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Two Phase Diffusion Model of Hydrogen in Steel[†]

Yukio UEDA* and Hidekazu MURAKAWA**

Abstract

Two phase diffusion model of hydrogen in steel is derived based on random motion of hydrogen atoms. Lattice dissolved and trapped hydrogen is considered. It is shown that the two phase diffusion model can be reduced to some of the existing models under proper assumptions. Further, it is applied to investigate the peculiar phenomena in measuring permeability by electrochemical method.

KEY WORDS: (Hydrogen) (Diffusion) (Random Motion) (Two Phase Diffusion) (Trapped Hydrogen) (Nonequilibrium Model) (Equilibrium Model) (Finite Difference Method) (Electrochemical Method)

1. Introduction

Hydrogen in steel exhibits peculiar behaviors around room temperature, at which delayed cracking occurs and unusually small diffusivity is observed. The reason for this phenomenon is commonly understood as a result of trapping of hydrogen by defects such as dislocations. Although various models, in which the effect of traps is considered, are proposed, real physical phenomena have not been thoroughly explained.

To provide better understanding of the phenomena, authors derived a two phase diffusion model in which lattice and trapped hydrogen atoms are considered. It is shown that some of the existing models^{1),2)} can be reduced from the proposed model as special cases. Further, the two phase diffusion model is applied to explain the peculiar phenomena observed in measuring the diffusivity by electrochemical method which are reported by Asano³⁾ and Fujishima⁴⁾.

2. Two Phase Diffusion Model

To describe the hydrogen diffusion in mathematical form, the following assumptions are made.

- Diffusive hydrogen in steel have two possible stable sites, namely lattice and trap sites, as shown in Fig. 1. The activation energies of the hydrogen in these sites are assumed to be Q^0 and Q^* , respectively.
- Hydrogen atoms are oscillating around the stable positions and their frequencies are assumed to be ν^0 and ν^* for lattice and trapped hydrogen atoms.
- The probabilities that a hydrogen atom can pass the potential barrier for each cycle of the oscillation are

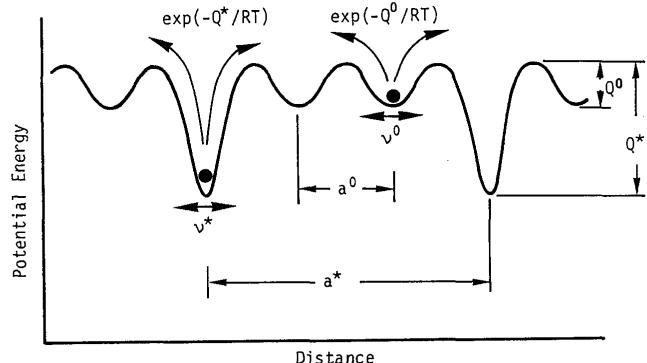


Fig. 1 Model of trap site and motion of hydrogen atoms.

given as

$$\exp(-Q^0/RT), \exp(-Q^*/RT)$$

where R is the gas constant and T is the absolute temperature.

- A hydrogen atom, which gets over the potential barrier, moves to the neighboring stable site a^0 or a^* away from the original site.
- The probabilities that the escaped hydrogen falls into the lattice and the trap sites are $(1-k)$ and k , respectively.
- Total hydrogen density is very small compared to that of possible stable sites.

Based on the above assumptions, two phase diffusion model is derived. For simplicity, one dimensional problem as shown in Fig. 2 is considered. The hydrogen can travel only in x direction and the bar is assumed to have unit crosssectional area. The hydrogen is separated into lattice and trapped hydrogen and their density distributions are denoted as $C^0(x)$ and $C^*(x)$. To derive the diffusion

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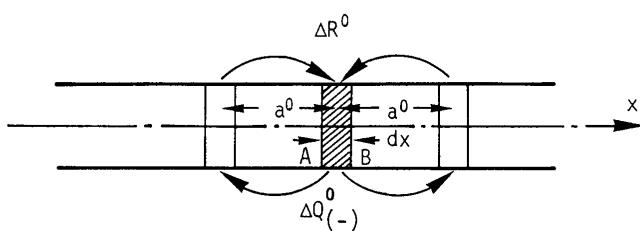


Fig. 2 Two phase diffusion model.

equation, a infinitesimal region A-B with length dx is considered as shown in Fig. 2. The lattice and the trapped hydrogen escape from the region dx during a small period dt are given as

$$\begin{aligned}\Delta Q_{(-)}^0 &= \nu^0 \exp(-Q^0/RT) C^0(x) dx dt \\ \Delta Q_{(-)}^* &= \nu^* \exp(-Q^*/RT) C^*(x) dx dt\end{aligned}\quad (1)$$

where $\Delta Q_{(-)}^0$ and $\Delta Q_{(-)}^*$ are those for lattice and trapped hydrogen, respectively.

On the other hand, the half of the lattice hydrogen which escaped from the regions with length dx at $x-a^0$ and $x+a^0$ flows into the region A-B and its magnitude is given as

$$\begin{aligned}\Delta R^0 &= \frac{1}{2} \nu^0 \exp(-Q^0/RT) [C^0(x-a^0) \\ &+ C^0(x+a^0)] dx dt\end{aligned}\quad (2)$$

Similarly, the trapped hydrogen flows into A-B from the regions dx at $x-a^*$ and $x+a^*$ is given as

$$\begin{aligned}\Delta R^* &= \frac{1}{2} \nu^* \exp(-Q^*/RT) [C^*(x-a^*) \\ &+ C^*(x+a^*)] dx dt\end{aligned}\quad (3)$$

Further, probabilities that the hydrogen flowing into A-B drops in lattice and trap sites are assumed to be $(1-k)$ and k , respectively. Then the increase of the lattice and the trapped hydrogen $\Delta Q_{(+)}^0$ and $\Delta Q_{(+)}^*$ are shown to be

$$\begin{aligned}\Delta Q_{(+)}^0 &= (1-k)(\Delta R^0 + \Delta R^*) \\ \Delta Q_{(+)}^* &= k(\Delta R^0 + \Delta R^*)\end{aligned}\quad (4)$$

Considering the conservation of hydrogen in the region A-B, the following equations are derived.

$$\begin{aligned}\frac{\partial C^0}{\partial t} dx dt &= \Delta Q_{(+)}^0 - \Delta Q_{(-)}^0 \\ \frac{\partial C^*}{\partial t} dx dt &= \Delta Q_{(+)}^* - \Delta Q_{(-)}^*\end{aligned}\quad (5)$$

By substituting Eqs. (1) and (4), Eq. (5) can be rewritten as

$$\begin{aligned}\frac{\partial C^0}{\partial t} &= \frac{1}{2}(1-k) [\nu^0 \exp(-Q^0/RT) \{ C^0(x-a^0) \\ &+ C^0(x+a^0) \} + \nu^* \exp(-Q^*/RT) \{ C^*(x-a^*) \\ &+ C^*(x+a^*) \}] - \nu^0 \exp(-Q^0/RT) C^0(x) \\ \frac{\partial C^*}{\partial t} &= \frac{1}{2}k [\nu^0 \exp(-Q^0/RT) \{ C^0(x-a^0) \\ &+ C^0(x+a^0) \} + \nu^* \exp(-Q^*/RT) \\ &\{ C^*(x-a^*) + C^*(x+a^*) \}] - \nu^* \exp(-Q^*/RT) C^*(x)\end{aligned}\quad (6)$$

Further, the above equation is expanded in Taylar series assuming that the travelling distances a^0 and a^* are small. The following set of equations are derived as two phase diffusion equations if the terms higher than the second order of a^0 and a^* are neglected.

$$\begin{aligned}\frac{\partial C^0}{\partial t} &= (1-k) [D^0 \frac{\partial^2 C^0}{\partial x^2} + D^* \frac{\partial^2 C^*}{\partial x^2}] \\ &- [k\nu^0 \exp(-Q^0/RT) - (1-k)\nu^* \exp(-Q^*/RT)] \\ \frac{\partial C^*}{\partial t} &= k [D^0 \frac{\partial^2 C^0}{\partial x^2} + D^* \frac{\partial^2 C^*}{\partial x^2}] + [k\nu^0 \exp(-Q^0/RT) \\ &- (1-k)\nu^* \exp(-Q^*/RT)]\end{aligned}\quad (7)$$

where D^0 and D^* are diffusion constants which are defined as

$$D^0 = \frac{1}{2} \nu^0 (a^0)^2 \exp(-Q^0/RT)$$

$$D^* = \frac{1}{2} \nu^* (a^*)^2 \exp(-Q^*/RT)\quad (8)$$

As seen from Eq. (7), the first terms in the right hand side of the equation represent diffusion of hydrogen. While, the second terms represent the reaction which moves toward the equilibrium between lattice and trapped hydrogen densities. In other words, these terms represents the accumulation of hydrogen in traps. Thus, if the state is in equilibrium the second terms vanishes and the ratio of trapped and lattice hydrogen in equilibrium is given as

$$C^*/C^0 = k\nu^0 \exp(-Q^0/RT) / (1-k)\nu^* \exp(-Q^*/RT)\quad (9)$$

3. Comparison with Existing Models

The concentration of hydrogen in weld joints can not be explained by conventional Fick type models, in which the diffusion is assumed to be driven by the hydrogen

density gradient. Various alternative models are proposed in which the effect of traps is considered. They may be classified into nonequilibrium and equilibrium models. In the former model, local equilibrium between the hydrogen in lattice sites and traps is not assumed and their reaction is considered. While in the latter, the equilibrium between the two phases of the hydrogen is postulated.

3.1 Assumptions

The two phase diffusion model discussed in the preceding chapter can be reduced to some of the existing non equilibrium and equilibrium models under proper assumptions. The assumptions introduced are

- The diffusivity of the trapped hydrogen D^* is small enough compared to that of lattice hydrogen D^0 and can be neglected.
- The reaction between the lattice and trapped hydrogen is fast enough so that the equilibrium are reached instantly.
- Ratio of the trap site density k compared to that of total stable sites is small.

3.2 Simplified two phase model

When the assumption a) is introduced, Eq. (7) can be reduced to the following equations.

$$\frac{\partial C^0}{\partial t} = (1 - k) D^0 \frac{\partial^2 C^0}{\partial x^2} - \beta^0 C^0 + \beta^* C^* \quad (10)$$

$$\frac{\partial C^*}{\partial t} = k D^0 \frac{\partial^2 C^*}{\partial x^2} + \beta^0 C^0 - \beta^* C^* \quad (11)$$

where

$$\beta^0 = k \nu^0 \exp(-Q^0/RT),$$

$$\beta^* = (1 - k) \nu^* \exp(-Q^*/RT) \quad (12)$$

Further if the assumption c) is introduced and minor terms involving k are neglected, the following set of equations are derived.

$$\frac{\partial C^0}{\partial t} = D^0 \frac{\partial^2 C^0}{\partial x^2} - \beta^0 C^0 + \beta^* C^* \quad (13)$$

$$\frac{\partial C^*}{\partial t} = \beta^0 C^0 - \beta^* C^* \quad (14)$$

where

$$\beta^0 = k \nu^0 \exp(-Q^0/RT),$$

$$\beta^* = \nu^* \exp(-Q^*/RT) \quad (15)$$

According to Eq. (13), the diffusion or the flow of the hydrogen is possible only in the form of the lattice hydrogen and it is driven by the gradient of its density. At the

same time, the reaction between the two phases occurs. For convenience, the above model is referred to as simplified two phase diffusion model. Although the detail is not shown here, Eqs. (13) and (14) are basically same as the nonequilibrium diffusion model proposed by McNabb and Foster¹⁾.

3.3 Equilibrium model

If the assumption b) is introduced in addition to the assumption a), the equilibrium is achieved instantaneously. Thus, the second terms in the right hand side of Eqs. (10) and (11) vanish under this assumption and it is shown to be

$$\frac{\partial C^0}{\partial t} = (1 - k) D^0 \frac{\partial^2 C^0}{\partial x^2} \quad (16)$$

$$\frac{\partial C^*}{\partial t} = k D^0 \frac{\partial^2 C^*}{\partial x^2} \quad (17)$$

By adding Eqs. (16) and (17), it is obtained that,

$$\frac{\partial}{\partial t} (C^0 + C^*) = D^0 \frac{\partial^2 (C^0 + C^*)}{\partial x^2} \quad (18)$$

Hence, the following set of equations are derived under the assumptions a) and b).

$$\begin{aligned} \frac{\partial C}{\partial t} &= D^0 \frac{\partial^2 C}{\partial x^2} \\ \beta^0 C^0 &= \beta^* C^* \end{aligned} \quad (19)$$

where C is the total hydrogen density, such that

$$C = C^0 + C^*$$

The above equation can be rewritten by eliminating C^0 and C^* . Then, the diffusion equation is reduced to the following form.

$$\frac{\partial C}{\partial t} = D^0 \frac{\partial^2}{\partial x^2} \left(\frac{1}{1 + \beta^*/\beta^0} C \right) \quad (20)$$

If the term in the parentheses is considered as activity, Eq. (20) can be related to the diffusion model proposed by Yurikawa²⁾ in which hydrogen is assumed to be driven by the gradient of the activity. For convenience, the above model is referred to as equilibrium two phase diffusion model.

4. Numerical Examples

Using the simplified two phase diffusion model, permeation curves are computed. Finite difference method is used to solve Eqs. (13) and (14). The lattice hydrogen density on the charging side of the surface is assumed to be \bar{C} as shown in Fig. 3. While, that on the discharging

side is assumed to be zero.

As the first example, the permeation curves are computed for cases in which the ratio of the trapped and the lattice hydrogen densities in equilibrium, C^*/C^0 , is constant. Permeation curves for three different values of k and Q^* are compared in Fig. 4. Also, the curve corresponding to the case without trap and that computed by the equilibrium model are shown. As seen from the figure, the permeation curve approaches to that of the equilibrium model when the trap density k is large. On the contrary, it approaches to the case without trap when k is small. It is interesting to notice that the curve is clearly divided into two stages if k takes intermediate value. The first stage shows rapid increase as that of the case without trap and gradual increase is observed in the second stage.

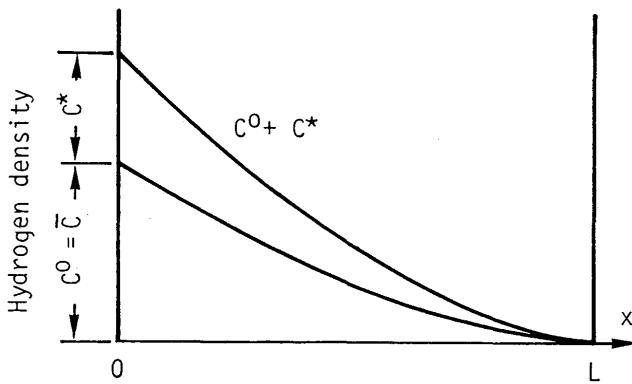


Fig. 3 Boundary condition.

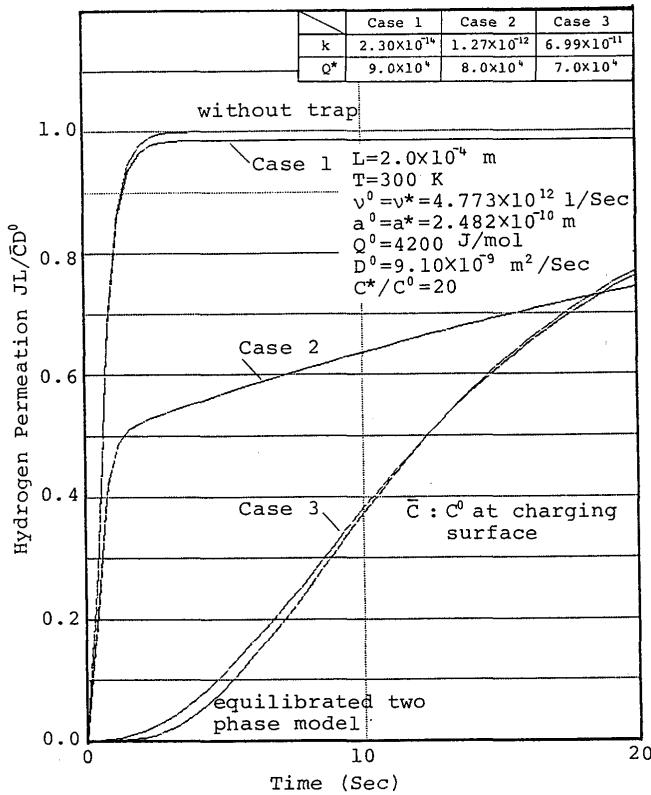


Fig. 4 Permeation curves for various cases with same C^*/C^0 .

Such peculiar phenomenon can be found in experimental data reported by Asano³⁾.

Further, the effects of k and Q^* are examined and the computed results are shown in Figs. 5 and 6. It can be

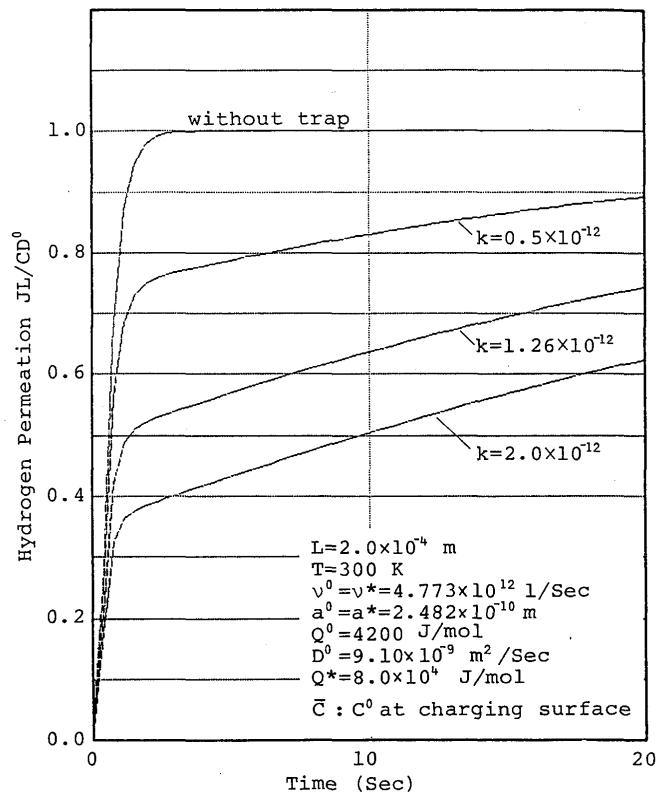


Fig. 5 Effect of trap density k .

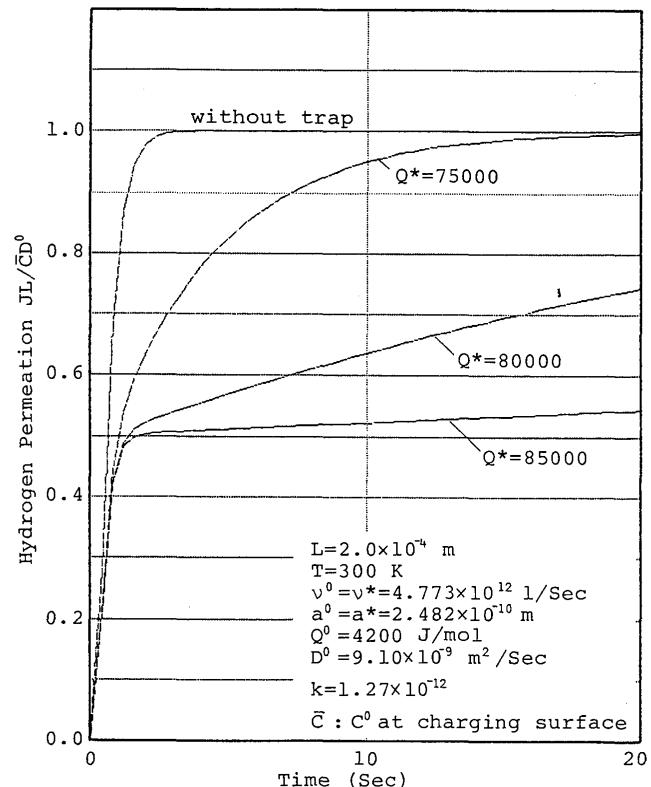


Fig. 6 Effect of activation energy Q^* .

seen from Fig. 5 that the permeation rate at the transition point from the first stage to the second stage is governed by k and it becomes higher for smaller value of k . On the other hand, Q^* is reflected in the slope of the permeation curve after the transition and the slope becomes bigger for small Q^* . These numerical results suggest that it may be possible to determine k or Q^* through comparison between theoretical computation and proper experiments using nonequilibrium diffusion. Though the detail is not discussed here, nonequilibrium diffusion can be observed clearly when the thickness of the specimen L is small.

5. Peculiar Phenomena in Hydrogen Diffusion

5.1 Simulation by simplified two phase diffusion model

Electrochemical method is one of the popular means to measure diffusivity of hydrogen in metal and detailed experimental data have been accumulated. Among these data, peculiar phenomenon, which can not be explained by conventional Fick type theory, was reported by Fujishima⁴⁾. He measured the permeation rates under three successive chargings with one and thirty minutes resting times after the first and the second chargings. Each charging is continued for one hour. The measured permeation rates are shown in Fig. 7. As seen from the figure, the curves for the first and the third runs can be divided into two stages. The first stage shows the similar curve as the permeation curve obtained by Fick's diffusion model.

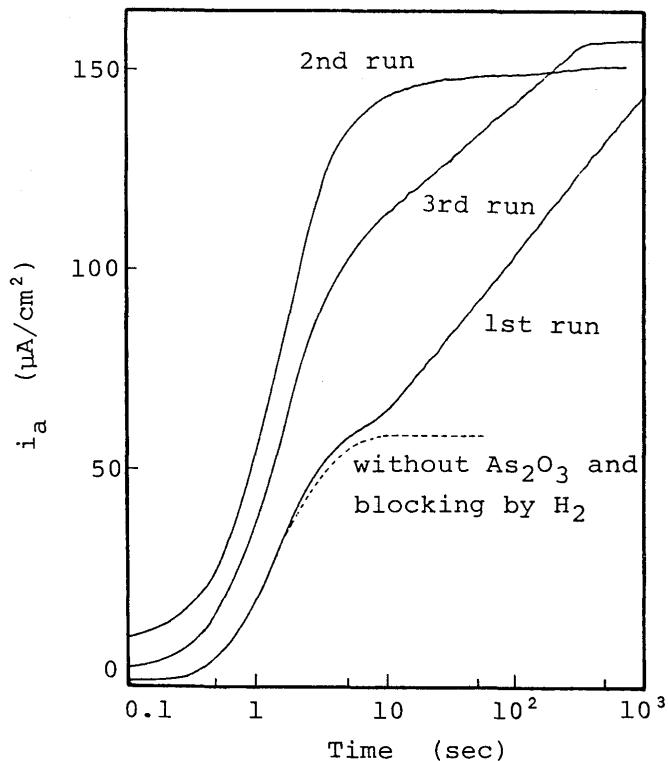


Fig. 7 Permeation curves measured by Fujishima.

Then, linearly increasing curve is observed in the second stage. On the other hand, only the first stage is observed in the second run. This phenomenon is explained by Fujishima as a result of chemical reaction in the electrolyte which forms AsH_3 .

However, it may be possible to explain the same phenomenon as a result of diffusion itself rather than the chemical reaction. To examine the possibility, the permeation curves are computed by finite difference method using the simplified two phase diffusion model. The physical constants are chosen so that the closest permeation curve is obtained for the first run. The computed permeation curves are shown in Fig. 8. As seen from the figure, the computed curves differ significantly from the measured curves shown in Fig. 7. The computed curve for the second run shows high permeation at the moment when the charging starts. Such high permeation rate is caused by the hydrogen released from the trap site which was filled during the first run. Also, the third run shows almost same curve as that of the first run. This means that the release rate of the hydrogen from the trap is too fast and the most trapped hydrogen is escaped during the thirty minutes resting time.

To reduce the release rate, Q^* is increased from 82000J/mol to 84000J/mol with keeping other constants same. The computed result for this case is shown in Fig. 9. Though slight improvement is observed, the in-

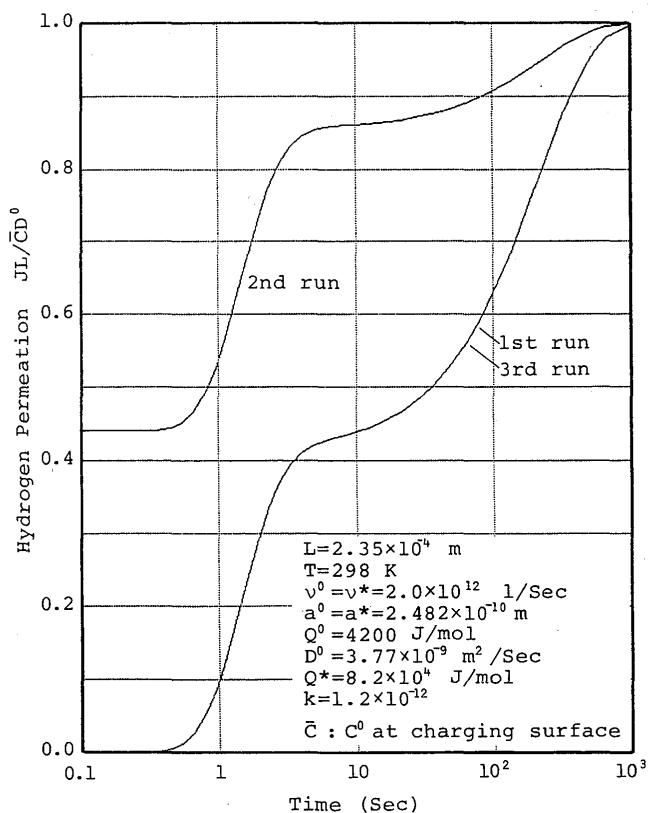


Fig. 8 Permeation curves computed by simplified two phase diffusion model ($Q^* = 82000$ J/mol).

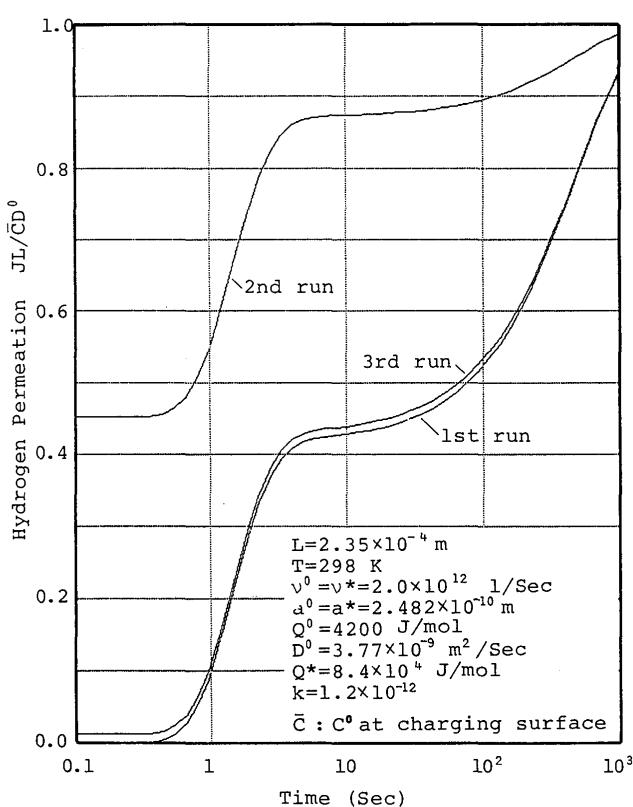


Fig. 9 Permeation curves computed by simplified two phase diffusion model ($Q^* = 84000 \text{ J/mol}$).

crease of Q^* result in bigger deviation of the computed curve for the first run from that of the measured one. Thus, it is concluded that it is not possible to reproduce the measured curve by choosing proper physical constants. In other words, the phenomenon can not be represented by the simple two phase diffusion model.

5.2 Simulation by modified two phase diffusion model

In the simplified two phase diffusion model, it is assumed that the hydrogen density is much smaller than that of the possible sites. However, the density of the trap site is small compared to that of lattice sites. Thus, it may be possible that the trapped hydrogen density becomes close to that of trap site itself even under normal conditions.

When the saturation of the trapped hydrogen is considered, Eqs. (13) ~ (15) are modified and the following diffusion equations can be derived.

$$\frac{\partial C^0}{\partial t} = D^0 \frac{\partial^2 C^0}{\partial x^2} - \beta^0 C^0 + \beta^* C^* \quad (21)$$

$$\frac{\partial C^*}{\partial t} = \beta^0 C^0 - \beta^* C^* \quad (22)$$

where

$$\beta^0 = \bar{k} v^0 \exp(-Q^0/RT), \beta^* = v^* \exp(-Q^*/RT) \quad (23)$$

$$\bar{k} = k (1 - C^*/C_{\max})$$

and C_{\max} is the density of the trap site. Eqs. (21) and (22) are solved numerically for the same boundary and initial conditions. The density of trap site C_{\max} is assumed to be

$$C_{\max} = 40 \bar{C}$$

where \bar{C} is the lattice hydrogen density at the charging surface. The computed results are shown in Fig. 10. Though some differences are observed, the measured curves are reproduced well by the computation based on the modified two phase diffusion model in which the saturation of the trapped hydrogen is considered.

6. Conclusion

Two phase diffusion model is derived based on the random motion of hydrogen atoms. It is also shown that the two phase diffusion model can be reduced to McNabb and Foster's nonequilibrium model and Yurikawa's equilibrium model by introducing proper assumptions. Using the proposed model, explanation of the peculiar behavior observed in measurement of permeation is attempted. It is found that if the saturation of the trapped hydrogen is considered, the peculiar behavior can be reproduced numerically.

Further, it is shown through this study that the non-equilibrium model of diffusion and proper experiments

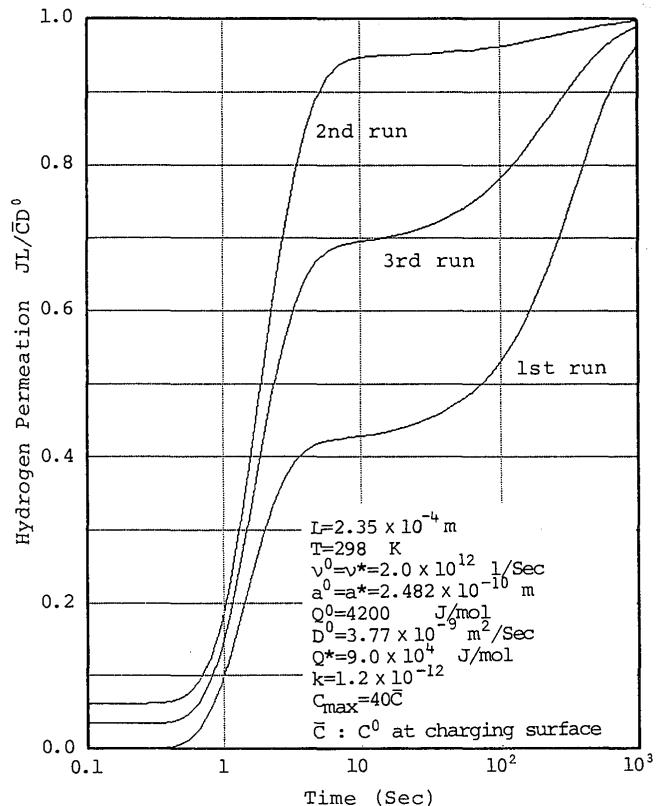


Fig. 10 Permeation curves computed by modified two phase diffusion model.

are useful to study the mechanism of the hydrogen diffusion.

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