equation (3) and D_L is

$$\begin{aligned} D &= D_L \frac{dc_L}{dc_T} = D_L \left[1 + \frac{N_x N_L K}{(N_L + K c_L)^2} \right]^{-1} \\ &= D_L \frac{c_L}{c_L + c_x(1 - \theta_x)}. \end{aligned} \quad (5)$$

It will be noted that when $\theta_x \ll 1$, $D = D_L(c_L/c_T)$, which is the relation arrived at in the Appendices of Refs. (1) and (7) for the effective diffusivity calculable from the observed kinetics of subscale formation. This last relationship was also developed by Hill and Johnson⁽²⁾ by a simple argument.

Thus, a phenomenological diffusivity determined by measuring the negative ratio of a flux to a gradient of total concentration as per equation (3), or the equivalent, is related to that in the corresponding homogeneous lattice by equation (5). This equation gives a simple interpretation to the often observed asymmetry between the absorption and evolution kinetics of hydrogen in steel—that the absorption proceeds with a larger apparent diffusivity than does the evolution. Within the postulate of local equilibrium such an asymmetry may be expected whenever the activity, a_x , cannot be satisfactorily expressed linearly in θ_x , that is when θ_x departs appreciably from zero. Consider the region of a slab very near the free

surface, the surface being in equilibrium with a hydrogen gas environment and the slab absorbing hydrogen. The flux across a plane parallel to and just below the external surface will be controlled by an effective diffusivity given by equation (5) with a finite value of θ_x consistent with the value of c_x in that region. The evolution of hydrogen from a slab initially of uniform concentration equal to that which would be in equilibrium with the gas phase in the absorption experiment, is equal to the flux across a plane just below the external surface where c_x and c_L are very close to zero (though still in the ratio controlled by K) and consequently θ_x approaches zero more nearly than in the absorption experiment. Consequently, during evolution $D \approx D_L c_L / c_T$, whereas during absorption $D = D_L c_L / (c_T - \theta_x c_x)$, so that D (evolution) $<$ D (absorption), and therefore J (evolution) $<$ J (absorption) as may be inferred from an analysis by Wagner⁽⁸⁾ for concentration-dependent diffusivities. This inequality of fluxes was first quantitatively demonstrated by Darken and Smith⁽¹⁾ and was understood by them in the way here described.

3. RANGE OF VALIDITY OF TREATMENT

It is pertinent now to inquire into the domain of validity of the assumption of local equilibrium between the normal and the trapped populations. This assumption fails phenomenologically if, within the accuracy of the experiment, the flux cannot be expressed solely in terms of the gradient of c_T . Atomistically the assumption breaks down if the time in which a change, δc_L , occurs by lattice diffusion in the normal population is not sufficiently long to accomplish the change in the trapped population required by the equilibrium equation (4).

Consider an infinite slab of half-thickness l of initial uniform normal lattice concentration $c_{L,0}$. If the concentration at the free surfaces is maintained at $c_s = 0$ at all times $t > 0$, at time $10^{-2}l^2/D_L$ the mean concentration c_M will be⁽⁹⁾ $(c_M - c_{L,0})/c_{L,0} = -0.110$. The change in concentration will be much larger in a layer very near the external surface; over the same time interval at $x/l = 0.95$ (where x is measured from the center line of the slab) the local concentration would be⁽⁹⁾ $(c_L - c_{L,0})/c_{L,0} = -0.7$, or $-\delta c_L = 0.7c_{L,0}$. Hence, we can develop a very stringent condition for the validity of the local equilibrium postulate if we demand that the trapped population be able to undergo in the outermost layer of the slab the change of concentration required by equation (4). This change is

$$\delta c_x = \frac{N_x}{N_L} (1 - \theta_x)^2 K \delta c_L \quad (6)$$

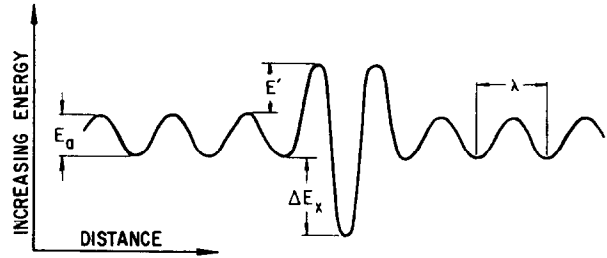


FIG. 1. Model for trapping site.

which, for $x/l = 0.95$ becomes

$$\delta c_x = \frac{N_x}{N_L} (1 - \theta_x)^2 K (0.7c_{L,0}) \quad (7)$$

δc_x is the number of trapped atoms per unit volume that must become untrapped in a time equal to or less than $10^{-2}l^2/D_L$ in order that the postulate of local equilibrium be obeyed. If \mathcal{R} is the rate of escape per trap, then the condition for local equilibrium is

$$\frac{\delta c_x}{\mathcal{R} N_x \theta_x} \leq 10^{-2}l^2/D_L. \quad (8)$$

The rate \mathcal{R} must be evaluated from a specific model for the trapping site. We will use a slight elaboration of that used in Ref. 6. Referring to Fig. 1, the trapping site represents an energy level lower than that of a normal site by $|\Delta E_x|$, and it is bounded by an energy barrier of height $E' + E_a$, where E_a is the activation energy for jumping between normal lattice sites separated by the distance λ . \mathcal{R} may be expressed as

$$\mathcal{R} = \nu \exp [(\Delta E_x - E_a - E')/RT]$$

in which ν is the vibration frequency of the trapped hydrogen, taken to be the same as that of hydrogen upon a normal lattice site, and in which we neglect the entropy factors. We can express D_L and K as

$$D_L = \lambda^2 \nu \exp (-E_a/RT) \quad (9)$$

and

$$K = \exp (-\Delta E_x/RT) \quad (10)$$

again neglecting the entropy contribution. With equations (9) and (10) we can express \mathcal{R} by

$$\mathcal{R} = K^{-1} \lambda^{-2} D_L e^{-E'/RT}. \quad (11)$$

Substituting equations (7) and (11) in equation (8) the condition for the validity of the postulate of local equilibrium becomes

$$70K(\lambda/l)^2 e^{E'/RT} (1 - \theta_x) \leq 1. \quad (12)$$

Taking reasonable values of these parameters, relevant to hydrogen in steel, of $\theta_x = 10^{-1}$,

$\lambda \approx 2 \times 10^{-8}$ cm, and $l = 10^{-1}$ cm, and restricting the model to the case $E' = 0$, one finds that equation (12) gives $K \leq 4 \times 10^{11}$ which at $T = 300^\circ\text{K}$ means $-\Delta E_x \leq 16.0$ kcal/mol. Remembering that the condition was developed for the section in the specimen which undergoes the most rapid concentration change, we conclude that in the systems of present interest we shall in all probability be in the domain of the postulate of local equilibrium.

4. EVALUATION OF PARAMETERS FROM EXPERIMENT

Whereas equation (5) is formally correct, within the assumption of local equilibrium, it is not useful in general because the phenomenological diffusivity is a function of the concentration of the diffusing species. The lack of usefulness stems directly from this functional dependence, since one cannot use the standard solutions of the diffusion equations in order to relate observable quantities to a meaningful effective diffusivity. However, in the domain of low coverage, $\theta_x \approx 0$, equation (5) is independent of concentration, and becomes

$$D = D_L(1 + KN_x/N_L)^{-1}. \quad (13)$$

Hence the phenomenological diffusivity, D , may be obtained by application of the standard equations of diffusion theory to the results of the usual experiments. For example, one may measure the cumulative amount, $G(t)$, of hydrogen that permeates through a sheet of metal of thickness a as a function of time where the environment over the input surface is maintained at a constant, finite fugacity and that over the output side is maintained at zero fugacity. The intercept, τ_i , upon the time axis of the straight-line asymptote to the $G(t)$ curve is related to the normal diffusivity in the absence of trapping effects by⁽¹⁰⁾

$$\tau_i = \frac{a^2}{6D} \quad (14)$$

provided that surface processes furnish negligible impedances. In the case of trapping behavior at $\theta_x \approx 0$ the D of equation (14) is to be interpreted according to equation (13). Similarly, one may expose one side of a thick slab of initially zero hydrogen content to a constant environmental hydrogen fugacity. For conditions where the slab simulates a semi-infinite volume and surface impedance does not play a significant role, the total amount of hydrogen, $q_a(t)$, absorbed per unit area in time t is related to the normal diffusivity by⁽¹⁰⁾

$$q_a(t) = 2c^0(Dt/\pi)^{1/2} \quad (15)$$

where in the absence of trapping behavior c^0 would

be the normal lattice solubility, c_L^0 , in equilibrium with the environmental fugacity just below the input surface. When trapping does exist and $\theta_x \approx 0$, again D is to be interpreted according to equation (13) and c^0 of equation (15) becomes the total hydrogen concentration, just below the input surface, in equilibrium with the environmental fugacity:

$$c^0 = c_L^0(1 + KN_x/N_L). \quad (16)$$

Hence for this situation equation (15) becomes

$$q_a(t) = 2c_L^0(1 + KN_x/N_L)^{1/2}(D_L t/\pi)^{1/2}. \quad (17)$$

Evolution of hydrogen into a vacuum from one side of a thick slab of initial content c^0 could also be followed. In the domain of $\theta_x \approx 0$ equation (17) would apply, replacing $q_a(t)$ by $q_e(t)$, since kinetic symmetry is expected in this domain. Indeed, obtaining the same value of the effective diffusivity irrespective of the type of experiment (all at the same c_L^0 , however) may be used as the diagnostic test for determining whether or not the $\theta_x \approx 0$ domain prevails. In this domain the temperature dependence of the apparent diffusivity yields an apparent activation energy which is composed of two terms,

$$\frac{\partial \ln D}{\partial (1/T)} = -\frac{E_a}{R} + \frac{KN_x/N_L}{1 + KN_x/N_L} \frac{\Delta E_x}{R}. \quad (18)$$

These equations are the same as those to which the more general relations of McNabb and Foster⁽⁵⁾ may be reduced for the stated conditions and under the assumption of local equilibrium. This shows that when the postulate of local equilibrium is valid, the results of McNabb and Foster are independent of the specific trapping model employed.

When the system departs from linearity between a_x and θ_x , the phenomenological diffusivity is a function of the concentration of the diffusing species. The usual solutions of the diffusion equations cannot be used to obtain an effective diffusivity, but if these equations are used one obtains values of " D " which are different for different experiments all of which should yield the same diffusivity in the absence of the trapping phenomenon. This behavior can in practice be employed as a diagnostic criterion for establishing the existence of the non-linear domain. In this domain the diffusion equations must be written with terms for sources and sinks and solved to some degree of approximation by techniques such as the method of Laplace transforms or numerical integration. Crank⁽¹⁰⁾ (Chap. 7) gives several examples, and McNabb and Foster⁽⁵⁾ others. The latter authors have considered the problem of diffusion

accompanied by trapping in very general terms. By describing the rate of release of trapped hydrogens per occupied trapping site by the parameter p and by letting the number of hydrogens captured per second per unit volume equal $kc_L N_x(1 - \theta_x)$, differential equations for diffusion with trapping were formulated for various specimen geometries and experimental arrangements without the necessity of making the assumption of local equilibrium. The differential equations are soluble with difficulty to obtain usually approximate solutions valid for various ranges of the parameters $\alpha \equiv N_x k/p$ and $\beta \equiv c_L^0 k/p$.

As we have seen, the domain of validity of the local equilibrium hypothesis is very broad for the systems of present interest, and because its use leads to considerable simplification of the McNabb-Foster equations we transcribe some of their relations for the domain of local equilibrium, for which the parameters α and β reduce to

$$\begin{aligned}\alpha &= N_x K/N_L \\ \beta &= c_L^0 K/N_L = \theta_L^0 K.\end{aligned}\quad (19)$$

(a) Permeation through a sheet

For the same experimental conditions as those underlying equation (14), but for large α and large β

$$\tau_i = \frac{a^2}{6D_L} \left(1 + \frac{3N_x}{c_L^0} \right), \quad (20)$$

and it follows from equation (20) that

$$\frac{\partial \ln \tau_i}{\partial (1/T)} = \frac{E_a}{R} + \frac{3N_x}{c_L^0 + 3N_x} \left(\frac{\Delta H^0}{R} \right)_p \quad (21)$$

in which ΔH^0 represents the enthalpy change in the reaction by which the metal just below the input surface is maintained in equilibrium with the environment of constant fugacity p . If, for example, the environment is gaseous hydrogen at a fixed pressure, ΔH^0 would be the heat of solution for the reaction $\frac{1}{2}H_2(g) = H$. Equation (20) reduces to a relation developed by Darken and Smith⁽¹⁾ for $3N_x/c_L^0 \gg 1$ and $\theta_x = 1$.

(b) Absorption into semi-infinite slab

With the initial hydrogen content zero and the lattice hydrogen concentration just below the input surface held constant at c_L^0 and in equilibrium with the environment from $t = 0$ on, the amount of hydrogen absorbed per unit area up to time t is

$$\begin{aligned}q_a(t) &\approx (2N_x N_L/K)^{1/2} (1 + c_L^0 K/N_L)^{1/2} (D_L t)^{1/2} \\ &\approx (2N_x c_L^0)^{1/2} (D_L t)^{1/2}\end{aligned}\quad (22)$$

for large α , large β .

(c) Evolution from semi-infinite slab

With the initial lattice hydrogen (i.e. mobile component only) content in slab uniform and equal to c_L^0 , and the metal just below the surface of the slab of zero hydrogen concentration from $t = 0$ on, the amount of hydrogen evolved per unit area is

$$q_e(t) \approx (N_x N_L/K)^{1/2} (D_L t)^{1/2} \ln (c_L^0 K/2N_L) \quad (23)$$

for large α and large β . The kinetic asymmetry for these conditions can be illustrated by forming the ratio

$$\frac{q_a(t)}{q_e(t)} \approx \frac{(2c_L^0 K/N_L)^{1/2}}{\ln (c_L^0 K/N_L)}.$$

We wish to emphasize that all of the above equations do not depend upon an explicit kinetic model, but only on the thermodynamic assumption of local equilibrium. The kinetic model of Fig. 1 has been used only to establish the range of validity of the postulate of local equilibrium. We now proceed to apply these equations to suitable data in the literature.

5. APPLICATION OF THEORY TO LITERATURE DATA

The ideal kind of kinetic data to which to apply the foregoing body of theory would have been those obtained on iron or steel of well characterized thermal and mechanical history, of a geometry for which mathematical solutions exist, and where the absence of a surface impedance has been ascertained. It would be highly desirable that the environmental hydrogen fugacity be controlled and be known in magnitude. The most direct method for accomplishing this is to use gaseous hydrogen at measured pressures. However, cathodic charging or acid attack may be used provided that a steady-state permeation experiment also is carried out, with identical surface conditions, from which the input fugacity may be calculated as shown below. Data, taken over ranges of temperature and of hydrogen fugacity, of both equilibrium and of kinetic character for the self-same specimens would be valuable.

We have found only a small amount of literature data suitable for our present purpose, which is to calculate the trapping parameters N_x and ΔE_x for well characterized steels. These data, the approximations involved in treating the data, and the results are presented here.

(a) Data of Hill and Johnson⁽²⁾

Hill and Johnson exposed small cylinders of 0.16% C-steel to 1 atm H_2 gas at 230°C to achieve uniform hydrogen contents in the specimens. Some specimens had been swaged at room temperature

to 30% reduction in area and others to 60% R.A. The evolution of the hydrogen from the metal into a vacuum was followed at various temperatures, and the apparent diffusivity was calculated as per an earlier analysis from the time in which the hydrogen content of the specimen decreased to $\frac{1}{10}$ of the initial value after the log rate-time curve becomes linear. It was ascertained that surface effects were negligible.

We may initially assume that the diffusivity data may be analyzed on the low- θ_x domain; this assumption will be checked a posteriori. Therefore equation (18) applies. E_a is taken as 1.9 kcal/mol H, following the analysis of Gonzalez.⁽¹¹⁾ N_L is calculated for the octahedral sites in bcc iron as 2.6×10^{23} sites/cm³. The term KN_x/N_L in the coefficient of $\Delta E_x/R$ may be approximated by applying equation (16) to the ratio c^0/c_L^0 at the hydrogen charging temperature of 230°C. c^0 was measured by Hill and Johnson and c_L^0 may be calculated from the equation established by Gonzalez⁽¹¹⁾

$$c_L^0 = 3.7p^{1/2} \exp(-6500/RT) \quad (24)$$

where c_L^0 is expressed in cm³ H₂ (N.T.P.)/cm³ Fe, R is the gas constant in cal/mol deg, and p is the hydrogen fugacity, in atmospheres, of the environment. In this way one calculates ΔE_x of -6.0 and -8.7 kcal/mol H for the 30% and 60% R.A. alloy, respectively.

Remembering that $K = \exp(-\Delta E_x/RT)$, one may now use these values of ΔE_x in equation (13) at each evolution temperature at which D (the apparent diffusivity) was measured in order to calculate N_x . D_L is calculated from Gonzalez's⁽¹¹⁾ evaluation of the steady-state permeability and from equation (24) yielding

$$D_L = 0.78 \times 10^{-3} \exp(-1900/RT). \quad (25)$$

The data and the calculated values are shown in Table 1. Finally, we form the ratio $\theta_x \approx c^0/N_x$ and find that for both the 30% R.A. alloy and the 60% R.A. alloy the low- θ_x treatment is appropriate. We defer to a subsequent section any discussion of these results.

Because Hill and Johnson also measured c_T as a function of charging temperature for the 60% R.A. alloy, it is also possible to use equation 16 to calculate ΔE_x from these equilibrium data (not shown in Table 1). Using the N_x already established from the kinetic analysis we calculate $\Delta E_x = -9.5$ kcal. The disparity with the -8.7 from the diffusivity measurements is an indication of experimental uncertainty and of crudity of the theoretical analysis. Hill and Johnson⁽²⁾ inferred a trapping energy of -9.4 kcal from the $c_T(T)$ data, and in a later publication⁽¹²⁾ they deduced a $\Delta E_x = -4.8$ kcal from kinetic evolution data on non-cold-worked, low-carbon iron. However, the only reason for the difference from the -6.0 kcal of the present analysis is that they used 3.0 instead of 1.9 kcal/mol H for E_a .

(b) Measurements of Eschbach et al.⁽¹³⁾

These investigators measured the permeation transient of hydrogen across the wall of a tube made of a variety of ferritic steels of unspecified thermal and mechanical history. The hydrogen gas pressure over the input side was variable but of the order of $\frac{1}{2}$ atm and ultra-high vacuum techniques and high-purity hydrogen were used to avoid surface impedances. The apparent diffusivity was established by a technique that is somewhat doubtful at the lower-temperature end of the 40 to 400° temperature range. This problem, the almost complete absence of experimental points in the published curves and the unknown history of the steels make extensive treatment of the data of doubtful value. It seems sufficient to assume the low- θ_x domain and to use equation (18) with the published apparent activation energies, assuming that the coefficient of $\Delta E_x/R$ is unity. This procedure yields ΔE_x between -4.7 to -5.0 kcal/mol H.

(c) Data of Beck et al.⁽¹⁴⁾

Hydrogen was cathodically deposited on one side of a steel diaphragm under 0.1 N NaOH solution at

TABLE 1.* Data and calculated values based on Hill and Johnson⁽²⁾ (0.16% C steel)

| % R.A. | $c^0(230^\circ)$ ($\times 10^{19}$) | $c_L^0(T_{ev})$ ($\times 10^{17}$) | T_{ev} | D | D_L ($\times 10^{-4}$) | ΔE_x | N_x | θ_x |
|--------|--|---|----------|----------------------|-------------------------------|--------------|----------------------|------------|
| 30 | 1.4 | 3.6 | 250 | 8.3×10^{-6} | 1.26 | | 1.2×10^{22} | |
| 30 | 1.4 | 6.3 | 300 | 1.5×10^{-5} | 1.49 | -6.0 kca | 1.2×10^{22} | 0.001 |
| 30 | 1.4 | 9.8 | 350 | 2.8×10^{-5} | 1.69 | | 1.1×10^{22} | |
| 60 | 5.5 | 3.6 | 250 | 1.8×10^{-6} | 1.26 | | 4.3×10^{21} | |
| 60 | 5.5 | 6.3 | 300 | 3.6×10^{-6} | 1.49 | -8.7 | 5.3×10^{21} | 0.01 |
| 60 | 5.5 | 9.8 | 350 | 8.6×10^{-6} | 1.69 | | 4.4×10^{21} | |
| 60 | 5.5 | 14.6 | 400 | 17×10^{-6} | 1.90 | | 3.8×10^{21} | |

* c^0 , c_L^0 and N_x are expressed in number per cm³, D and D_L in cm² s⁻¹, and temperatures in °C. T_{ev} is the temperature at which the evolution kinetics was measured.

various current densities and detected after permeation to the other side by electrochemical oxidation. The apparent diffusivity was calculated from the time taken to reach a specified fraction of the steady-state permeability. The fact that the same D was obtained independently of membrane thickness was taken as evidence of freedom from surface problems.

The diffusivity was measured from 40 to 80°C, yielding an apparent activation energy of 9.2 kcal/mol H, for AISI 4340 steel which had been heat-treated to an ultimate tensile strength of 260,000 psi. Neither the total hydrogen content nor the input fugacity was measured for this system. However, the steady-state permeation of hydrogen was measured for a diaphragm of zone-refined iron in the same electrolyte at 10 mA/cm² charging current. Using Gonzalez's equations this yields an input fugacity of 2030 atm. If we assume that the AISI 4340 was under an equal input fugacity we can conclude that this system departs appreciably from the low- θ_x domain. The reason for this conclusion is that Frank *et al.*⁽¹⁵⁾ found markedly faster absorption than evolution kinetics under charging conditions where the environmental fugacity corresponds* to about 660 atm. Hence we should use an equation of the type of equation (20) in order to evaluate N_x/c_L^0 . However, Beck *et al.*⁽¹⁴⁾ do not give the transient times from which they evaluated their " D " values, which in the high- θ_x domain are not meaningful parameters. We can, however, regain the transient time τ from the reported value of " D " using the equation the authors employed. Doing this, one finds

$$\frac{D_L}{\text{"}D\text{"}} - 1 = \frac{3N_x}{c_L^0}.$$

At 282°K, " D " = 1×10^{-7} and $D_L = 2.6 \times 10^{-5}$ cm² s⁻¹ from equation (25), so that $N_x = (259/3) c_L^0$. The lattice concentration can be estimated from equation (24) if we are willing to assume the same input fugacity of 2030 atm for the steel as for the zone-refined iron. Doing this yields $N_x = 1.4 \times 10^{19}$ cm⁻³.

To get an estimate of the trap depth, we can use this value of N_x in equation (18). The measured apparent activation energy of 9.2 kcal/mol H and $E_a = 1.9$ kcal/mol H give $\Delta E_x \approx -7.3$ kcal/mol H; this is only an approximation in view of the inappropriateness of equation (18).

* These authors⁽¹⁵⁾ charged steel with hydrogen by abrading the steel under water. If one assumes that the relevant reaction is $\frac{1}{2}\text{Fe} + \text{H}_2\text{O}(l) = \frac{1}{2}\text{Fe}_3\text{O}_4 + \text{H}_2(g)$ for which the free energy change is 3.9 kcal, $p_{\text{H}_2} \approx 660$ atm at room temperature.

(d) Data of Andrew *et al.*⁽¹⁶⁾

These investigators charged hydrogen cathodically at various current densities, using an unspecified electrolyte, onto the outer surface of steel tubes of various dimensions, carbon contents, and metallurgical treatments. The hydrogen which permeated at room temperature through the cylindrical wall was collected inside the tube and was measured volumetrically. The surfaces of the specimens were cleaned in an unspecified manner to maintain them free of machining marks, cracks, sludge, and oxides.

Because the permeation was carried out long enough, as judged from the published figures, to have achieved steady state, one can use Gonzalez's equation⁽¹¹⁾ to calculate c_L^0 and hence the input fugacity. This is found to be variable, but it is of the order of 10^6 atm. Hence we must treat these data by the large- θ_x approximation of equation (20). Table 2 summarizes the relevant data and the results. θ_x values cannot be calculated because total hydrogen contents were measured only on specimens using geometries and charging currents different from those employed in the permeation experiments.

(e) Data of Darken and Smith⁽¹⁾

Bars of steel (0.15% C, 0.38% Mn, 0.14% Si) were immersed in 1N H₂SO₄ for measured times at room temperature (Table 8 of Ref. 1). The amounts of hydrogen absorbed were measured by extraction at 170°C. The amount absorbed is linear in the square root of the time of exposure up to a time, t_s , after which no further absorption occurs. The amount absorbed at t_s , divided by the amount of steel, yields the total hydrogen concentration in equilibrium with the input fugacity of hydrogen imposed by the acid-iron reaction. The electrical potential of the steel immersed in the acid was measured with respect to a hydrogen electrode immersed in the same solution. If we follow the authors' assumption that the emf gives a rough measure of the input fugacity of hydrogen, one finds $p_{\text{H}_2} \approx 10^8$ atm. Hence we must use the high- θ_x approximation embodied in equation (22).†

However there are two obstacles to the application of this equation. The first is that the specimens used in this investigation depart widely from the geometry of the semi-infinite slab for which the equation was developed. The second obstacle is that we do not know c_L^0 well enough since the e.m.f. method cannot

† Figure 6 of Ref. 1 enables an estimate of θ_x to be made for an SAE 1020 steel with an unspecified amount of cold work. With the acid of lowest pH used the $\theta_x \approx 0.9$.

TABLE 2. Data and calculated values based on Andrew *et al.*⁽¹⁶⁾

| Steel designation and composition | Treatment of steel | R.A. % | P_{∞} cm ³ H ₂ (NTP)/hr | c_L^0 (atoms H/cm ³) | τ_i (hr) | N_x (sites cm ⁻³) |
|-----------------------------------|--------------------|--------|---|---------------------------------------|------------------|------------------------------------|
| A-2, 0.06% C | a | 25.4 | 0.32 | 5.5×10^{18} | 1.0 | 1.0×10^{20} |
| | | 41.5 | 0.32 | 5.5 | 1.3 | 1.3 |
| | | 60.8 | 0.30 | 5.1 | 2.8 | 3.7 |
| | | 81.4 | 0.30 | 5.1 | 3.1 | 3.0 |
| | | 88.6 | 0.30 | 5.1 | 3.5 | 3.4 |
| | c | 0 | 0.44 | 3.6 | 0.3 | 0.12 |
| | | 20 | 0.42 | 3.5 | 0.9 | 0.39 |
| | | 30 | 0.36 | 3.0 | 1.7 | 0.60 |
| | | 40 | 0.27 | 2.2 | 2.5 | 0.66 |
| | | 60 | 0.20 | 1.7 | 3.2 | 0.65 |
| | | 70 | 0.16 | 1.3 | 3.3 | 0.52 |
| D-2, 0.59% C | d | 0 | 0.39 | 7.3 | 0.8 | 0.68 |
| | | 20 | 0.24 | 4.5 | 1.2 | 0.64 |
| | | 30 | 0.18 | 3.4 | 1.5 | 0.61 |
| | | 40 | 0.14 | 2.6 | 3.1 | 0.96 |
| | | 70 | 0.03 | 0.6 | 5.0 | 0.34 |

P_{∞} = Steady-state permeation rate.

Treatments: a—Steel was cold-drawn by the amounts tabulated, then annealed for 1 hr at 650°C. (Table 4 of Ref. 16.)

b—Same as treatment a, except that anneal was $\frac{1}{2}$ hr at 600°C.

c—Steel normalized before cold-drawing by the amount tabulated. (Table 2 of Ref. 16.)

d—Steel lead-patented at 480°C before cold-drawing by the amount tabulated. (Table 2 of Ref. 16.)

be relied upon to give a measure of the fugacity of the hydrogen produced by acid attack. Hence we prefer to calculate only relative values of N_x from equation (22) applied to a series of bars of the same steel with various amounts of cold-work by wire drawing. Table 3 presents the results of this procedure, where

TABLE 3. Data and analysis based on Darken and Smith⁽¹⁾

| % R.A. | Total hydrogen ($\times 10^{19}$ atoms/cm ³) | Relative N_x | Relative θ_x |
|----------|--|----------------|---------------------|
| 0 | 0.44 | 1 | 1 |
| 16.5 | 2.2 | 2.8 | 1.4 |
| 30.6 | 4.7 | 6.5 | 1.3 |
| 46.2 | 6.6 | 7.8 | 1.5 |
| 60.8 | 10.9 | 14 | 1.4 |
| 75.9 | 15.5 | 19 | 1.5 |
| Annealed | 11.7 | 3 | 7 |

we have assumed that because the acid strength and temperature are the same for all samples the input fugacity, and hence c_L^0 is constant for the whole series. The designation "green rod" refers to the original hot-rolled rod. The annealing referred to in Table 3 is that given to the bar with 76% R.A.; it consisted of 72 hours at 840°C.

(f) *The work of Foster et al.*⁽¹⁷⁾

The evolution of hydrogen from bars of steel previously uniformly saturated with hydrogen was studied. The steel composition was 0.23% C, 0.65% Mn, and was normalized before use; the initial charging was done by immersion at room temperature in water saturated with H₂S. The curve of the evolution kinetics was analyzed by the methods of

McNabb and Foster,⁽⁵⁾ yielding a temperature coefficient for the evolution which, upon subtraction of $E_a = 1.9$ kcal/mol H, yields $\Delta E_x = -6.0$ kcal/mol H. A major shortcoming of this paper is that the dimensions of many of the quantities of Table 2 are not given. If, however, our assignment to column 10 of the units cm³H₂(NTP)/100 g Fe, is correct, then N_x has an average value of 3.6×10^{19} cm⁻³ and $\theta_x \approx$ unity.

(g) *The work of Kim and Loginow*⁽¹⁸⁾

A Ni-Cr-Mo steel was heat-treated in various ways to produce four levels of yield strengths. The treated steels were used in two types of experiments, in each case exposing the steels to an aqueous solution of acetic acid saturated with hydrogen sulfide. In one set of experiments these workers measured the permeation of hydrogen through a slab one side of which was in contact with the acid medium. Because the permeation was followed to steady state one can use these data to calculate input fugacities. One may calculate τ_i from the curves of total hydrogen throughput versus time and with equation (20) calculate N_x , since these conditions correspond to high θ_x . The data and the analyses are given in Table 4-A.

The second set of experiments consisted in totally immersing small cubes of the same steels in the acid medium and determining the amount of hydrogen absorbed by the cubes as a function of time of immersion by a hot-extraction method. The amount absorbed was found to be roughly linear in the square root of time until the saturation amount was reached.

TABLE 4-A. Permeation experiments on slabs as function of strength level⁽¹⁸⁾

| Steel, yield strength (ksi) | P_{∞} (mA/cm ²) | c_L^0 ($\times 10^{17}$ atom cm ⁻³) | τ_j s | N_x ($\times 10^{19}$ cm ⁻³) |
|-----------------------------|------------------------------------|--|------------|---|
| 150 | 0.051 | 3.7 | 1820 | 3.0 |
| 138 | 0.057 | 4.1 | 1270 | 2.3 |
| 103 | 0.055 | 3.9 | 830 | 1.5 |
| 95 | 0.066 | 4.8 | 680 | 1.5 |

Thus we can use equation (22) (valid only approximately since the specimens are not semi-infinite solids) to analyze these data. The necessary value of c_L^0 is not available directly from these experiments but if one assumes that for the same acid and steel the same input fugacity is generated on the slab as on the cube specimens then one may use the c_L^0 obtained in the permeation experiments. The results of these calculations are also presented in Table 4-B.

Kim and Loginow also measured the saturation amount of total hydrogen in the steel cubes in total immersion, so that, using again the assumption that the same hydrogen fugacities were generated on the same steel in both types of experiments, one may calculate ΔE_x from the relation

$$\frac{c_{tot}}{c_L^0} = 1 + \frac{KN_x}{N_L + Kc_L^0}$$

remembering that $K = \exp(-\Delta E_x/RT)$. The values of ΔE_x calculated this way are given in Table 4-B.

6. DISCUSSION OF RESULTS

It is clear that, because the limited number of calculated values that we have been able to accumulate is too small, because the original data are of such fragmentary nature and because the analyses are necessarily approximate, any conclusions can only be very tentative at this time. Perhaps the most striking result of these calculations is the approximate uniformity of the trap depth, ΔE_x . There is an indication that $|\Delta E_x|$ increases with increasing cold work and with increasing strength level of the steel. Similarly, there is a remarkable consistency in N_x , the volume density of trapping sites, for the steels that have not received cold work; N_x is always of the order of 10^{19} cm⁻³. There is also a trend of increasing N_x with either increasing carbon content or increasing strength level of the steel.

The calculations based on the work of Darken and Smith and on that of Andrew *et al.* indicate increasing trapping site density with increasing amount of cold work. It is also satisfying that the annealing treatment given by Darken and Smith considerably reduced N_x below the value for the corresponding cold-worked steel. The results based on the work of Hill and Johnson do not follow this pattern, but instead we find that increasing the amount of cold work increases the energy of binding but at a smaller number of trapping sites. It is also disturbing that N_x is so much larger for the Hill-Johnson data than for the case of Andrew *et al.* for corresponding amounts of cold work.

Because the magnitude of ΔE_x that we have calculated closely resembles the value of -6.4 kcal/mol found by Gibala⁽¹⁹⁾ for the interaction free energy between dislocation cores and dissolved hydrogen atoms, it might be tempting to conclude that the trapping sites are to be identified as sites at dislocation cores. However, this interpretation must be tempered by a consideration of the magnitudes found for N_x . One would need a dislocation density of 10^{11} cm⁻² in order to achieve $N_x = 3.5 \times 10^{19}$ cm⁻³, assigning 5 trapping sites per dislocation line per atomic plane (Chou and Li⁽²⁰⁾). Consideration of the amount of solute that can be held in the stress fields⁽²¹⁾ of dislocations may increase the effective N_x due to dislocations by a factor of two or three. A non-cold-worked steel could have a dislocation density of 10^8 – 10^{10} cm⁻². Thus a contribution from another kind of trapping site is needed and the most likely such site is that at interfaces.

Non-cold-worked steels have internal interfaces because of the presence of carbides, nitrides, and other second-phase particles. That adsorption of hydrogen at such solid-solid interfaces is likely may be inferred

TABLE 4-B. Immersion experiments on cubes⁽¹⁸⁾

| Steel, yield strength (ksi) | Assumed c_L^0 ($\times 10^{17}$ atom cm ⁻³) | Measured c_{tot} ($\times 10^{19}$ atom cm ⁻³) | t_s (hr) | N_x ($\times 10^{19}$ cm ⁻³) | θ_x | ΔE_x (kcal/mol H) |
|-----------------------------|--|---|------------|---|------------|---------------------------|
| 150 | 3.7 | 2.9 | 5.8 | 5.9 | 0.5 | -8.0 |
| 138 | 4.1 | 2.6 | 5.3 | 4.7 | 0.55 | -8.1 |
| 103 | 3.9 | 1.6 | 4 | 2.5 | 0.64 | -8.3 |
| 95 | 4.8 | 1.1 | 4 | 0.9 | (1.2) | — |

from the demonstration of Podgurski *et al.*⁽²²⁾ that nitrogen is strongly adsorbed at the interface between AlN particles and ferrite. Indeed, Podgurski⁽²³⁾ has obtained strong indications that hydrogen is also adsorbed at such an interface. The extent of internal interface cannot now be estimated for the steels for which we have calculated N_x . The best that can be done at this stage is to demonstrate the likelihood that these steels had a sufficiently large area of internal interface to contribute significantly to N_x . We can do this by pointing out that the measurements of Kramer *et al.*⁽²⁴⁾ show that, near the middle of the range of pearlite spacings that they studied, the extent of the ferrite-cementite interfacial area was about $10^4 \text{ cm}^2/\text{g}$ for a pearlitic steel of 0.8% C. On the basis that the ferrite side of the interface is composed of (100) planes and that the hydrogen sites would be at the octahedral interstitial positions in those planes, this means that $N_x = 28 \times 10^{19}$ interfacial sites/ cm^3 of steel. Thus, even a 0.1% C steel of the same pearlite spacing would have $N_x(\text{interface}) = 3.5 \times 10^{19}$. If the same amount of cementite were in particles whose average dimension is equal to the thickness of the cementite lamellae in the corresponding pearlitic steel the interfacial area would be larger; if the pearlite were spheroidized, the area would be smaller. Remembering that steels usually have other inclusions as well, we consider that solid-solid interfaces probably represent the predominant trapping sites for hydrogen in steels that have not been cold worked.

When a steel is mechanically deformed, the number of dislocation-core sites for hydrogen trapping is increased but also microcracks are produced. This is known from the density decrement that accompanies cold work^(25,26) as well as from the work of Podgurski⁽²⁾ on the formation of methane within microvoids in steel Hill and Johnson⁽²⁾ have suggested that microcrack surfaces furnish important trapping sites in cold-worked steels. Insofar as trapping of hydrogen is concerned, the relative importance of microcracks and of the increasing dislocation density will depend on the mode of deformation and upon the microstructure of the steel. Garofalo and Wriedt⁽²⁸⁾ showed that steel deformed in tension suffered a larger density decrement than the same steel deformed in compression. One would expect therefore that the former would have a larger volume of microcracks than the latter and, if the crack morphologies are the same, that the ferrite-vacuum interfaces thus developed would play a more important role in the former. An additional complication lies in the predominant location of the microcracks produced by cold work. If the majority of these are the result of parting at the solid-solid interface,

then the trap depth and/or number of traps for hydrogen would be smaller than for the same crack area produced in the bulk of the ferrite matrix. The reason for this statement is that the crack surface developed from an internal surface would retain the adsorbate that was probably already upon the internal surface. This would lead to a decreased energy of adsorption of hydrogen as compared with a clean iron surface⁽⁶⁾ such as would be produced by cracking the ferrite matrix.

Thus we suggest that the increasing amount of hydrogen absorption with increasing amount of cold work, observed by many investigators for a variety of steels, is due to the increasing dislocation density and to the increasing amount of microcrack surface produced by the cold work. In addition, at large charging fugacities the amount of hydrogen held within the volumes of the microcracks as molecular hydrogen would become a significant contribution. Annealing of a pre-cold-worked steel probably would reduce the dislocation density, reducing N_x thereby, but the microcrack network would not be as easily reduced.⁽²⁹⁾ The annealed steel therefore presents to hydrogen a smaller total population of trapping sites but one of larger mean trap depth since the energy involved in hydrogen going from the dissolved state to the adsorbed state at an atomically clean iron surface is⁽⁶⁾ about -20 kcal/mol H , to be compared with -6.4 for trapping at dislocation cores.⁽¹⁹⁾ This may be the explanation of the Darken-Smith result. Annealing the cold-worked steel resulted (see Table 3) in a marked reduction in N_x but in only a small decrease in the amount of hydrogen absorbed so that θ_x rose sharply. Evidently the cold-worked alloy had microcrack surfaces as the major contributing element to c_x . Annealing decreased the already relatively small contribution from dislocations, leaving only that contribution from the surfaces. However, it is also possible that annealing a cold-worked steel causes adsorption upon microcrack surfaces of dissolved interstitial elements. This would decrease the adsorption energy of hydrogen, and if such surfaces had been the major contribution to N_x in the cold-worked state, annealing would markedly reduce the occlusive capacity for hydrogen, as was in fact observed by Harhai *et al.*⁽⁴⁾

We have thus been led to the concept of a multiplicity of traps for dissolved hydrogen. Clearly the simple analysis that has been developed, characterized by non-interacting hydrogens upon a single population of traps, is inadequate to comprehend this situation, but nevertheless some insight can be gained by its judicious application. More realistic and

complicated analyses can be developed, but of greater need are experiments on the equilibrium hydrogen absorption and on the kinetics of absorption, evolution, and permeation all on the same material. In these experiments the environmental fugacity of hydrogen should be controlled and measured so that gaseous hydrogen is preferable as a charging medium. Gaseous hydrogen offers the additional advantage that since the low- θ_x regime is practically assured for reasonable numbers of trapping sites, the analysis of the kinetics is both easier and more fruitful. The microstructure of the steel used should be carefully controlled and characterized both as to chemistry and morphology. The effects of cold work on second-phase morphology, dislocation structure, and microcrack generation should be carefully examined. Systems should be sought where the variety in the kinds of trapping sites is as restricted as possible. Finally, it goes without saying that input and output surface conditions must be rigorously controlled to preclude surface impedance to permeation, and that the geometry of the specimen used should be appropriate for the mathematical solutions that will be employed in the analysis.

7. SUMMARY

A thermodynamic analysis of trapping of dissolved hydrogen atoms, in which the trapped population is in local equilibrium with the mobile population, may be used to rationalize the whole range of anomalous diffusion behavior of hydrogen in steels. Application of the analysis, which is independent of a specific kinetic model, to selected sets of data leads to a fair internal consistency of interaction energy of dissolved hydrogen with trapping sites and of numbers of trapping sites. Consideration of these quantities and of trends in these quantities with degree of cold work leads to the suggestion that whereas dislocations furnish trapping sites, solid-solid interfaces are the more important structural feature in non-cold-worked steels for the trapping of hydrogen. With increasing cold work, microcrack surfaces increase in importance over the augmented dislocation network. Suggestions are made for more definitive experiments.

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