

# Effect of trapping on the solubility and diffusivity of hydrogen in palladium ( $\alpha$ -phase)

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The solubility and diffusivity data of hydrogen in palladium with different concentrations of defects are discussed within the framework of the two-level model with local equilibrium (Oriani's model). Analytical expression of the solubility isotherm and of the variation of the apparent diffusion coefficient depending on the total bulk concentration are derived. A good agreement is found between the experimental results on the solubility and diffusivity of hydrogen and the calculated values using the theoretical expressions.

## 1. Introduction

The solubility and diffusivity of hydrogen in polycrystalline metals depend strongly on the nature and concentration of defects these metals hold [1]. The behaviour of hydrogen in these metals is therefore affected by their previous "history" and reliable data may be obtained from samples with a well controlled "history".

The influence of defects (mainly dislocations) on the solubility of hydrogen in palladium was reported for the first time by Flanagan and co-workers, using the gas-phase technique [2, 3]. Further investigations on the effect of defects upon both the solubility and diffusivity of hydrogen in palladium have been carried out using electrochemical permeation methods by Hasegawa and Nakajima [4], Kirchheim [5, 6] and Züchner and Schöneich [7]. More recently, we have produced new data on the solubility [8] and diffusivity [9] of hydrogen in defected palladium by applying an improved electrochemical technique, namely galvanostatic permeation [10-12]. In this way reliable and reproducible data have been acquired concerning the simultaneous measurement of the solubility isotherm, the dependence of the apparent diffusion coefficient of hydrogen on its concentration and the concentration of defects, all on the same sample. These features of the method enabled us to correlate consistently the equilibrium and transport properties of hydrogen in well-characterized defected palladium samples.

In this work attempts are made to discuss, as a whole, the data on the solubility and diffusivity of hydrogen in palladium on the basis of the two-level model. This model assumes that the hydrogen atoms moving within a real metal sample should be distributed between two different levels of energy (sites) and that a rapid equilibrium occurs between the atomic populations.

The model seems to originate in the earlier works of Hill and Johnson [13] and McNabb and Foster [14], as reformulated under certain conditions of local equilibrium by Oriani, and applied by him to selected data on a variety of steel with and without cold work [15].

The  $\alpha$ -phase of the palladium-hydrogen system has recently been examined by Schöneich *et al.* who used the model to discuss the dependence of the exchange current of Volmer reaction on the degree of deformation of palladium samples [16]. Moreover, this model has also proved to be useful in the explanation of the initial non-linear region of the solubility isotherms on palladium samples having a large number of defects [8].

## 2. Discussion

### 2.1. Equilibrium measurements

The solubility isotherms of hydrogen in defected palladium samples are shown in Fig. 1. The data were obtained by stationary galvanostatic permeation measurements on a palladium membrane (curves 1 and 2), and on thin palladium films evaporated on polymer substrates (curve 3), thickness 67 nm on Teflon, and curve 4, thickness 184 nm on Mylar) respectively. In the latter case, measurements were carried out by linear sweep voltammetry [17]. The dotted lines in Fig. 1 correspond to the isotherm on a well-annealed palladium sample and are displayed for comparison. The defects were generated in the palladium membrane in the course of the  $\alpha \rightleftharpoons \beta$  phase transition following successive addition and removal of hydrogen, respectively [8, 9]. In the thin palladium films the defects were generated by the deposition process itself on the plastic substrate [18].

The solubility isotherms all exhibit an initial deviation from Sieverts' law which is more marked and extended over a larger concentration range for the thin films than for the palladium membrane. Beyond this non-linear region the solubility data again obey a linear relationship. These findings are similar to those reported by Flanagan *et al.* for cold-worked palladium chips [3].

This non-linear initial behaviour of the solubility data may be theoretically predicted by the two-level model mentioned in Section 1 [8]. The hydrogen atoms dissolved in a palladium sample should be distributed between two different states: a weakly bonded state

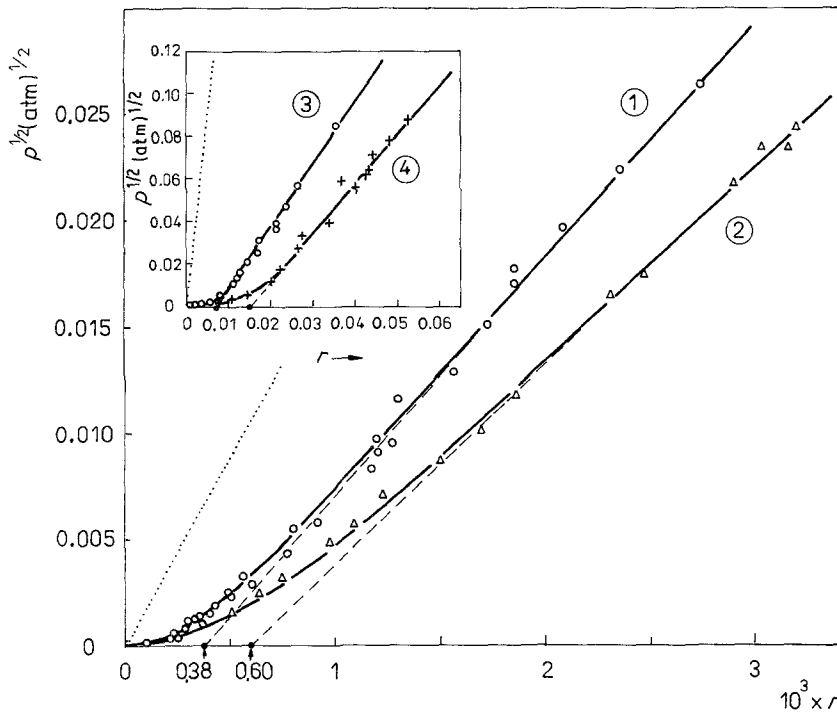
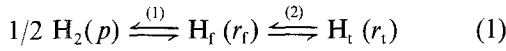


Figure 1 Solubility isotherm at 293 K of hydrogen in palladium with different defect concentrations,  $r_t^0$ : membrane, curve 1,  $r_t^0 = 3.8 \times 10^{-4}$ ; curve 2;  $r_t^0 = 6 \times 10^{-4}$ ; thin films on polymer substrate; curve 3,  $r_t^0 = 7.75 \times 10^{-3}$  and curve 4,  $r_t^0 = 1.56 \times 10^{-2}$ .

which corresponds to the normal sites in its crystalline structure (an unlimited amount in diluted  $\alpha$ -phase), and a strongly bonded state associated with a limited amount of defects (trapping sites). The two states are in reciprocal rapid local equilibrium and with the hydrogen gas, namely



Here  $p$  is the hydrogen pressure and  $r_j$  are the hydrogen concentration expressed by the hydrogen-to-palladium ratio,  $r = \text{H}/\text{Pd}$ , of weakly ( $j = f$ ) and strongly ( $j = t$ ) bonded hydrogen, respectively. The equilibrium relationships are

$$K_s = \frac{r_f}{p^{1/2}} \quad (2)$$

and

$$K_t = \frac{r_t}{r_t(r_t^0 - r_t)} \quad (3)$$

respectively, with their constants,  $K_s$  (Sieverts' constant) and  $K_t$ . Here  $r_t^0$  is the concentration of the saturable sites.

Taking into account that the total bulk concentration is the sum of the two components

$$r = r_f + r_t \quad (4)$$

and combining that with the appropriate forms of Equations 2 and 3 one has immediately

$$r = r_t^0 \frac{p^{1/2}}{K + p^{1/2}} + \frac{p^{1/2}}{K_s} \quad (5)$$

with  $K = K_s/K_t$ .

The solubility isotherm, Equation 5, is composed of two terms corresponding to the two bonding states mentioned above. Theoretically, the first term on the right-hand side, which is associated with the trapped hydrogen, cancels at an ideal material free of defects,  $r_t^0 = 0$ , while practically it becomes negligibly lower in

comparison with the second term, at well-annealed real materials. In this case the solubility data obey Sieverts' law within the usual range of experimental error. On the other hand, this term becomes constant and equal to  $r_t^0$  for a sufficiently high equilibrium pressure ( $p^{1/2} \gg K$ ), and the solubility data again obey a linear relationship, but shifted along the abscissa.

The validity of Equation 5 in describing the solubility data is shown in Fig. 1 by the solid lines: these represent the calculated isotherms using the parameters estimated in the linear portion of the solubility isotherms,  $K_s$  and  $r_t^0$ , and the adjusted value of the equilibrium constant  $K$ , which has been chosen to fit the best curves drawn through the experimental points. The corresponding value are given in Table I.

The dependence of Sieverts' constant,  $K_s$ , on the concentration of the defects,  $r_t^0$  is shown in Fig. 2a: its value decreases in so far as the concentration of defects increase, but it seems to exhibit two limits: a higher value of about  $K_s \approx 20 \text{ atm}^{1/2}$  for  $r_t^0 \rightarrow 0$  (a perfect crystal structure) and a lower value of about  $K_s \approx 2 \text{ atm}^{1/2}$  for a large concentration of defects.

Simultaneously, the standard relative partial molar enthalpy,  $\overline{\Delta H}^0$  of the weakly bonded hydrogen also changes, as shown in Fig. 2b. This parameter has been calculated using a value of the standard relative partial molar entropy,  $\overline{\Delta S}^0 = -60.8 \text{ J (g atom H)}^{-1}$  previously measured under similar conditions [12]. Flanagan *et al.* [3] have found that this value essentially remains unchanged after generation of defects in the sample. The strength of the weak hydrogen bond in the normal sites increases by generation of the defects in palladium, but again seems to vary between two limits: the higher one of  $\overline{\Delta H}^0 = -10.4$  to  $-10.5 \text{ kJ (g atom H)}^{-1}$  (for perfect crystal growth structure) and the smaller limit of about  $\overline{\Delta H}^0 = -17 \text{ kJ (g atom H)}^{-1}$ .

On the other hand, the value of the constant  $K$ ,

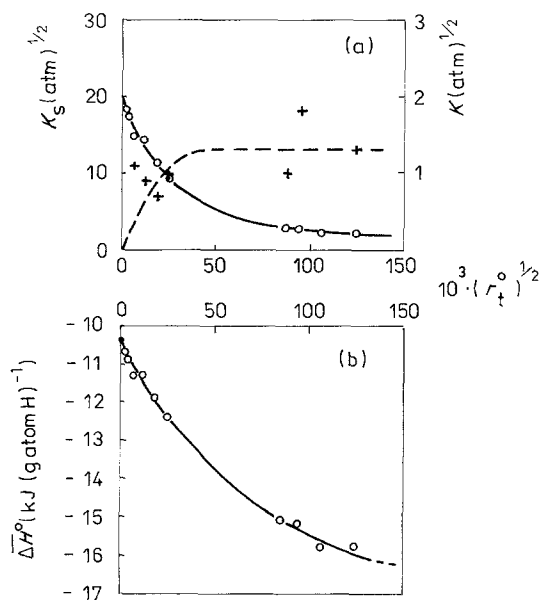


Figure 2 Variation of (a) the equilibrium constants,  $K_s$  and  $K$ , and (b) the standard relative partial molar enthalpy,  $\Delta\bar{H}^0$ , with the concentration of defects,  $(r_t^0)^{1/2}$ , at 293 K.

which corresponds to the equilibrium between the strongly bonded hydrogen (trapped) and the molecular hydrogen, seems to rise with the concentration of defects up to a certain value ( $r_t^0 \simeq 6 \times 10^{-4}$ ) beyond which it tends towards a constant value. This tendency can be observed in Fig. 2a, the dashed curve, despite the fact that the estimated individual values of the equilibrium constant are quite scattered.

Accordingly, the trapping free enthalpy change increases from  $\Delta\bar{G}_i^{293} = -23 \text{ kJ (g atom H)}^{-1}$ , for well-annealed palladium, to  $\Delta\bar{G}_i^{293} = -16 \text{ kJ (g atom H)}^{-1}$ , for  $r_t^0 > 6 \times 10^{-4}$ . These facts suggest that either by the  $\alpha \rightleftharpoons \beta$  phase transition or vacuum evaporation on plastic substrates, both the concentration and the Gibbs' energy of the normal sites and of the traps in palladium undergo alterations. This is in agreement with the conclusion of Schöneich *et al.* [16] that in the mechanically deformed palladium samples only the concentrations of traps change, and not their interaction energy with hydrogen.

## 2.2. Diffusion measurements

The variation of the apparent diffusion coefficient,  $D$ , depending on the total bulk concentration of hydrogen in palladium,  $r$ , is shown in Fig. 3. The experi-

mental points correspond to measurements carried out by the galvanostatic permeation method on a palladium membrane with different concentrations of defects: curve 1,  $r_t^0 = 5.5 \times 10^{-5}$ ; curve 2,  $r_t^0 = 2.72 \times 10^{-4}$ ; curve 3,  $r_t^0 = 3.83 \times 10^{-4}$  and curve 4,  $r_t^0 = 6.5 \times 10^{-4}$ , respectively. As already reported, the apparent diffusion coefficient increases smoothly with the total bulk concentration of hydrogen and finally tends towards a plateau value,  $D_f$  [9]. Moreover, the rate of the rise together with the plateau value sensibly depends on the concentration of the defects.

This behaviour of the apparent diffusion coefficient is also predictable within the framework of the two-level model. Indeed, the diffusion flux measured at the exit side of the membrane only has a contribution from the hydrogen moving freely in the normal sites of the lattice [15]. Therefore, in the stationary state, one has

$$\phi^\infty = -D \frac{dc}{dx} = -D_f \frac{dc_f}{dx} \quad (6)$$

where  $\phi^\infty$  is the stationary diffusion flux,  $c$  is the total bulk concentration of hydrogen (in  $\text{g atom cm}^{-3}$ ),  $D$  is the apparent diffusion coefficient associated to its gradient,  $D_f$  and  $c_f$  are the diffusion coefficient and the concentration of the freely moving hydrogen, respectively. Equation 6 involves the assumption that the trapped hydrogen does not contribute to any significant extent or not at all to the diffusion flux.

By substitution of the concentration by its atomic ratio,  $r$  ( $= \text{H/Pd}$ ) and the appropriate combination with Equations 3 and 4, Equation 6 becomes finally

$$D = D_f \left( 1 + \frac{K_t r_t^0}{1 + K_t r_t} \right)^{-1} \quad (7)$$

This equation describes the variation of the apparent diffusion coefficient in the framework of the two-level model with rapid local equilibrium and neglecting the contribution to the diffusion flux of the trapped hydrogen. It differs from Oriani's equation by the square of the denominator which originates from the fact that Equation 6 was applied to the transient state [15] and not to the stationary state, as in our case.

Equation 7 can be further simplified in two limited cases.

*Case 1:*  $K_t r_t \ll 1$ , hence the apparent diffusion coefficient no longer depends on the hydrogen

TABLE I Characteristic parameters of hydrogen in defected palladium

Equilibrium measurements			Diffusion measurements		
$K_s$ (atm <sup>1/2</sup> )	$K$ (10 <sup>3</sup> atm <sup>1/2</sup> )	10 <sup>6</sup> $r_t^0$	10 <sup>6</sup> $r_t^0$	$K$ (10 <sup>3</sup> atm <sup>1/2</sup> )	$D_f$ (10 <sup>7</sup> cm <sup>2</sup> sec <sup>-1</sup> )
18.2	—	5.4	—	—	3.6
17.3	—	17 ± 7	15 ± 40	—	—
14.7	—	60 ± 30	50 ± 20	1.07	3.31
14.2	—	160 ± 20	150 ± 15	0.9	2.47
11.3	0.7	380 ± 20	370 ± 30	0.7	2.13
9.34	1.0	600 ± 30	650 ± 30	1.13	2.08
3	1.0	7 750	—	—	—
2.91	1.8	8 980	—	—	—
2.29	—	11 380	—	—	—
2.32	1.3	15 600	—	—	—

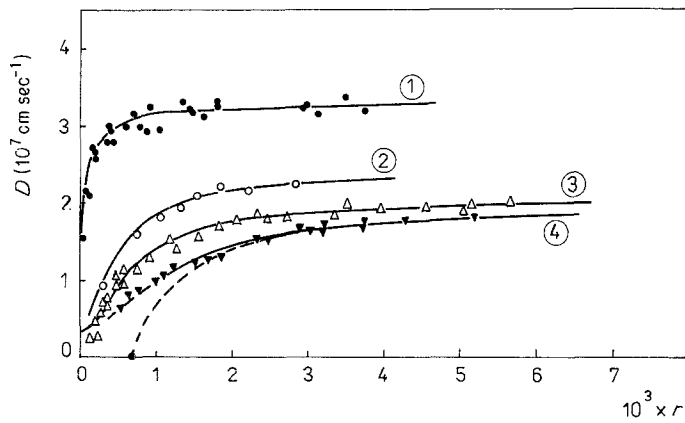


Figure 3 Effect of the total bulk concentration of hydrogen,  $r$ , on its apparent diffusion coefficient,  $D$ , for different defect concentrations: (1)  $r_t^0 = 5.5 \times 10^{-5}$ ,  $D_f = 3.31 \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$ ; (2)  $r_t^0 = 2.72 \times 10^{-4}$ ,  $D_f = 2.47 \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$ ; (3)  $r_t^0 = 3.83 \times 10^{-4}$ ,  $D_f = 2.13 \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$  and (4)  $r_t^0 = 6.50 \times 10^{-4}$ ,  $D_f = 2.08 \times 10^7 \text{ cm}^2 \text{ sec}^{-1}$ , 293 K.

concentration in palladium, namely

$$D = D_f (1 + K_t r_t^0)^{-1} \quad (8)$$

This relation is identical to Oriani's simplification [13].

Case 2:  $K_t r_t \gg 1$ , hence the concentration of the trapped hydrogen approaches the saturation value,  $r_t \approx r_t^0$  and

$$D = D_f \frac{r - r_t^0}{r}, \quad r > r_t^0 \quad (9)$$

or, in its linear form,

$$Dr = D_f r - D_f r_t^0 \quad (10)$$

The data shown in Fig. 3 are plotted in Fig. 4 in accordance with Equation 10: the numbers correspond to those marked on the curves in Fig. 3. As can be seen, Equation 10 is well satisfied in all cases for  $r > r_t^0$  and the parameters of the straight lines enabled us to calculate both the diffusion coefficient of the freely moving hydrogen,  $D_f$ , and the concentration of the defects,  $r_t^0$ . The latter values are given in Table I, for comparison with the value estimated from equilib-

rium measurements: the agreement between the two rows of data is satisfactory.

The validity of the two-level model in the case of the diffusion of hydrogen in palladium has been checked using an alternative form of Equation 7

$$D = D_f [1 + K_t (r_t^0 - r_t)]^{-1} \quad (11)$$

together with the relation

$$r = r_t \left[ 1 + \frac{1}{K_t (r_t^0 - r_t)} \right] \quad (12)$$

and the values of the constants given in Table I.

The solid curves in Fig. 3 were calculated using Equations 11 and 12 and show a good fit to the experimental points except for very low concentrations of hydrogen. The dashed line attached to curve 4 has been calculated using Equation 10 and they practically overlap for total bulk concentrations higher than the concentrations of defects,  $r > 1.5 \times 10^{-3}$ . It must be mentioned that Oriani's relation, with the square of the denominator does not fit the experimental points, giving values for the apparent diffusion constant much higher than those measured.

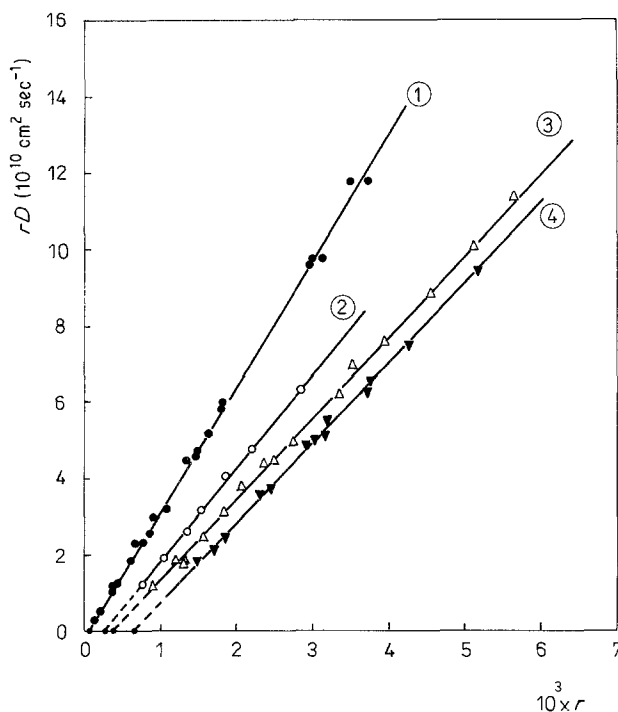


Figure 4 Linear plot of diffusion measurements of Fig. 3 in accordance with Equation 10  $r_t^0 =$  (1)  $0.055 \times 10^3$ , (2)  $0.272 \times 10^3$ , (3)  $0.383 \times 10^3$ , (4)  $0.650 \times 10^3$ , 293 K.

### 2.3. Correlation between the diffusion and the equilibrium measurements

The two-level model with a constant energy level of activated complex state is frequently used in the study of alloys [19]. The generation of defects in palladium by the  $\alpha \rightleftharpoons \beta$  phase transition seems to occur without

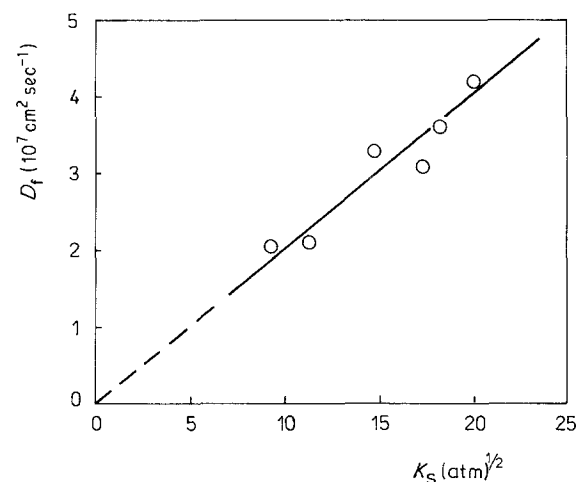


Figure 5 Correlation between the diffusion coefficient of free hydrogen,  $D_f$  and Sieverts' constant,  $K_s$ . SLP =  $2.04 \times 10^{-8}$ , 293 K.

any discernible change in the energy level of the hydrogen atoms in the saddle-point configuration, despite the fact that their energy in the normal and trapped sites changes. If that is true the activation energy for diffusion,  $E_d$ , and the standard enthalpy,  $\overline{\Delta H}^0$ , are related by the equation

$$W = E_d + \overline{\Delta H}^0 = \text{constant} \quad (13)$$

where  $W$  is the energy level of the activated complex state with respect to the molecular state.

Taking into account Equation 13 together with the expression of the diffusion coefficient of free hydrogen,  $D_f$  and Sieverts' constant,  $K_s$

$$D_f = D^0 \exp\left(-\frac{E_d}{RT}\right) \quad (14)$$

and

$$K_s = \exp\left(\frac{\overline{\Delta H}^0 - T\overline{\Delta S}^0}{RT}\right) \quad (15)$$

one finally has

$$D_f = \varepsilon K_s \quad (16)$$

with

$$\varepsilon = D^0 \exp - \frac{(W - T\overline{\Delta S}^0)}{RT} \quad (17)$$

Indeed, the diffusion coefficient of the free hydrogen,  $D_f$ , changes proportionally to Sieverts' constant, as shown in Fig. 5. It follows that there is quite a good linear correlation between these two constants as predicted by Equation 16, having a correlation coefficient of  $r = 0.987$  for seven points. The experimental slope,  $\varepsilon_{\text{exp}} = 2.04 \times 10^{-8} \text{ cm}^2 \text{ atm}^{1/2} \text{ sec}^{-1}$ , agrees well with that calculated using the following data [10–12]:  $E_d = 21.83 \text{ kJ (g atom H)}^{-1}$ ;  $\overline{\Delta H}^0 = -10.9 \text{ kJ (g atom H)}^{-1}$ ;  $\overline{\Delta S}^0 = -60.8 \text{ J (K g atom H)}^{-1}$ ;  $D^0 = 2.48 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$  and  $W = 10.93 \text{ kJ (g atom H)}^{-1}$ , namely  $\varepsilon_{\text{calc}} = 1.9 \times 10^{-8} \text{ cm}^2 \text{ atm}^{-1/2} \text{ sec}^{-1}$ .

The practical result of this correlation is that the stationary diffusion flux of hydrogen through a palladium membrane depends only on its pressure at the entrance side and not on the concentration of the defects. The stationary diffusion flux expressed by the diffusion current,  $I^\infty$  is given by the equation

$$I^\infty = \frac{FS}{l} Dc = \frac{FS}{lV_{\text{Pd}}} \frac{D_f}{K_s} p^{1/2} \quad (18)$$

as, in accordance with Equations 2 and 6, the product of the apparent diffusion coefficient,  $D$ , and the total bulk concentration,  $c$ , can be written

$$Dc = \frac{D_f}{V_{\text{Pd}} K_s} p^{1/2} \quad (19)$$

where  $F$  is the Faraday constant,  $S$  is the surface area of the membrane,  $l$  is the thickness and  $V_{\text{Pd}}$  is the atomic volume of palladium. Because the ratio  $(D_f/K_s)$  does not depend on the concentration of defects, Equation 16, the stationary diffusion current,  $I^\infty$ , should increase with the hydrogen pressure, as shown in Fig. 6: the concentration of the defects changed within the range of  $5 \times 10^{-6}$  to  $6 \times 10^{-4}$  without affecting this linear dependence. From the slope of the straight line  $\text{SLP} = 0.32 \text{ A atm}^{-1/2}$  one can estimate again the value of constant  $\varepsilon = D_f/K_s$  and it is found

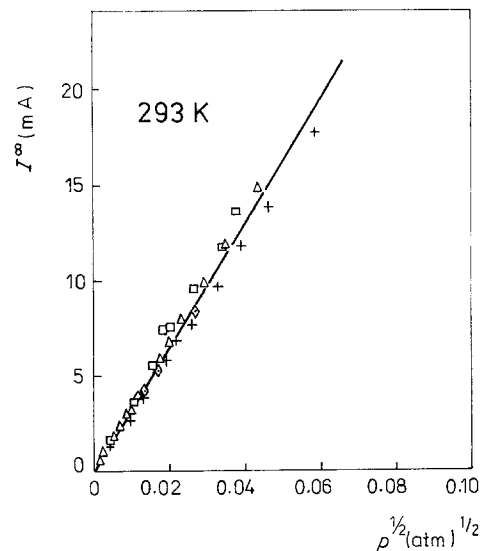


Figure 6 Stationary diffusion current,  $I^\infty$ , plotted against hydrogen pressure,  $p^{1/2}$ , at the entrance side of the palladium membrane with different defect concentrations:  $r_t^0 = (\diamond) 5 \times 10^{-6}$ ,  $(\square) 5 \times 10^{-5}$ ,  $(+)$   $3.83 \times 10^{-4}$  and  $(\Delta) 6.5 \times 10^{-4}$ . SLP =  $320 \text{ mA atm}^{-1/2}$ ,  $\pm 11\%$ ; 293 K.

to be  $\varepsilon_{\text{exp}} = 1.94 \times 10^{-8} \text{ cm}^2 \text{ atm}^{-1/2} \text{ sec}^{-1}$ , in very good agreement with the values given above.

### 3. Conclusion

The two-level model with rapid local equilibrium and a constant energy level of the activated complex state seems to explain in a satisfactory manner both the initial non-linear region of the solubility isotherm and the dependence of the apparent diffusion coefficient on the total bulk concentration of hydrogen in defected palladium.

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