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Non-ideality in H Permeation through Plate Membranes

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Introduction

It is known that at finite H concentrations in metals and alloys, the measured D_H , Fick's concentration-dependent diffusion constant, must be corrected for non-ideality effects in order to obtain the concentration-independent Einstein diffusion constant, D_H^* [1]. Such changes from D_H to D_H^* have been mostly applied to H in Pd and its alloys because of the easily obtained large H solubilities where non-ideality is important and because $\mu_H (= \frac{1}{2} \mu_{H_2(1 \text{ bar})}^0 + RT \ln p_{H_2}^{1/2})$ can be easily measured from the equilibrium p_{H_2} as a function of $(H/M)=r$ [1,2,3,4].

For one-dimensional diffusion, Fick's first law is

$$J = -c \cdot \frac{dc}{dx} = -D_H (dc/dx) \quad (1)$$

where c is the H concentration. The real driving force however, is known to be the gradient of the chemical potential and therefore the general expression for flux is

$$J = -(D_H^*/RT)c(d\mu_H/dx) = -(D_H^* c /RT)(d\mu_H/dc)(dc/dx) \quad (2)$$

where c is the concentration of H. Since

$$(d\mu_H/dc) = RT (d \ln p^{1/2}/dc), \quad (3)$$

equation (2) can be written as

$$J = -D_H^* c (d \ln p^{1/2} / d \ln c) (dc/dx) \quad (4)$$

and therefore

$$D_H(c) = D_H^* c (d \ln p^{1/2}) / (d \ln c) = D_H^* f(c) \quad (5)$$

where $f(c)$ is the thermodynamic factor [2]. It is convenient to substitute r for c where r is the H-to-metal, atom ratio because this concentration unit is more commonly employed for metal-H systems and they are directly proportional to each other. It is easy to determine $f(r)$ for metal-H systems from $\ln p_{H_2}$ vs. $\ln r$ isotherms because it is given by the slopes, $d \ln p^{1/2} / d \ln r$, as a function of r .

Conversions from D_H to D_H^* have been made by Bohmholdt and Wicke [2], Küssner [3] and Züchner and co-workers [4]. They employed time-lapse methods for the determination of D_H where

the initially uniform H content of the membrane is perturbed on the upstream side and the perturbation is detected on the downstream side of the membrane at a later time. Because the concentration does not vary much over the membrane in these time-lapse measurements a mean concentration of H can be employed for the evaluation of $f(r)$ and the measured D_H is easily converted to D_H^* . These workers were able to determine values of D_H^* in the high H content regions with this approach [2,3,4]. It is of considerable interest that D_H is ~10 times as great in the hydride phase region of Pd-H as in the dilute phase due to the thermodynamic factor.

Derivation of Equation for the Determination of D_H^* from D_H

In permeation determinations based on steady state H fluxes through membranes where the upstream and downstream concentrations differ significantly, it is not a valid approximation to employ a mean concentration for the evaluation of $f(r)$. Often the upstream side is maintained at a given r value while the downstream side kept at $r=0$ by continuous evacuation. D_H is generally evaluated from equation (1) in the form

$$J = -D_H(c) (dc / dx) = D_H (c_{up} / d) \quad (6)$$

where d is the membrane thickness and downstream concentration, $c_d = 0$ and the steady-state flux can be determined experimentally from p_{H_2} changes on the upstream side of the membrane. The main purpose of this paper is to derive an expression for D_H^* from the measured D_H value for this situation. D_H is the diffusion constant determined from equation (6) and it is dependent upon p_{up} , T , and the nature of the alloy, which is dependent upon c indirectly through p_{up} . The experimental value will not be considered to be an explicit function of c .

Jost [5] and Barrer [6] have also considered gas permeation through membranes where D_H is concentration-dependent and they desired to obtain D_H^* . They approached the problem from the opposite viewpoint however, by assuming that the experimental concentration profiles in the membranes are known and from these they determined the non-ideality and D_H^* . For diffusion of H through membranes the concentration profiles are generally unknown but the non-ideality as a function of c is known. They assumed that the non-ideality is of the form $(1 + f(c))$ which differs from the usual form for metal-H systems [1]. These workers give an expression for obtaining D_H^* from $D_H(c)$ which is generally not for real metal-hydrogen systems.

For steady state H permeation through a plate membrane, there will be a spectrum of thermodynamic factors affecting $D_H(c)$ from the different concentrations within the membrane, i.e., $D_H^* \cdot f(r_i) \cdot r_i / r_{up}$ where $f(r_i)$ is the non-ideality at r_i . For the ideal case, $f(r_i)=1$ and therefore $f(r_i) \cdot r_i = r_{up}$ and $D_H = D_H^*$.

In the limit, the summation can be written as an integral

$$D_H = D_H^* \left(\int_0^{r_{up}} f(r) dr \right) / r_{up} \quad (7)$$

where r_{up} is the upstream H-to-metal ratio which is known from the isotherm and the upstream p_{H_2} .

Application of the Equation relating D_H to D_H^*

Equation (7) will be applied for steady-state H permeation through a Pd_{0.81}Ag_{0.19} alloy membrane at 423 K with $p_{up}=20.3$ kPa and $p_d=0$. This alloy does not have a two phase region at this temperature but its non-ideality is significant. It has been found that the steady-state is established quickly in these membranes.

Figure 1 shows an experimental isotherm for the Pd_{0.81}Ag_{0.19} alloy plotted as $\ln p^{1/2}$ against $\ln r$ (423 K). The slopes of this isotherm, $(\bullet \ln p^{1/2} / \bullet \ln r)_{(T,r)}$, give $f(r)$ as a function of r . The ideal slope of 1.0 is shown by the dashed line. The slopes, $f(r)$, have been plotted as a function of r in Figure 2 to $r_{up}=0.148$ which corresponds to $p_{up}=20.3$ kPa. D_H^* can be calculated for this alloy from equation (7).

From the experimentally measured D_H (423 K, $p_{up}=20.3$ kPa) of 2.73×10^{-6} cm²/s and from the isotherm at 20.3 kPa, $r_{up}=0.148$, we obtain from equation (7) $D_H^*=5.11 \times 10^{-6}$ cm²/s. This is a reasonable value judging from the literature. The smaller area under the non-ideal relation in Figure 2 as compared to the ideal area ($=r_{up}$) means that D_H is smaller than D_H^* .

For a Pd_{0.77}Ag_{0.23} alloy membrane, D_H values were determined at 473 K and at H₂ pressures of 20.3 kPa and 77.3 kPa. The corresponding D_H were 6.65×10^{-6} and 6.09×10^{-6} cm²/s, respectively. If these are converted to D_H^* using equation (7) and the known $f(r)$, we obtain 8.07×10^{-6} and 8.12×10^{-6} cm²/s, respectively, which are nearly the same as compared to the two experimental D_H values. The deviations from non-ideality are greater for the determination at 77.3 kPa, as expected and, as for the Pd_{0.81}Ag_{0.19} alloy, $D_H^* > D_H$.

Non-ideal H Concentration Profile in Pd-based Membranes

It is of interest to determine the concentration profile through a membrane under conditions where r_{up} is large and $r_d=0$ and the temperature is moderate so that non-ideality is significant. A procedure can be carried out to determine the profiles using equation 7. The equation for steady-state diffusion through a plate is

$$J = -(\bullet / \bullet x)(D_H \bullet c / \bullet x) = 0. \quad (8)$$

Upon integration of equation (8) we obtain

$$-D_H(\bullet c / \bullet x) = -D_H^* f(r) (\bullet c / \bullet x) = \mathbf{A} \quad (9)$$

where \mathbf{A} is a constant for a membrane at a given p_{up} and temperature. Integration of equation (9) gives

$$D_H^* \bullet_o^r f(r) dr = \mathbf{A}x + \mathbf{a}, \quad (10)$$

where \mathbf{a} is another constant. The boundary conditions are: at $x=0$, $r=r_{up}$ and at $x=d$, $r=0$ where x varies between 0 and d , the membrane thickness. These can be employed to determine \mathbf{A} and \mathbf{a} from equation 10, giving $\mathbf{a} = D_H^* F(r_{up})$ and $\mathbf{A} = (D_H^*/d)F(r_{up})$ where $F(r) = \bullet_o^r f(r)dr$. With these substitutions, equation (10) then gives

$$x / d = [F(r_{up}) - F(r)] / F(r_{up}) \quad (11)$$

or

$$F(r) = F(r_{up}) (1 - x/d). \quad (12)$$

$F(r_{up})$ can be obtained from the integration of

$$j_o^{rup} (d \ln p^{1/2} / d \ln r) dr. \quad (13)$$

$F(r)$ can be determined for each (x/d) from a plot of $f(r)$ against r for a given membrane and p_{up} .

Concentration Profile for the Pd_{0.77}Ag_{0.23} Alloy Membrane at $p_{up}=20.3$ kPa ($x=0$) and $p_{down}=0$ ($x=d$) (423 K)

The concentration profile, $r-(x/d)$, is obtained from equation (11). The area under the curve in Figure 2 for a given r corresponds to $F(r)$ and from these $F(r)$, the corresponding (x/d) is obtained from equation (11). The (x/d) values obtained in this way are then plotted as a function of r to give the steady-state concentration profile for the Pd_{0.81}Ag_{0.19} alloy membrane for $p_{up}=20.3$ kPa and 423 K (Fig. 3).

In Figure 3 it can be seen that the non-ideal H concentration at a given (x/d) is smaller for this Pd_{0.81}Ag_{0.19} alloy than for the ideal case given by the linear decrease of r between $(x/d)=0$ and 1.0 as shown. If the non-ideality is in the opposite direction, then the flux would be greater than the ideal flux which is the case for higher Ag concentration alloys.

In the steady-state, the flux is constant across the membrane but it is smaller (Fig 3) for this non-ideal situation than for the ideal case. Constant flux requires that the product $D_H^* f(r)(dr/dx)$ is constant across the membrane and, since D_H^* is a constant, the other two quantities must compensate each other. From Figure 3 it can be seen that when $(x/d) \sim 1.0$, (dr/dx) is small but $f(r)$ is large, i.e., ~ 1.0 , whereas at $(x/d) \sim 0$, (dr/dx) is large but $f(r)$ is small so that their product is constant and equal to the value at $(x/d) \sim 1.0$. If the product is examined over the whole range of (x/d) values in Figure 3, it is found to be constant within the range of error.

Why are the H concentrations smaller for the non-ideal Pd_{0.81}Ag_{0.19} alloy as compared to the ideal case? From equation (12) it can be seen that if $F(r_{up})$ is smaller than the ideal value at r_{up} for a given (x/d) , $F(r)$ will also be smaller and therefore r is smaller a given (x/d) than its ideal value.

An Approximation for ($j_o^{rup} f(r) dr$)

An approximation for $(j_o^{rup} f(r) dr)$ is to employ $(j_o^{rid,up} f(r) dr)$ with $f(r) = 1.0$, i.e., from p_{up} , the corresponding r is determined for the system as though it were behaving ideally. The results from this approximation are not exact but much better than not correcting the D_H values for non-ideality. For the Pd_{0.81}Ag_{0.19} alloy discussed earlier, the approximate correction give 6.52×10^{-6} cm²/s as

compared to the accurately corrected value of $5.54 \times 10^{-6} \text{ cm}^2/\text{s}$ and the experimental value of $2.96 \times 10^{-6} \text{ cm}^2/\text{s}$.

Conclusions

Under the commonly employed experimental conditions of a significant upstream concentration of H and $c_H \sim 0$ downstream, expressions are given for obtaining the concentration-independent D_H^* from the concentration dependent D_H employing the known non-ideality. A procedure is given for determining the concentration profile for a given upstream concentration for an alloy where the non-ideality is known as a function of H concentration. For the $\text{Pd}_{0.81}\text{Ag}_{0.19}$ alloy (423 K) the non-ideality, $f(r) < 1$ decreases the flux but for alloys where the non-ideality is in the opposite direction, $f(r) > 1$, the flux will be greater which would be an advantage for the experimental purification of H_2 .

Acknowledgement

This work was supported by Westinghouse Savannah River Company under U.S. Department of Energy Contract Number DE-AC09-96SR185000.

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Figure Captions

Fig. 1 Isotherm plotted as $\ln(p_{\text{H}_2})^{1/2}$ as a function of $\ln r$ for the $\text{Pd}_{0.81}\text{Ag}_{0.19}$ alloy (423 K) and the ideal behavior..

Fig. 2 Plot of the thermodynamic factor, $f(r) = \bullet \ln p^{1/2} / \bullet \ln r$ as a function of r for the $\text{Pd}_{0.81}\text{Ag}_{0.19}$ alloy (423 K) for $p_{\text{up}} = 20.3 \text{ kPa}$.

Fig. 3 Plot of $r (=H/M)$ in the membrane as a function of (x/d) for the $\text{Pd}_{0.81}\text{Ag}_{0.19}$ alloy (423 K) for $p_{\text{up}} = 20.3 \text{ kPa}$. \bullet , calculated values; solid line, ideal values.

Figure 1.

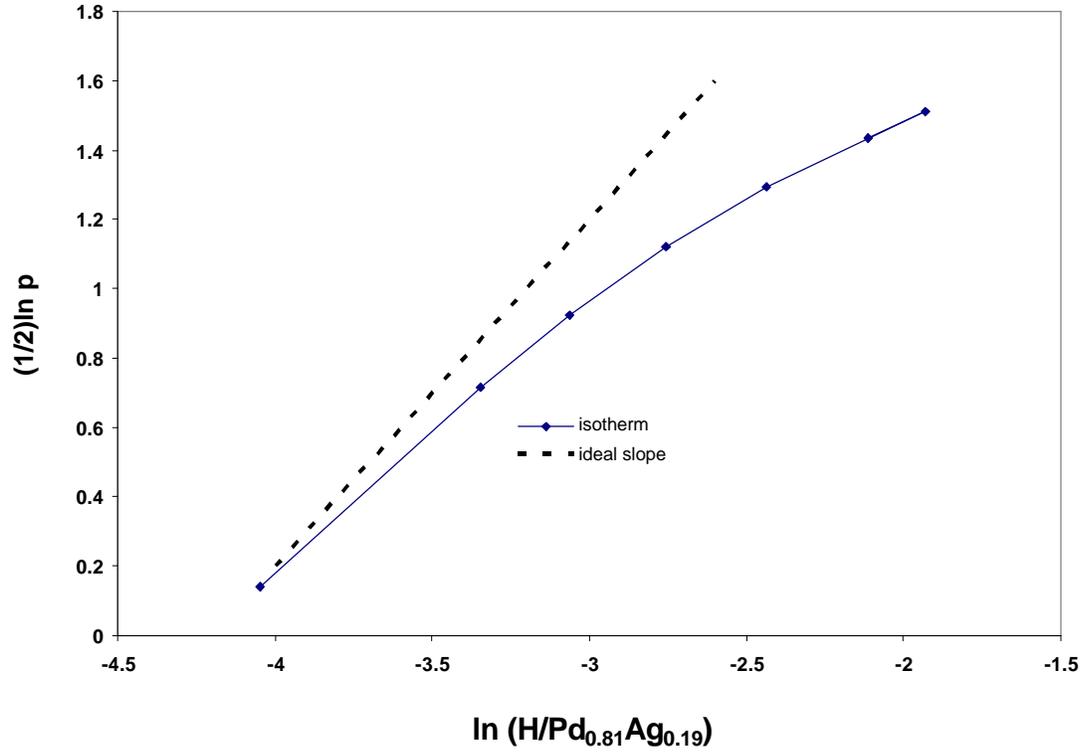


Figure 2.

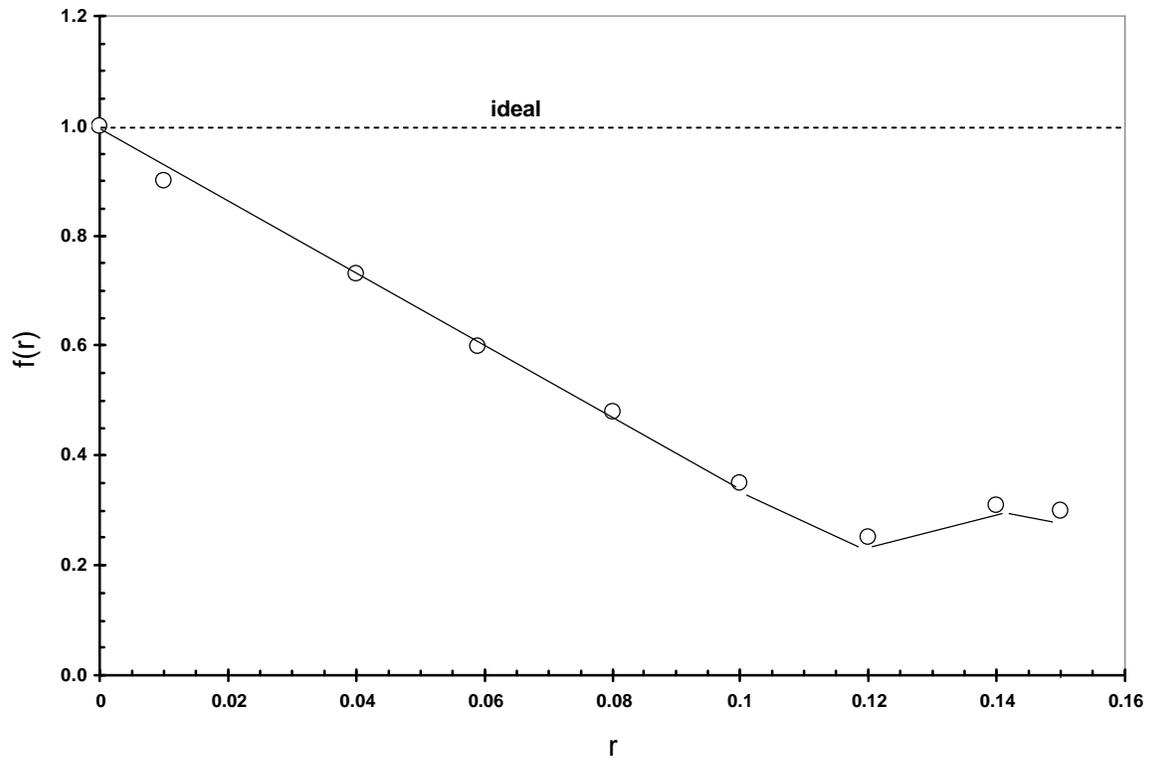


Figure 3.

