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Abstract

Hydrogen diffusion constants decrease with increase of atom fraction Y, X_Y , for the Pd–Y alloys investigated here, however, the H permeabilities increase because the H_2 solubility increase is greater than the diffusion constant decrease. D_H values have been measured for some of the Pd–Y alloys over a large range of H contents and for the $Pd_{0.94}Y_{0.06}$ alloy there is a minimum at $r=(H/metal)$, mol ratio, ≈ 0.20 (453 K) due to non-ideality from the thermodynamic factor. The effect of CO on the permeation of H through Pd–Y membranes has been determined and compared to effect of CO on the permeability of a $Pd_{0.77}Ag_{0.23}$ alloy. The poisoning effect of CO is consistently greater for the un-oxidized $Pd_{0.77}Ag_{0.23}$ alloy membranes than for the internally oxidized Pd–Y alloy membranes, however, the differences are small.

Introduction

Pd–*Y* alloy membranes are of interest for H purification because, as first shown by Harris and coworkers [1, 2, 3, 4], the H permeabilities are greater in some of these alloys than in the alloy membrane commonly used for H₂ purification, Pd_{0.77}Ag_{0.23}. *Pd*–*Y* alloys are complicated by a disorder-order transition, *i.e.*, the formation of Pd₇Y [3, 4, 5, 6], which influences the solubility and diffusion of H. In this research ordering will be largely avoided by employing low atom fraction Y alloys, X_Y ≤ 0.06, and by heating the alloy membranes to an elevated temperature and then cooling rapidly. A Pd_{0.905}Y_{0.095} membrane will also be employed which is also believed to be disordered after cooling from an elevated temperature in H₂.

Employing an electrochemical technique, both Sakamoto *et al* [7] and Ishikawa and McLellan [8] determined diffusion constants for H in *Pd*–*Y* alloys from 280(285) to 333(322) K where the parenthesis refers to the temperature range employed by the latter authors. The results of these two investigations disagree. The diffusion constants were found to increase with X_Y by Sakamoto *et al* [7] for small X_Y and then decrease for greater values whereas they decreased sharply with X_Y according to Ishikawa and McLellan [8]. The activation energy for diffusion, E_D, determined by Ishikawa and McLellan [8] increased from 21.6 (Pd) to 39.0 kJ/mol H (Pd_{97.4}Y_{0.026}) while D_H^o increased from 1.1 × 10^{−3}/cm²/s(Pd) to 1.1/cm²/s (Pd_{97.4}Y_{0.026}). Sakamoto *et al* [7] found that E_D decreased with X_Y while D_H^o did not change appreciably, *e.g.*, from 1.05 × 10^{−3}/cm²/s(Pd) to 1.08 × 10^{−3}/cm²/s (Pd₉₈Y_{0.02}), however, D_H^o decreased at larger X_Y. These parameters appear in the familiar Arrhenius' equation for diffusion

$$D_H = D_H^o \exp^{-E_D/RT}. \quad (1)$$

Also employing an electrochemical technique (293 K), Yoshinari *et al* [9] found that D_H increased with X_Y in agreement with Sakamoto *et al* [7] although the increase was reported to be much greater in the study of Yoshinari *et al*. In a very dilute region $r=10^{-4}$ to $\approx 3 \times 10^{-3}$ where $r=H/(Pd_{1-x}Y_x)$, mol ratio, Yoshinari *et al* found that D_H decreased with r . Activation energies for diffusion were not determined [9].

In the work of Hughes and Harris [1] an Arrhenius plot is given for D_H for a Pd_{0.92}Y_{0.08} alloy and, if a straight line is drawn through the data, the slope and intercept give: E_D=28.7 kJ/mol H and D_H^o=6.0 × 10^{−3}cm²/s, respectively. Since these data were determined with a p_{H₂} differential of 0.34 MPa across the membrane, the results will be influenced by different degrees of non-ideality at the different temperatures. It has been shown earlier, *e.g.*, [10], that Fick's diffusion constant, D_H, is related to the concentration-independent diffusion

constant, D_H^* , by eq (2),

$$D_H = D_H^* f(r) \quad (2)$$

where the thermodynamic factor, $f(r)$, is defined as

$$f(r) = \left(\partial \ln p_{H_2}^{1/2} / \partial \ln r \right)_T. \quad (3)$$

Wicke and coworkers demonstrated that $f(r)$ affects the H diffusion parameters in Pd and its alloys at moderate temperatures [10, 11, 12] and recently, non-ideality has been shown to be a factor even at moderately high temperatures, 423 to 523 K [13, 14].

Salomons [16] determined D_H values for a $Pd_{0.91}Y_{0.09}$ alloy at elevated temperatures from relaxation times following application of sudden p_{H_2} changes to a H-containing $Pd_{0.91}Y_{0.09}$ alloy. The diffusion constants were found to increase with r . Salomons appears to be the first investigator who examined in some detail the r -dependence of E_D ; he investigated the $Pd_{0.91}Y_{0.09}$ and $Pd_{0.8}Cu_{0.2}$ alloys. E_D decreases with r for the $Pd_{0.91}Y_{0.09}$ alloy, which is reasonable in view of the results below but for the $Pd_{0.8}Cu_{0.2}$ alloy there was no trend of E_D with r .

Later Stonadge *et al* [17] carried out a similar investigation with a disordered $Pd_{0.90}Y_{0.10}$ alloy using the same technique as Salomons [16]. They also employed their experimental diffusion constants, D_H , (403-540 K) to obtain the concentration-independent diffusion constant from eq (2). The results gave quite constant D_H^* values for the higher temperatures but, at the lower ones, D_H^* increased with r . It seems that their lower temperature data may be questionable, *e.g.*, D_H increases at 463 K by a factor of $\approx 30\times$ as r increases from 0.05 to 0.17 and the Einstein diffusion constant, D_H^* , obtained from eq (2) was not constant. Activation energies for diffusion, E_D , were not determined in their study but an attempt to estimate them from their D_H values at various temperatures [17] gives anomalously large values of E_D at small r compared to the 28 kJ/mol H ($r=0.05$) found by Salomons [16].

The trends of the diffusion parameters with X_Y in the studies by Sakamoto *et al* [7], Yoshinari *et al* [9] and Ishikawa and McLellan [8] differ and, hopefully, the correct trends will be established in this research. D_H will be determined as a function of r for several low Y content alloys, from $X_Y=0.03$ to 0.060. In addition, some data will be measured for a $Pd_{0.905}Y_{0.095}$ membrane.

One purpose of this research will be to determine how the non-ideality of the dissolved H affects the diffusion parameters of disordered *Pd*-Y alloys. The effect of the H concentration on D_H is an important aspect of the investigation of the role of non-ideality of solutes on diffusion in solid phases and such an investigation can best be carried out with H in Pd and its alloys because of the

relatively easy determination of $f(r)$ (eq 3) and the large range of H concentrations available at moderate p_{H_2} in Pd and some of its alloys. The dependence of E_D and D_H on r will be determined here for some fcc, disordered Pd-Y alloys. It should also be emphasized that diffusion through Pd-Y membranes is of some practical interest for H_2 purification. It should also be noted that the $Pd_{0.905}Y_{0.095}$ alloy is above its critical temperature at 300 K so that there is no possibility of hydride formation at $T \geq 300$ K which can lead to embrittlement and membrane cracking.

It has been shown that some Pd alloys, *e.g.*, Pd-Al, are more resistant to the gaseous poison CO after partial internal oxidation [18]. It will be determined here if the internally oxidized Pd-Y alloy membranes are more resistant to CO than a $Pd_{0.77}Ag_{0.23}$ alloy membrane.

Experimental

Alloys were prepared by arc-melting the pure components under argon and then annealing the resulting buttons for 72 h at 1133 K. The arc-melted buttons were rolled into foils of the appropriate thickness for the diffusion membranes, *i.e.*, 100-250 μm . Since the lower content Y alloys, $X_Y \leq 0.052$, do not order significantly, they can be considered to be disordered. There is evidence for some partial ordering in the diffusion behavior of the $Pd_{0.94}Y_{0.06}$ alloy and consequently it was cooled in 0.2 MPa H_2 from above its order/disorder temperature which Harris *et al* [2] have shown maintains the disordered state. The $Pd_{0.905}Y_{0.095}$ alloy is known to order; the foils were therefore heated to an elevated temperature in H_2 and cooled in H_2 and evidence that this treatment gives the disordered state has been given elsewhere [19].

Diffusion parameters were determined from the H fluxes, J , through planar alloy membranes 1.77 cm^2 in area with p_{up} at a desired value and $p_{down}=0$. Fick's diffusion constants are obtained from

$$J = \frac{D_H c_{up}}{d} \quad (4)$$

where c_{up} is the upstream H concentration, mol H/ cm^3 , d is the membrane thickness and D_H is the measured diffusion constant for the specific c_{up} employed. Values of c_{up} can be obtained from the measured p_{H_2} vs c_H isotherms. In the present paper instead of c_H , the H concentrations will frequently be expressed as $r=(H\text{-to-metal})$, mol ratio and $c_H=r\rho/M$, where ρ is the density, and M the molar mass of the H-containing Pd alloy. If D_H is independent of H concentration, eq (4) will give the true concentration-independent diffusion

constant, D_{H}^* , but if non-ideality, which depends on c_{H} , is a factor, the varying H concentrations in the membrane must be allowed for [13, 20, 14].

Recently it has been found that partial internal oxidation of some Pd-based alloys such as *Pd*-Al [21] renders membranes more resistant to the gaseous poison CO. In the present case, however, even a partial internal oxidation of, *e.g.*, 5% decreased the permeability significantly because the alloys have greater permeabilities than Pd. Internal oxidation was employed to demonstrate that permeation in the present alloys is bulk-diffusion controlled.

Some experiments were also carried out to determine whether partially internally oxidized membranes were more resistant to CO poisoning than $\text{Pd}_{0.77}\text{Ag}_{0.23}$ membranes. The membranes were pre-exposed to CO(g) by introducing them to a given p_{CO} in the small volume, 3 cm^3 , adjacent to the membrane. A valve connecting this small volume and the adjoining large volume, either 600 or 1000 cm^3 , was then closed and the larger volume was evacuated to remove the CO and then H_2 was introduced into the larger volume. When the H_2 was at the desired p_{H_2} , the valve connecting the larger and smaller volumes was opened to allow permeation to proceed.

Results and Discussion

Demonstration that Bulk Diffusion is the Slow Step using H Permeabilities through Partially Internally Oxidized *Pd*-Y Alloys.

A novel and convenient way to verify that bulk diffusion is the slow step for H permeation through a *Pd*-M membrane, where M is more oxidizable than Pd, is to measure fluxes as a function of the extent of internal oxidation of an alloy membrane at a given p_{up} . Figure 1 shows plots of $1/J$ against % internal oxidation for a $\text{Pd}_{0.97}\text{Y}_{0.03}$ membrane at 473 K and at 523 K . The linearity of the plots supports the assumption that bulk diffusion is the slow step. The equation describing the flux was derived earlier [21] as

$$J^{-1} = (J_{\text{Pd}}^{-1} - J_{\text{alloy}}^{-1}) f_{\text{IO}} + J_{\text{alloy}}^{-1} \quad (5)$$

where f_{IO} is the fraction of internal oxidation, J_{Pd}^{-1} and J_{alloy}^{-1} are the fluxes of Pd and the alloy under the same conditions of p_{up} , membrane thickness and temperature. If the slow step were not bulk diffusion, this equation would not

Table 1: Permeability/ $10^{-8}(\text{mol H/s})\cdot\text{cm}/\text{cm}^2$

$p_{\text{up}}=50.6 \text{ kPa}$	Permeability		
alloy	523 K	473 K	423 K
$\text{Pd}_{0.97}\text{Y}_{0.03}$	6.94	5.88	5.32
$\text{Pd}_{0.956}\text{Y}_{0.044}$	9.75	8.85	8.55
$\text{Pd}_{0.948}\text{Y}_{0.052}$	11.60	10.90	11.07
$\text{Pd}_{0.94}\text{Y}_{0.06}$	13.60	12.77	14.49
$\text{Pd}_{0.905}\text{Y}_{0.095}$	29.1	27.0	21.2
$\text{Pd}_{0.77}\text{Ag}_{0.23}$	8.80	9.47	10.49
$p_{\text{up}}=20.3 \text{ kPa}$	Permeability		
alloy	523 K	473 K	423 K
$\text{Pd}_{0.97}\text{Y}_{0.03}$	4.20	3.41	2.81
$\text{Pd}_{0.956}\text{Y}_{0.044}$	5.63	5.05	4.55
$\text{Pd}_{0.948}\text{Y}_{0.052}$	6.83	6.19	5.34
$\text{Pd}_{0.94}\text{Y}_{0.06}$	8.03	7.22	7.79
$\text{Pd}_{0.905}\text{Y}_{0.095}$	16.7	16.5	14.3
$\text{Pd}_{0.77}\text{Ag}_{0.23}$	5.58	5.31	5.97

be obeyed. Recall that the result of complete internal oxidation is a Pd/oxide composite [22], *i.e.*, in this case, Pd/yttria, and the oxide precipitates will not play a role in the H diffusion after a very small amount of trapping at the interfaces takes place [23].

A similar plot is shown in Figure 2 for the $\text{Pd}_{0.94}\text{Y}_{0.06}$ alloy at 473 K and again the data seem to obey equation (5) although only relatively small amounts of % internal oxidation were employed for both alloys.

H Permeabilities in Pd -Y Alloys

H permeabilities of Pd -Y alloy membranes (un-oxidized) are shown in Table 1 at several temperatures for $p_{up}=50.6$ kPa and 20.3 kPa. They are compared to the permeabilities of a $Pd_{0.77}Ag_{0.23}$ alloy membrane under comparable conditions. As noted above, the permeabilities of partially internally oxidized Pd -Y alloys are smaller than those of the same un-oxidized alloys and therefore the internally oxidized alloys are not given in the Table. The permeability is defined here as $P = D_H c_{up}$ since $c_{down}=0$.

The $Pd_{0.905}Y_{0.095}$ alloy membrane has the greatest permeability at all of the temperatures investigated and at both p_{up} values as might be expected since this is close to the composition suggested as a membrane for hydrogen purification, *e.g.*, [4]. The permeability of the $Pd_{0.77}Ag_{0.23}$ alloy is its greatest at 423 K than at higher temperatures because, although D_H is smaller, the H_2 solubility at 423 K is significantly greater than at the higher temperatures. For the Pd -Y alloys there is not much difference in permeabilities at the three temperatures because, while D_H increases with temperature, c_{up} decreases. The permeability of the $Pd_{0.94}Y_{0.06}$ alloy is smaller at 473 K than at 423 K or 523 K because the solubility increases significantly at 423 K and D_H increases significantly at 523 K whereas neither factor increases significantly at 473 K.

The permeabilities of the $Pd_{0.905}Y_{0.095}$ alloy membrane appear to be anomalously large, however, this can be explained by its relatively large hydrogen solubility together with the increase in D_H with r which is due to non-ideality of the H solution at these relatively high values of p_{up} . These results confirm the large H permeabilities of Pd -Y alloys as reported earlier by Harris and co-workers [1, 2, 3, 4]. Pd -Y alloy membranes have the advantage compared to the $Pd_{0.77}Ag_{0.23}$ alloy membrane that not as much metal solute is needed, *e.g.*, 9 at.%Y versus 23 at. % Ag, which may reduce fabrication problems resulting from solid solution hardening.

It is common practice to employ Arrhenius-like plots of permeabilities at constant p_{up} , *e.g.*, for Pd-H [24] and for other metallic membranes, to obtain so-called permeability activation energies. It has been shown recently [25] for the $Pd_{0.77}Ag_{0.23}$ and $Pd_{0.94}Y_{0.06}$ alloys that such plots can be nearly independent of temperature. For example, for the $Pd_{0.77}Ag_{0.23}$ alloy, $\ln P$ is almost invariant with $1/T$ in the investigated p_{up} range from 16 to 81 kPa (423–523 K) and for the $Pd_{0.94}Y_{0.06}$ alloy, plots of $\ln P$ against $1/T$ exhibit minima. The slopes of such psuedo-Arrhenius plots of permeability should *not* be referred to as activation energies because they are composed of kinetic and equilibrium terms, *e.g.*, at infinite dilution this psuedo-activation energy is given as $E_{perm}=E_D^* + \Delta H_H^\circ$ where ΔH_H° is a thermodynamic term, *i.e.*, the relative partial enthalpy of solution for one-half mol of $H_2(g)$ in the solid phase at infinite dilution of

H.

A plot of $\ln P$ against $1/T$ for a $\text{Pd}_{0.956}\text{Y}_{0.044}$ alloy membrane is shown in Figure 3 where there are minima in the plots at both 101.3 kPa and at 50.3 kPa and consequently, the slopes are positive at lower temperatures. That is, the apparent activation energies would be negative, which is unlikely and reinforces the view that the slopes of such plots should not be regarded as activation energies.

Concentration-Independent Diffusion Parameters, D_H^*

E_D^* and $D_H^{\circ,*}$

Diffusion Equations for $p_{\text{up}} \gg p_{\text{down}}=0$.

Concentration-dependent diffusion constants, D_H , have been derived from the permeabilities P using eq (4) and they have been determined at a series of temperatures and p_{up} for each alloy. D_H is found to depend on r as it does for pure Pd [10, 11, 13, 16] and for Pd alloys such as Pd-Ag [11, 14]. The r -dependence is due to non-ideality arising from the thermodynamic factor, eqs (2) and (3). Recently the dependence of E_D and D_H° on r have also been determined experimentally for several Pd-Ag alloy membranes [14]. Earlier studies of the dependence of E_D on r were carried out by Salomons [16] for Pd-H and the two alloy-H systems: $\text{Pd}_{0.91}\text{Y}_{0.09}$ and $\text{Pd}_{0.80}\text{Cu}_{0.20}$. The dependence of these diffusion parameters on H concentration is important for the understanding of diffusion and information gained from Pd-H and its alloy-H systems may be relevant for other solutes and solvents where the measurement of the effects of non-ideality may be experimentally more difficult than for H in Pd and its alloys.

If Fick's diffusion constant is concentration-independent, *i.e.*, $D_H=D_H^*$, then D_H^* can be obtained directly from equation (4), however, for the present experimental situation where $p_{\text{up}} \gg p_{\text{down}}$, the D_H values measured using equation (4) are generally affected by non-ideality, the degree of which is a function of the penetration distance of H through the membrane since $f(r)$ depends on r . A common experimental situation is for $p_{\text{up}} \gg p_{\text{down}} = 0$ and, for H_2 purification, although $p_{\text{down}} \neq 0$, a large p_{H_2} gradient is desirable.

Equation (6), which has been given elsewhere [13], provides a method to determine D_H^* from D_H under conditions where $p_{\text{up}} \gg p_{\text{down}}=0$ and where non-ideality of the H solution is a factor

$$D_H = D_H^* \int_0^{r_{up}} f(r) dr / r_{up} = D_H^* F(r) / r_{up}. \quad (6)$$

D_H is the experimental diffusion coefficient determined from equation (4) for a given p_{up} with $p_{down}=0$.

It has been shown before [13, 20] that at small r , the insertion of the expression for $\ln p^{1/2}$ from mean field theory into equations (2) and (3) gives

$$RT \ln D_H = RT \ln D_H^* + RT \ln \left(\frac{g_1 r_{up}}{2RT} - \frac{\ln(1 - r_{up})}{r_{up}} \right) \quad (7)$$

which, at small r , reduces to

$$RT \ln D_H \approx RT \ln D_H^* + g_1 r_{up} / 2. \quad (8)$$

where g_1 is the first order term of a polynomial expansion in r of the excess chemical potential of H. According to equation (8), at small r , a plot of $RT \ln D_H$ against r_{up} will be linear with a slope of $(g_1/2)$.

Differentiation of the $\ln D_H$ term in equation (8) with respect to $(1/T)$ gives [13]

$$E_D = E_D^* + \frac{h_1 r_{up}}{2 \ln(1 - r_{up}) / r_{up} - g_1 r_{up} / RT} \quad (9)$$

where $g_1 = h_1 - Ts_1$ and g_1 . At small r_{up} , equation (9) reduces to

$$E_D \approx E_D^* - \frac{h_1 r_{up}}{2}. \quad (10)$$

It is important to emphasize that E_D in eq (10) refers to the condition of $p_{down}=0$. The values of h_1 are negative for alloys with $X_Y \leq 0.06$ and therefore according to eq (10), E_D should increase with r for these alloys.

Values of g_1 can be obtained from plots of $RT \ln p^{1/2}(1 - r)/r$ against r (eq (8)). h_1 can be determined from equilibrium p_{H_2} - r data, *e.g.*, from the slopes of plots of g_1/T against $1/T$ or from the slopes of ΔH_H against r . Those from the former method are not as accurate as the g_1 values because they are obtained from slopes of g_1/T against $(1/T)$ and small errors in g_1 cause significant error in h_1 . h_1 from the slope of ΔH_H against r is also not very accurate because of the small range of r over which ΔH_H is generally measured. Diffusion data, eq 10 can also be employed to determine h_1 .

Dependence of $RT \ln D_H$ on r at Small r

The variation of $RT \ln D_H$ with r has been examined for the Pd -Y alloys at relatively low H concentrations as shown in Figure 4. The third column of Table

2 gives g_1 values determined from slopes of $RT \ln D_H$ against r_{up} (eq (8)). It can be seen that the g_1 values determined from the diffusion- and equilibrium-based equations are comparable except for the $X_Y=0.052$ alloy where equation (8) gives a result which is too negative. It is noteworthy to be able to determine thermodynamic values such as g_1 from both diffusion and equilibrium data.

Table 2: Values of g_1 and h_1 at small r (423-523 K)

X_Y	g_1^* (473 K)	g_1^{**}	h_1^{***}	h_1^{****}
0	-40.0	-34 (473 K, [13])	-82.5 ([26])	—
3	-33.5	-33.8	-56.5	-65
4.4	-31.9	-28.2	-50.2	-45.8
5.2	-28.0	-20.1	-39.4	—39.4
6	-20.9	-16.5	-21.2	-19.8

* determined from equilibrium data from plots of $RT \ln p^{1/2}(1-r)/r$, **, determined from diffusion data (eq (8)), $RT \ln D_H-r$ plots, ***, from eq (10), ****, from plots of ΔH_H against r .

Yoshinari *et al* [9] report an increase of D_H with r in the very dilute H solution in Pd and $Pd-Y$ alloys and the D_H vs r slopes became less positive with X_Y as found here, however, the numerically derived values of g_1 from their data, using eq (8), appear to be unlikely. They did not attempt to analyze the increases of D_H with r . Salomons [16] finds that D_H increases with r for the $Pd_{0.91}Y_{0.09}$ alloy by about a factor of 2 as the H content increases from $r=0.05$ to 0.20 (473 K). Stonadge *et al* [17] report an increase of D_H for the $Pd_{0.9}Y_{0.1}$ alloy at 463 K of "over two orders of magnitude" [17] as r — *increases* from $r=0.05$ to 0.17. It seems from the isotherms for the present Pd-Y alloys [19] that D_H should increase with r but two orders of magnitude seems too large.

The h_1 values obtained from slopes of ΔH_H against r , *i.e.*, $(d\Delta H_H/dr) = h_1$, agree reasonably well with those using equation (10) from the present diffusion data (Table 2). The values of h_1 are more negative than g_1 as was also found for Pd-H [26].

The concentration-independent diffusion parameters can be determined directly from eq (6) with $f(r)$ obtained from equilibrium isotherms and integration of $f(r)$ from $r=0$ to r_{up} as described elsewhere for H diffusion in Pd-Ag alloys [13]. A method applicable at small r , which avoids the integration, is to

use the approximation that $(r_{\text{up}}/2)=\bar{r}$ where \bar{r} is an average r to be used in equation (2), *i.e.*,

$$D_{\text{H}} = D_{\text{H}}^* f(\bar{r}) \quad (11)$$

where $f(\bar{r})$ is the thermodynamic factor for \bar{r} . D_{H}^* values can also be obtained from extrapolation of $RT \ln D_{\text{H}}$ against r .

Table 3 shows some D_{H}^* values where there is seen to be little difference between D_{H}^* for Pd and the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy. The values for the $\text{Pd}_{0.956}\text{Y}_{0.044}$ and $\text{Pd}_{0.948}\text{Y}_{0.052}$ alloys are similar which is probably due to some experimental uncertainty. D_{H}^* values from eq (6) are considered more accurate than the extrapolation procedure because often there are little data available at small r . Generally from Table 3 it can be concluded that there is a steady decrease of D_{H}^* with X_{Y} . The results of Yoshinari *et al* [9] where D_{H}^* increases significantly with X_{Y} appear unlikely since there are few disordered fcc Pd-rich alloys where D_{H}^* increases significantly with X_{M} . Small increases at low X_{M} followed by decreases have been reported for Pd–Au alloys [25] and Pd–Ag alloys [12]. Sakamoto *et al* [7] find a small increase of D_{H} with X_{Y} followed by a decrease whereas Ishikawa *et al* [8] find a sharp initial decrease which seems unlikely.

Results using the approximation that equation (2) can be employed with $\bar{r}=r_{\text{up}}/2$ are not shown, however, at, *e.g.*, 473 K for the $\text{Pd}_{0.94}\text{Y}_{0.06}$ alloy at $r_{\text{up}}=0.08$, $D_{\text{H}}^*=8.7 \times 10^{-6} \text{cm}^2/\text{s}$ which is slightly smaller than that determined by the other methods. For the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy at 473 K and $r_{\text{up}}=0.08$, $D_{\text{H}}^*=12.3 \times 10^{-6} \text{cm}^2/\text{s}$ using $r=r_{\text{up}}/2$ which is also slightly smaller than the value in the Table.

Figure 5 shows Arrhenius' plots of D_{H}^* obtained using an average of the values in Table 3. It can be seen that the slopes and intercepts, E_{D}^* , $D_{\text{H}}^{\circ,*}$, are nearly identical for Pd and for the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy despite the fact that the $\Delta H_{\text{H}}^{\circ}$ for H_2 absorption (423–523 K) the values differs significantly, *i.e.*, -8.2 and -14.3 kJ/mol H for Pd and the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy, respectively [19]. Table 4 shows E_{D}^* and $D_{\text{H}}^{\circ,*}$ values derived from this Figure and aside from the $X_{\text{Y}}=0.03$ alloy, they are seen to increase steadily with X_{Y} .

Although the trends in Table 4 are in the direction found by Ishikawa *et al* [8], as noted above, the present trend differs from theirs because there is negligible change of D_{H}^* and E_{D}^* up to $X_{\text{Y}} \approx 0.052$ and then there is a sharp fall-off whereas Ishikawa *et al* find a sharp increase of both E_{D} and D_{H}^* for the $X_{0.026}$ alloy.

Figure 6 shows a plot of E_{D} against r for the Pd–Y alloys with $X_{\text{Y}}=0.03$, 0.044, 0.052 and 0.06 where it can be seen that the slopes are positive indicating that h_1 is negative (eq 12). It is also apparent that the slopes decrease with X_{Y} . The extrapolated values at $r \rightarrow 0$ do not correspond exactly to those in

Table 3: $D_H^*/10^{-6}$ in units of cm^2/s Obtained by Two Different Methods.

X_Y	$D_H^*(423 \text{ K})$	$D_H^*(453 \text{ K})$	$D_H^*(473 \text{ K})$	$D_H^*(503 \text{ K})$	$D_H^*(523 \text{ K})$
0	6.3	9.9	12.9	18.5	23.0
0.03	6.3(6.2)	10.0(9.9)	12.8(12.9)	18.1(18.2)	22.3(22.2)
0.044	4.8(5.1)	8.3(8.7)	12.1(12.0)	14.7(16.2)	19.7(20.8)
0.052	4.8(4.9)	8.3(8.5)	11.0(11.4)	16.5(16.8)	20.7(21.3)
0.06	3.2(4.0)	5.4(7.7)	9.6(9.9)	15.7(16.7)	16.4(20.1)
0.095	(3.7)	-	(7.4)	-	(14.0)

The D_H^* values without parenthesis are from extrapolation of D_H to $r=0$; those with the parenthesis are from integration of eq (6).

Table 4 because the latter is based on average values of $D_H^{\circ,*}$, *i.e.*, those from eq (6) using several values of D_H and the corresponding $F(r)$.

$D_H^{\circ,*}$ can be derived from

$$\ln D_H^{\circ,*} = \ln D_H^* + E_D^*/RT \quad (12)$$

where $\ln D_H^*$ values employed for eq (12) are taken from the average values in Table 3 and E_D^* is determined from the Arrhenius' plots of the $\ln D_H^*$ values. The values of $D_H^{\circ,*}$ (Table 4) are all of the expected magnitude, *i.e.*, $\approx 10^{-3}$, except for the $\text{Pd}_{0.948}\text{Y}_{0.052}$ and the $\text{Pd}_{0.94}\text{Y}_{0.06}$ alloys. One determination of the diffusion parameters of the $\text{Pd}_{0.94}\text{Y}_{0.06}$ alloy membrane employed a membrane which had been palladized giving a very active surface and since these results were similar to those for the un-palladized membrane, the values for this alloy are believed to be correct (Table 4).

Diffusion Parameters over a Large Range of H Contents.

$\text{Pd}_{0.97}\text{Y}_{0.03}$

In this section plots of $RT \ln D_H$ against r , *e.g.*, Fig. 7, extend over a larger r range than those shown in Figure 4. D_H values were measured at 453 K for the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy up to $r_{\text{up}}=0.14$, ≈ 30 kPa. Surprisingly, the $RT \ln D_H$ against

Table 4: E_D^* and $D_H^{\circ,*}$ from Figure 7

X_Y	$E_D^*/\text{kJ/mol H}$	$D_H^{\circ,*}/10^{-3}\text{cm}^2/\text{s}$
0	23.9	5.6
0.03	23.4	4.0
0.044	25.4	6.6
0.052	26.9	9.8
0.06	28.9	14.5

the values in the Table are averages of those given in Table 732

r relation is nearly linear over this range. In order to convert the experimental D_H to D_H^* , the thermodynamic factor must be known as a function of r and this was derived from the isotherm (453 K) and is shown elsewhere [19]. On close examination of this Figure the $f(r)$ *vs* r relation appears to be very similar at all of the temperatures measured, 423-473 K, at the higher r range but shows differences in the lower range. For the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy the $f(r)$ *vs* r relationship [19] is also nearly linear up to $r=0.14$ which leads to a linear dependence of $RT \ln D_H$ with r . If a $f(r)$ - r plot is linear, then it follows that $\bar{r}=r_{\text{up}}/2$ can be employed in equation (2) rather than having to employ eq (8). Figure 7 shows that the $RT \ln D_H^*$ values calculated from $D_H(r)$ using eq (8) gives nearly constant values up to about $r \approx 0.10$ and the $F(r)=r_{\text{up}}/2$ also works reasonably well. For $r > \approx 0.10$ both methods give values which are lower than the expected one found at the lower r values. More constant values of D_H^* are obtained if D_H is corrected by the $F(r)$ value and if a blocking factor $(1-r)$ is included (Fig. 7).

$\text{Pd}_{0.948}\text{Y}_{0.052}$

D_H was measured for the $\text{Pd}_{0.948}\text{Y}_{0.052}$ alloy over a large range of r_{up} and

is shown for three temperatures in Figure 8. Nearly linear decreases of $\text{RTln } D_{\text{H}}$ with r are observed over a large range. The initial slopes become more negative with decreasing temperature since $|g_1|$ increases in magnitude with decrease of temperature. The linear regions are followed by minima (Fig. 8) which are not as pronounced as the temperature increases and they shift to lower r_{up} values. A minimum in the $\text{RTln } D_{\text{H}}$ *vs* r relation was also found for a $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloy [14] and earlier for the $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloy by Küssner [11] while Salomons [16] found a minimum for a $\text{Pd}_{0.80}\text{Cu}_{0.20}$ alloy at 473 K.

$\text{Pd}_{0.94}\text{Y}_{0.06}$

For this alloy, D_{H} values were measured up to $r_{\text{up}}=0.30$ at 473 K and the results are plotted in Figure 9. This alloy can be investigated to higher r than the lower X_{Y} alloys because its equilibrium p_{H_2} are lower. There is a minimum in the $\text{RTln } D_{\text{H}}$ *vs* r_{up} plot. The r value at the minimum is greater than the minimum in the $f(r)$ *vs* r plot [19].

If the D_{H} values in Fig. 9 are divided by $F(r)/r_{\text{up}}$, D_{H}^* values are obtained. The minimum in D_{H} is eliminated in the derived D_{H}^*-r relation but the values of D_{H}^* decrease somewhat with r especially at the larger values. If the $F(r)/r_{\text{up}}$ factor is divided by $(1-r)$, the D_{H}^* are more constant and correspond with the extrapolated value at $r=0$. The $(1-r)$ "blocking factor" has been employed by Bohmholdt and Wicke and co-workers [27] to account for blocking of interstices by H atoms. In this case D_{H}^* is significantly more constant improved by including this factor.

$\text{Pd}_{0.905}\text{Y}_{0.095}$

Figure 10 shows the variation of $\text{RT ln } D_{\text{H}}$ with r from about 0.058 to $r=0.24$ at three different temperatures for the disordered $\text{Pd}_{0.905}\text{Y}_{0.095}$ alloy membrane. Data at lower r are limited by the relatively low pressures at small values

r for this alloy. The agreement of D_H with the value reported by Salomons [16] is quite good (473 K), *i.e.*, the present data at $r_{up}=0.2$ ($\bar{r} = r_{up}/2$) are $9 \times 10^{-6} \text{cm}^2/\text{s}$ and the results of Salomon at $r=0.10$ are $8 \times 10^{-6} \text{cm}^2/\text{s}$. Conversion of D_H to D_H^* gives values of the latter which increase with r and it can be noted that Salomons [16] also found an increase of D_H^* with r after dividing D_H by the thermodynamic factor and blocking factor, *i.e.*, $D_H = D_H^* f(r)(1 - r)$.

The Variation of D_H° with r

The effect of H content on D_H° has not been the subject of much research. Flanagan and co-workers [13] found for Pd-H that D_H° increased from 5.83 to $7.12 \times 10^{-3} \text{cm}^2/\text{s}$ as the H content increased from $r=0.01$ to 0.03 at 423 K. Bohmholdt and Wicke [27] reported that D_H° increases from $3.65 \times 10^{-3} \text{cm}^2/\text{s}$ for the dilute phase to $5.7 \times 10^{-3} \text{cm}^2/\text{s}$ for the hydride phase for Pd-H at 293 K.

From the Arrhenius expression for D_H and eq (6) we obtain

$$\ln \left(\frac{D_H^\circ}{D_H^{\circ,*}} \right) = \left(\frac{E_D - E_D^*}{RT} \right) + \ln F(r) - \ln r_{up} \quad (13)$$

and according to the mean field model,

$$\frac{F(r)}{r_{up}} = -\ln(1 - r_{up})/r_{up} + g_1 r_{up}/2RT \quad (14)$$

If this result is inserted into eq (13), it gives

$$\ln D_H^\circ = \ln D_H^{\circ,*} - \Delta E_D/RT + \ln \left(\frac{g_1 r_{up}}{2RT} - \ln(1 - r_{up})/r_{up} \right) \quad (15)$$

where $\Delta E_D = E_D^* - E_D$. In the dilute range at 423 K for Pd-H, ΔE_D and g_1 are negative, however, the ΔE_D term dominates at $r_{up}=0.03$ predicting from eq (13) that $\ln D_H^\circ$ is greater than $\ln D_H^{\circ,*}$ as observed [13].

Under conditions where eq (2) can be employed, *i.e.*, when r is nearly constant as in electrochemical pulse methods, a simple expression for $\ln(D_H^\circ/D_H^{\circ,*})$

obtains. From the Arrhenius equation and eq (2), the following can be obtained

$$\ln D_H^\circ = \ln D_H^{\circ,*} - \Delta E_D/RT + \ln f(r) \quad (16)$$

and if ΔE_D is nearly zero, then

$$D_H^\circ/D_H^{\circ,*} = f(r) \quad (17)$$

which is a particularly simple result. Bohmholdt and Wicke [27] that there is little difference between E_D and E_D^* between the dilute and hydride phase of Pd-H.

The variation of D_H° with r for the $\text{Pd}_{0.948}\text{Y}_{0.052}$ and $\text{Pd}_{0.905}\text{Y}_{0.095}$ alloys are shown in Figure 11 where D_H° is seen to increase with r for the former alloy as predicted by eq (13).

It is of interest to examine the variation of D_H° with r for an alloy where the thermodynamic factor is mainly >1.0 , *i.e.*, the $\text{Pd}_{0.905}\text{Y}_{0.095}$ alloy, rather than < 1.0 as for the $\text{Pd}_{0.948}\text{Y}_{0.052}$ alloy. Results are shown in Fig. 11 where it can be seen that D_H° decreases with r . Since for this alloy $E_D^* > E_D$ and, since the \ln term is negative, it follows from eq (13) that D_H° should decrease with r as observed.

Generally it is found that D_H° is of the order of $10^{-3}\text{cm}^2/\text{s}$ for H in pure Pd and its alloys at small r , however, it becomes significantly greater than this at higher r and X_Y values, *e.g.*, for the $\text{Pd}_{0.948}\text{Y}_{0.052}$ alloy it is $25.5 \times 10^{-3}\text{cm}^2/\text{s}$ at $r=0.26$ and for the $\text{Pd}_{0.905}\text{Y}_{0.095}$ alloy, it is $74 \times 10^{-3}\text{cm}^2/\text{s}$ at $r=0.08$.

Table 4 shows that $D_H^{\circ,*}$ increases with X_Y except for a small decrease for the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy membrane. Although the absolute magnitudes appear unrealistically large for an average $r=0.02$, Ishikawa and McLellan [8] also found that D_H^* increased with X_Y whereas Sakamoto *et al* found a decrease.

Effect of Pre-adsorbed CO on H Permeation through Un-oxidized and Internally Oxidized Pd–Y and Pd_{0.77}Ag_{0.23} Membranes

With respect to H permeation it has been shown that partially internally oxidized, IOed, Pd–Al alloy membranes are more resistant towards CO poisoning than the corresponding un-oxidized Pd–Al alloys [15]. H permeation is smaller for Pd–Al alloys than for Pd because of the lower H solubilities in these alloys which results in the partially IOed alloys having lower permeation rates than Pd. For the Pd–Y alloys, however, H permeation is greater than in Pd and therefore the Pd–Y alloys may be more useful for H₂ purification from industrial gas streams which contain CO and other gaseous poisons. In this section the permeation rates of partially internally oxidized and an un-oxidized Pd_{0.77}Ag_{0.23} alloy will be compared in the presence of CO. Since the effect of CO has been found to depend on the permeation rate [15], comparisons will be made of membranes which have similar fluxes in the absence of CO.

The effect of CO on Pd–Y alloy membranes will be compared to its effect on Pd_{0.77}Ag_{0.23} alloy membranes rather than to Pd because the alloy is used commercially for H₂ purification and its permeation rates are more comparable to the Pd–Y alloys than to Pd. The thicknesses of the Pd_{0.77}Ag_{0.23} alloy membranes have been varied in order to obtain fluxes similar to those of the internally oxidized Pd–Y alloys. Although it was not always possible to exactly match the fluxes of the two alloy membranes, the rates were generally close. Comparisons are made between pairs of membranes after their pre-exposure to a given p_{CO} rather than to exposure to (CO+H₂) mixtures. At small times, the former procedure leads to less "swamping" than the latter, where "swamping" refers to the increasing enrichment of the non-permeating gas, CO, near the upstream membrane surface and consequent slowing of the permeation rate.

Many experiments were carried out in which the permeation rates were followed over 30 minute periods. In most of these experiments the initial $p_{\text{up}}=50.7$ kPa. Because the upstream volume is finite, *i.e.*, 500 or 1000 cm³, there is a small p_{up} decrease during permeation, and consequently a decrease of c_{up} , which leads, even in the absence of CO, to a small decrease of permeability during the 30 m periods the extents of which depend on the temperature and membrane thickness.

Firstly, the effect of CO on H permeation through a partially internally oxidized Pd_{0.97}Y_{0.03} membrane will be described in some detail and then results for other alloys will be given without as much detail. Plots of $\ln J$ versus time at three different temperatures in the presence and absence of pre-adsorbed CO (0.67 kPa) are shown in Figure 12 for the partially IOed (5%) Pd_{0.97}Y_{0.03} alloy membrane (126 m μ) and a Pd_{0.77}Ag_{0.23} membrane (various thicknesses). It can be seen that in the absence of CO the fluxes of the partially oxidized Pd_{0.97}Y_{0.03} and the Pd_{0.77}Ag_{0.23} alloy membranes are comparable and these fluxes show a small decline at the three temperatures as expected. Fluxes in the presence of CO for the two alloys are also shown where can be seen that the CO poisoning is greatest at the lowest temperature (Fig. 12).

Since CO chemisorption is expected to increase at lower temperatures, the greater effect of CO at 423 K on both alloy membranes is reasonable (Fig. 12). The decrease of $J(\text{CO})$ as compared to the CO-free J can be qualitatively understood from eq (4) because for a given p_{H_2} , equilibration of the surface layers with the gas phase H₂ cannot be maintained and c_{up} falls below its equilibrium value in the presence of chemisorbed CO. At 423 K the effect of CO is such that $J(\text{CO})$ is constant for the Pd_{0.77}Ag_{0.23} alloy membrane independent of p_{up} which may result from nearly complete coverage of the surface by CO allowing only a small amount of H to penetrate into the membrane the extent of which is independent of p_{up} .

Results for two other internally oxidized Pd -Y alloys with larger X_Y contents will be now discussed as shown in Figures 13-14 at 423, 473, and 523 K. The CO-free fluxes for the two internally oxidized Pd -Y and $Pd_{0.77}Ag_{0.23}$ alloys are nearly equal at the various temperatures.

Figure 13 shows results for an internally oxidized(10%) $Pd_{0.956}Y_{0.044}$ alloy membrane. The poisoning by CO is somewhat greater for the $Pd_{0.77}Ag_{0.23}$ alloy compared to the internally oxidized alloy at 423 K and the difference between the two alloy membranes appears to decrease with time of permeation. At 473 J(CO) is greater for the internally oxidized $Pd_{0.956}Y_{0.044}$ membrane but the resistance to CO poisoning of the internally oxidized alloy is not as great as at 423 K and the difference appears to decrease after $t=30$ m. At 523 K the fluxes after pre-exposure to CO for the internally oxidized(10%) $Pd_{0.956}Y_{0.044}$ and $Pd_{0.77}Ag_{0.23}$ membranes are nearly equal and constant with t (Fig. 13).

Figure 14 shows a plot of fluxes in the presence of pre-adsorbed CO (0.67 kPa), $J(CO)$, as a function of J , the flux in the absence of CO, at three different temperatures for the partially IOed $Pd_{0.94}Y_{0.06}$ alloy membrane and for the $Pd_{0.77}Ag_{0.23}$ alloy membrane at comparable permeation rates in the absence of CO. There is an increased poisoning with increase of J . For example, at 523 K for this partially internally oxidized alloy, $J=2.2\times 10^{-6}$ /mol H/s/cm² and $J(CO)=1.7\times 10^{-6}$ /mol H/s/cm² in the absence and presence of CO, respectively, or a reduction of about 23% whereas at a higher flux, $J=4.35\times 10^{-6}$ /mol H/s/cm², the corresponding $J(CO)=2.5\times 10^{-6}$ /mol H/s/cm² or a reduction of about 43% at the higher J .

Many experiments were carried out and, in all of these, the inhibition effect of CO was either the same or, more commonly, greater for the $Pd_{0.77}Ag_{0.23}$ alloy than for the internally oxidized Pd -Y alloys. The increased poisoning of the $Pd_{0.77}Ag_{0.23}$ alloy membrane compared to the internally oxidized Pd -Y

alloys was not as great as for other internally oxidized alloys such as *Pd*–Al alloys [18]. There was no clear trend with X_Y or % internal oxidation although it is difficult to compare different alloys with similar CO-free fluxes. No long term exposures to CO have been carried out with either alloy and these may show larger differences.

Conclusions

The $\text{Pd}_{0.905}\text{Y}_{0.095}$, $\text{Pd}_{0.94}\text{Y}_{0.06}$ and $\text{Pd}_{0.948}\text{Y}_{0.052}$ alloy membranes are shown to have greater permeabilities than the $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloy membrane confirming the general conclusions of Harris *et al* [1, 2, 3, 4]. D_H decreases with r for all of the *Pd*–Y alloys investigated but the decrease becomes smaller with increase of X_Y . D_H^* decreases slightly with X_Y up to ≈ 0.044 and then decreases more sharply. The slopes of $RT \ln D_H - r$ plots are given, at small r , by $g_1/2$ and the experimental values of g_1 agree reasonably well with those from thermodynamic measurements. Plots of $\ln(\text{ permeability})$ against $1/T$ give plots with minima indicating that these are not kinetic Arrhenius plots.

It is shown that partially internally oxidized *Pd*–Y alloy membranes have a greater resistance to CO poisoning especially at the lower temperatures. At 523 K there is not much difference between the CO resistance of the IOed *Pd*–Y alloys and the un-oxidized $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloy membrane. The temperature of internal oxidation may be a factor in the resistance and more research should be done on this aspect.

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References

- [1] D. Hughes, I. Harris, *Z. Physik. Chem. N.F.*, **117** (1979) 185.
- [2] D. Hughes, J. Evans, I. Harris, *J. Less-Common Mets.*, **74** (1980) 255.
- [3] M. Doyle, R. Wileman, I. Harris, *J. Less-Common Mets.*, **130** (1987) 79.
- [4] R. Wileman, M. Doyle, I. Harris, *Z. Physik. Chem. N.F.*, **164** (1989) 797.
- [5] E. Salomons, N. Koeman, J. Rector, R. Griessen, *J. Phys. Condens. Matter*, **2** (1990) 835.
- [6] P. Poyser, M. Kemali, D. Ross, *J. Alloys Compounds*, **253-254** (1997) 175.
- [7] Y. Sakamoto, H. Kaneko, T. Tsukahara, S. Hirata, *Scripta Metall.*, **21** (1987) 415.
- [8] T. Ishikawa, R. McLellan, *acta metall.*, **353** (1987) 781.
- [9] O. Yoshinari, H. Matsuda, K. Fukuhara, K. Tanaka, *Material Trans., JIM*, **38** (1997) 508.
- [10] E. Wicke, H. Brodowsky, *Hydrogen in Metals, II* G. Alefeld, J. Völkl, eds., Springer-Verlag, Berlin, 1978.
- [11] A. Küssner, *Z. Naturforschung*, **21a** (1966) 515.
- [12] L. Opara, B. Klein, H. Züchner, *J. Alloys Compounds*, **253-254** (1997) 378.
- [13] T. Flanagan, D. Wang, K. Shanahan, *J. Membrane Sci.*, **306** (2007) 66.
- [14] D. Wang, T. Flanagan, K. Shanahan, *J. Phys. Chem.*, **112** (2008) 1135.

- [15] D. Wang, T. Flanagan, K. Shanahan, *J. Membrane Sci.*, **253** (2005) 165.
- [16] E. Salomons, PhD thesis, Vrije University, Amsterdam, 1989.
- [17] P. Stonadge, M. Benham, D. Ross, C. Manwaring, I. Harris, *Z. Physik. Chem. N.F.*, **181** (1993) 125.
- [18] T. Flanagan, D. Wang, K. Shanahan, *Separation and Purification Tech.*, **79** (2011) 385.
- [19] D. Wang, T. Flanagan, *to be published*.
- [20] T. Flanagan, *Defect and Diffusion Forum*, **349** (2014) 1.
- [21] D. Wang, T. Flanagan, K. Shanahan, *Scripta Mat.*, **54** (2006) 1317.
- [22] R. Balasubramaniam, W. Zhang, S. Luo, D. Wang, T. Flanagan, *J. Alloys Compounds*, **330-332** (2002) 607.
- [23] X-Y Huang, W. Mader, R. Kirchheim, *Acta metall. mater.*, **39** (1991) 893.
- [24] B. Morreale, M. Ciocco, R. Enick, B. Howard, A. Cugini, K. Rothenberger, *J. Membrane Sci.*, **212** (2003) 87.
- [25] T. Flanagan, D. Wang, *J. Phys. Chem.A*, **116** (2012) 185.
- [26] T. Kuji, W. Oates, B. Bowerman, T. Flanagan, *J. Phys. F: Metal Phys.*, **13** (1983) 1785.
- [27] G. Bohmholdt, E. Wicke, *Zeit. Physik. Chem.N.F.*, **56** (1967) 133.

Figures

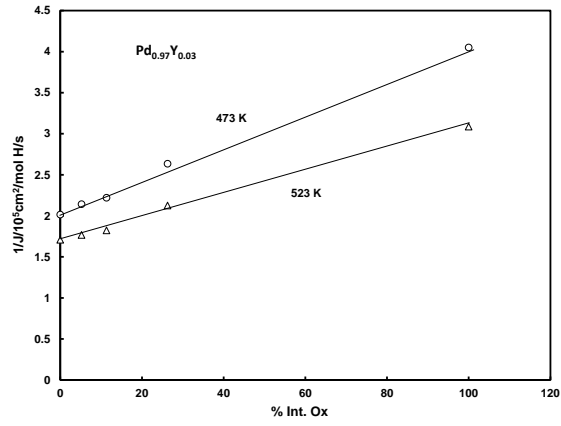


Figure 1: Plots of $(1/J)$ for the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy membrane as a function of internally oxidized. \bigcirc , 473 K; \triangle , 523 K.

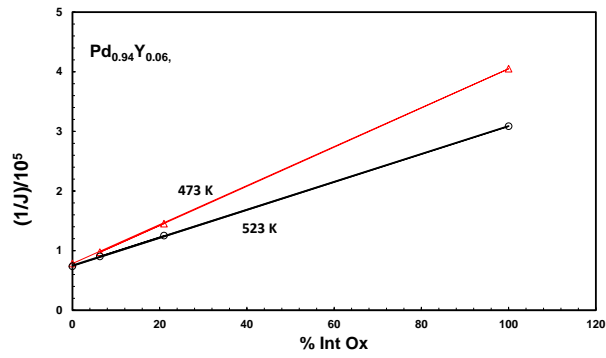


Figure 2: Plot of $(1/J)$ for the $\text{Pd}_{0.94}\text{Y}_{0.06}$ alloy membrane as a function of % internal oxidation at 473 K.

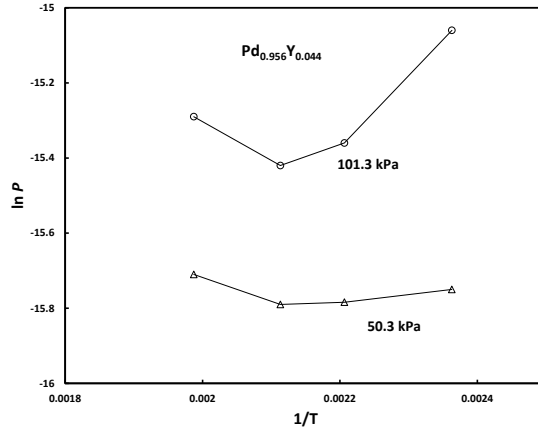


Figure 3: Plot of $\ln P$ against $1/T$ for the $\text{Pd}_{0.956}\text{Y}_{0.044}$ alloy membrane.

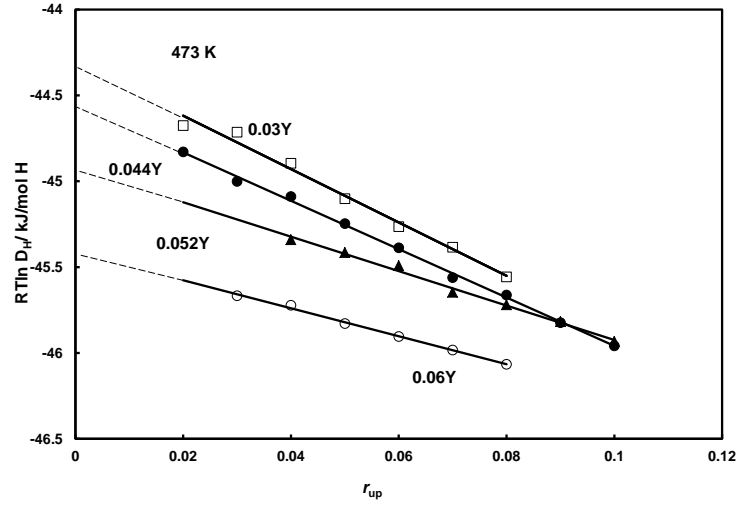


Figure 4: $RT \ln D_H$ against r for a series of Pd-Y alloys at 473 K.

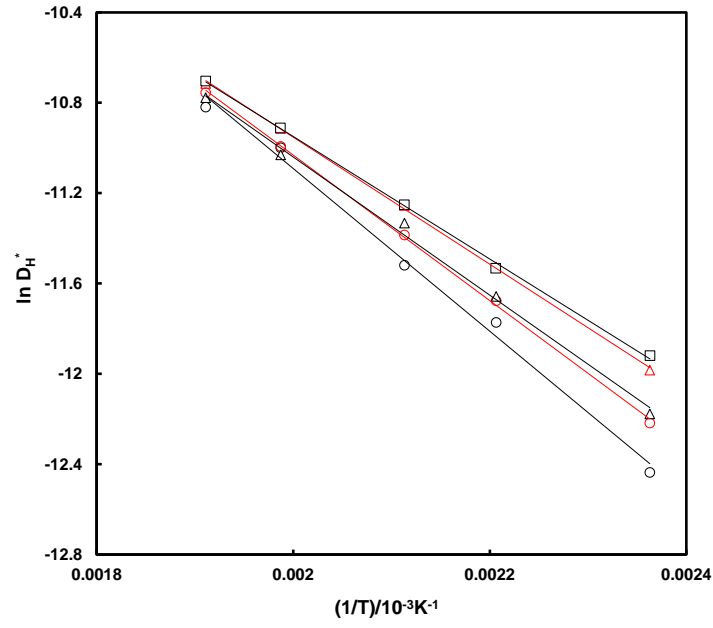


Figure 5: Arrhenius plots of D_H^* for some Pd -Y alloys and for Pd. \square , Pd; \triangle , $Pd_{0.97}Y_{0.03}$; \triangle , $Pd_{0.956}Y_{0.044}$; \circ , $Pd_{0.948}Y_{0.052}$; \circ , $Pd_{0.94}Y_{0.06}$.

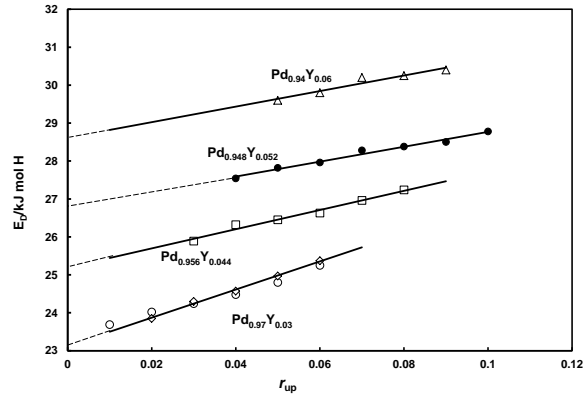


Figure 6: E_D against r for the Pd -Y alloys.

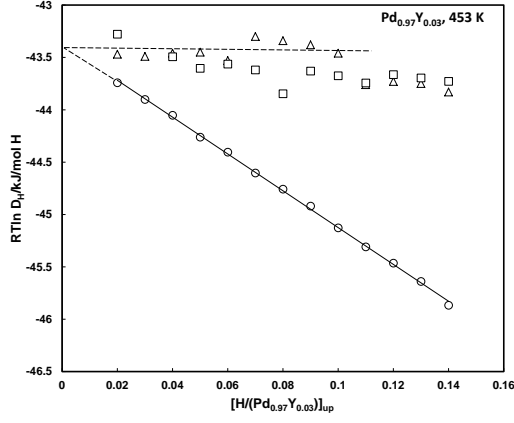


Figure 7: $RT \ln D_H$ against r (453 K) for the $\text{Pd}_{0.97}\text{Y}_{0.03}$ alloy membrane from $r=0$ to 0.14. \bigcirc , experimental; \triangle , D_H corrected using eq (6) and the values of $F(r_{up})$ for this temperature; \triangle , corrected using $F(r)=f(r_{up}/2)$.

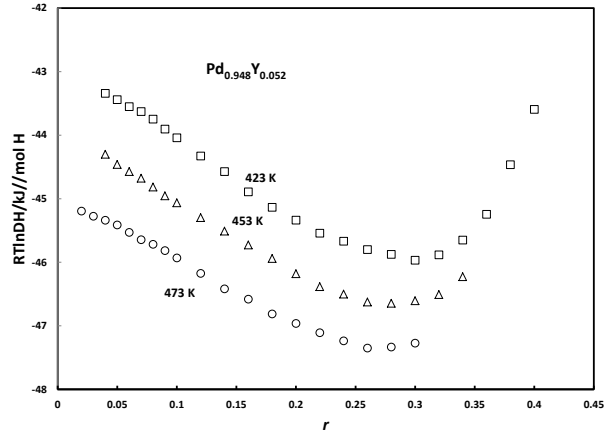


Figure 8: $RT \ln D_H$ for the $\text{Pd}_{0.948}\text{Y}_{0.052}$ alloy as a function of r . \square , 423 K; \triangle , 453 K; \bigcirc , 473 K.

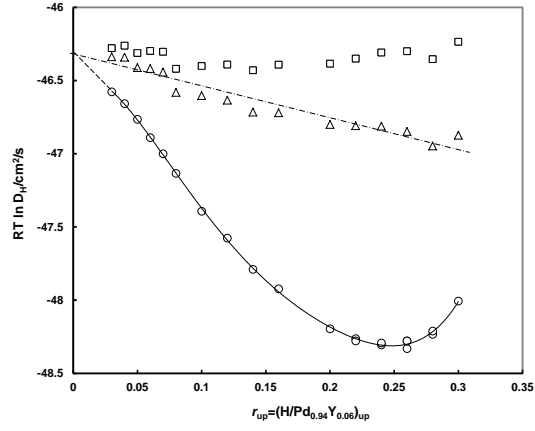


Figure 9: $RT \ln D_H(D_H^*)$ as a function of r at 473 K for the $\text{Pd}_{0.94}\text{Y}_{0.06}$ alloy. \bigcirc , D_H ; \triangle , D_H^* ; \square , $D_H^* \times (1-r)$.

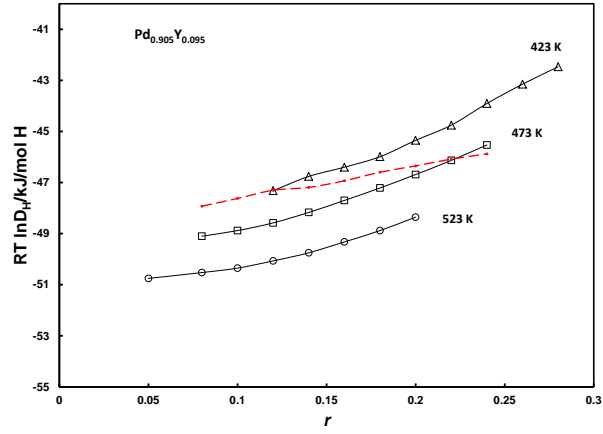


Figure 10: $RT \ln D_H$ as a function of r for the $\text{Pd}_{0.905}\text{Y}_{0.095}$ alloy. \square , 423 K; \circ , 473 K; \triangle , 523 K; $- - -$, $RT \ln D_H^*$ at 473 K.

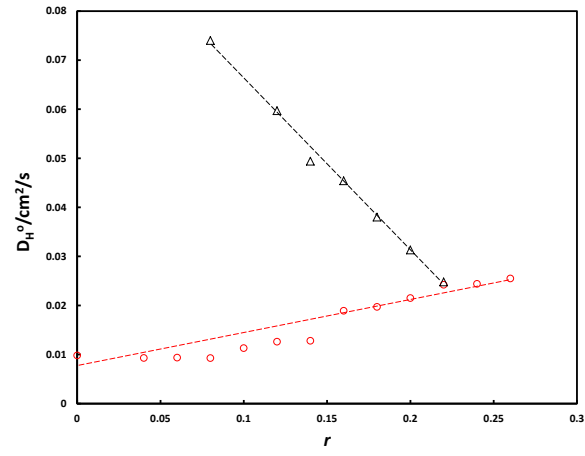


Figure 11: D_H^o as a function of r . \bigcirc , Pd_{0.948}Y_{0.052} membrane; \triangle , Pd_{0.905}Y_{0.095} membrane.

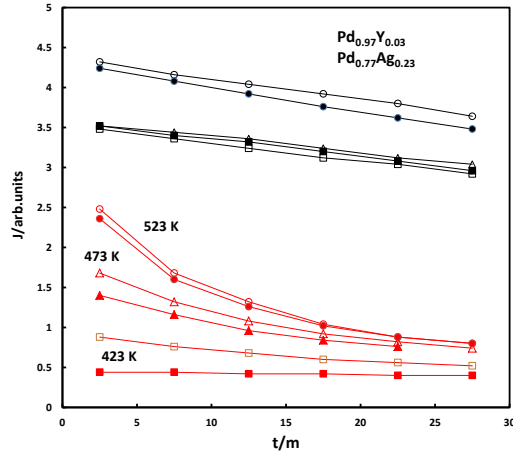


Figure 12: Flux as a function of time in the presence and absence of CO for the $\text{Pd}_{0.97}\text{Y}_{0.03}$ and $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloys. The open and closed symbols refer to the $\text{Pd}_{0.97}\text{Y}_{0.03}$ and $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloy membranes, respectively, and the lower (red) and upper (black) sets of plots refer to J in the absence and the presence of CO, respectively.

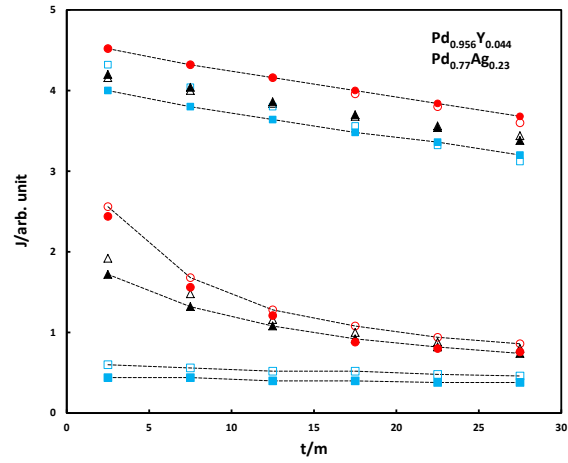


Figure 13: Flux as a function of time in the presence and absence of CO for the $\text{Pd}_{0.956}\text{Y}_{0.044}$ alloy membrane. The open and closed symbols refer to the $\text{Pd}_{0.956}\text{Y}_{0.044}$ and $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloys, respectively, and the upper and lower sets of plots refer to J in the absence and the presence of CO, respectively. \circ , 523 K; \triangle , 473 K; \square , 423 K.

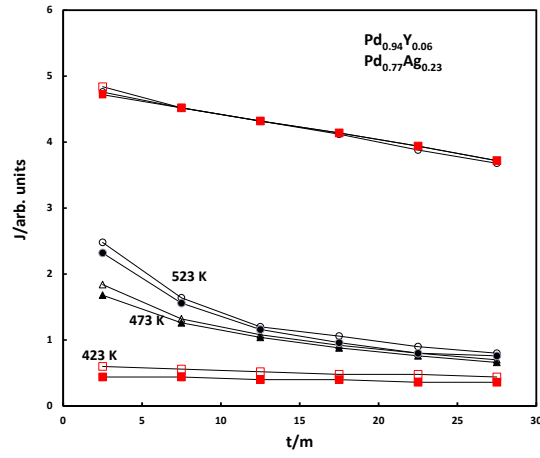


Figure 14: Flux as a function of time in the presence and absence of CO for the $\text{Pd}_{0.94}\text{Y}_{0.06}$ and $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloy membranes. The open and closed symbols refer to the $\text{Pd}_{0.94}\text{Y}_{0.06}$ and $\text{Pd}_{0.77}\text{Ag}_{0.23}$ alloys, respectively, and the upper and lower sets of plots refer to J in the absence and the presence of CO, respectively.