

Permeation of Hydrogen through Palladium-Silver Membranes

STRAIN-GRADIENT-INDUCED "UPHILL EFFECTS"

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The hydrogen content gradients that occur during hydrogen permeation through palladium-silver membranes produce complementary strain gradients of lattice expansion, which induce opposing Gorsky Effect components of Diffusion Flux. A body of observations of related "uphill effects" and allied diffusion phenomena have recently been studied, using sheet and tube membranes; these phenomena have been correlated with hydrogen pressure-hydrogen content relationships of the Pd₇₇Ag₂₃H_n system.

The suitability of employing palladium-silver alloys, of composition Pd₇₇Ag₂₃ and Pd₇₅Ag₂₅, as diffusion membranes for hydrogen permeation (1, 2) is related to the high solubility of hydrogen in these alloy compositions, which is accompanied by high hydrogen diffusion coefficient values and is also linked to the resistance of the alloys to deformation during cycles of absorption and desorption of hydrogen (3).

Particular advantages of these two alloy compositions, in regard to these factors, are centred around the forms of their corresponding equilibrium hydrogen pressure-hydrogen content relationships (p-n). At temperatures near 25°C these relationships are of critical- or super critical-type forms, with reference to structure damaging $\alpha \rightarrow \beta$ phase transitions and allied hysteretic effects (3-5).

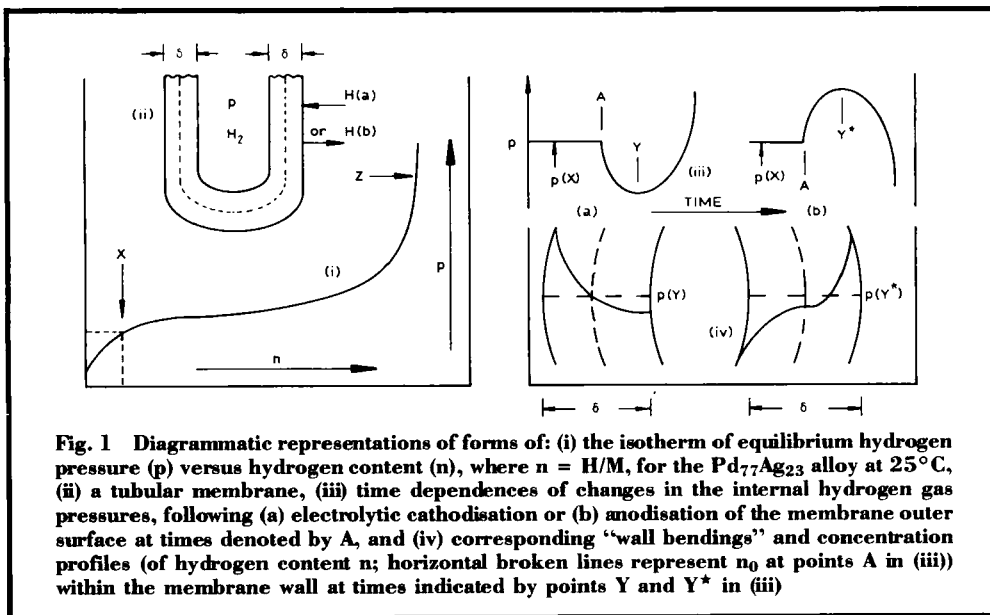
Associated with these considerations, substantial data on various experimental parameters have become available for the Pd-Ag-H system (4, 5). These have included estimations of hydrogen diffusion coefficients, both as functions of temperature and of hydrogen content (3-6).

One frequently employed means of deriving hydrogen diffusion coefficients has been by

"breakthrough technique" analyses of the time dependence of hydrogen permeation fluxes (3-6). Recently such derivations have, however, been shown to be temporarily complicated by the possibility of "uphill" processes related to Gorsky Effect responses to strain gradients developed by lattice-expanding hydrogen interstitials (7). Preliminary outlines of a substantial series of studies of "uphill effects", carried out with membranes of Pd₇₇Ag₂₃ alloys in the form of both sheet and tube, have been reported quite recently (8-10).

In addition to having a technological significance (1, 2), the form of the p-n isotherms of the Pd₇₇Ag₂₃H_n system at temperatures near to 25°C (illustrated in Figure 1) provides certain experimental advantages from the view point of the recent studies of "uphill effects" (8-11). For instance, the p-n isotherm at 25°C covers a conveniently wide range of hydrogen contents, n, (where $n = H/M$, the atomic ratio of hydrogen to metal atoms) for equilibrium hydrogen pressures $p < 1$ atm (6, 8-10), for example, with $p = 1$ atm at point Z in Figure 1 (i), $n \sim 0.42$. A practical advantage of a tubular form of membrane, Figure 1 (ii), is that in addition to

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possibilities of use as a bi-electrode, it has proved to be sensitively reliable – with respect to “leakage problems” associated with interstitial hydrogen expansive effects (1–10) – for accurately measuring changes in hydrogen gas pressures at inner surfaces. The tubular form of membrane has also been important for obtaining allied complementary measurements of actual changes of internal volume by a water displacement technique (12).

Analyses of “Uphill Effects”

The essential characteristics of “uphill effects” are shown in Figure 1 (iii). Thus when a quasi-static hydrogen pressure is established within the tube, corresponding (for surfaces having high catalytic activity) to a hydrogen content both on the surface and throughout the tube wall as given by the p - n isotherm in Figure 1 (i), the re-introduction of hydrogen to the outer surface, for example at point A in Figure 1 (iii(a)), will produce an initial “uphill” decrease of internal hydrogen pressure – or, in alternative experiments of a more electrochemical type, an equivalent increase of the internal surface electrode potential. The alternative procedure of

removal of hydrogen from the outer surface (point A in Figure (iii(b))) self-consistently produces the converse effect, namely an increase in the internal gas pressure or a decrease in the internal surface electrode potentials (12).

The magnitudes of “uphill effects” – as defined with reference to the maximum “uphill” decrease (or converse increase) Δp , of the internal tube pressure indicated by points Y and Y^* in Figure 1 (iii) and of their associated influences on “breakthrough time” parameters, and subsequently derived values on the hydrogen diffusion coefficient – have now been investigated for a series of initial hydrogen contents, n_0 , in both $\text{Pd}_{77}\text{Ag}_{23}$ (8–11) and $\text{Pd}_{81}\text{Pt}_{19}$ (12) membranes.

From these studies sound evidence has been obtained that hydrogen permeation, J_δ , through membranes of wall thickness δ can be described by an outline relation of the form

$$J_\delta = -D[\text{grad } n - f(n_0, \text{grad } \epsilon)] \quad (i)$$

indicative of the combined influences of a generally expected Fickian concentration gradient term, represented by $\text{grad } n$, and a second term representing an opposing Gorsky Effect flux – involving strain gradients, $\text{grad } \epsilon$, produced

by the expansion effects of the hydrogen interstitials, and initial concentrations, n_0 , of the interstitials in the wall. More pictorial representations of the influences of these factors at an intermediate stage (points Y and Y* in Figure 1 (iii)) of both increasing and decreasing pressure "uphill effects" are shown in Figure 1 (iv). Here, for a section of tube wall with an initial hydrogen content, n_0 , further entry of hydrogen into the outer surface has been represented as producing an outward distortion of the tube wall, corresponding to a developing strain gradient, represented by $\text{grad } \epsilon$. This strain gradient has produced a Gorsky Effect transfer of hydrogen away from the inner regions of the wall of a magnitude proportional to n_0 – with a reduction corresponding to Δp of the hydrogen chemical potential and, effectively, a simultaneous equilibration of hydrogen gas pressure within the tube. In complementary studies of permeation rate alterations – resulting from mechanically produced strain gradient responses to pressure changes at the outer surface, involving either hydrogen or any other gas likely to be encountered in technological working conditions – self-consistently clear evidence has now been obtained (10) that the corresponding Gorsky Effect hydrogen transfer in this case supplements the normally expected concentration gradient directed hydrogen flux.

From combined academic and technological standpoints, these studies of hydrogen permeation would now seem to represent particularly clear demonstrations of Gorsky Effect operation. As a consequence of the good opportunities provided through the p-n-T data to obtain quite accurate estimates of the hydrogen contents of both wall substrates and suitably activated surfaces, there has been good progress (13) in matching experimental permeation rates with quantitatively more precise forms of Equation (i) and analogous relationships.

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Protecting Rhodium Catalysts

An understanding of the relationship between the chemistry and structure of rhodium surfaces with their catalytic performance has already been gained from extensive surface spectroscopic investigations. Now, researchers at the University of Pittsburgh, Pennsylvania, have studied the protection of rhodium supported catalysts by potassium functionalisation, in connection with their performance in syngas-related industrial reactions and in automobile exhaust gas converters (M. I. Zaki, T. H. Ballinger and J. T. Yates, *J. Phys. Chem.*, 1991, 95, (10), 4028–4033).

They found that the exchange functionalisation of isolated aluminium-hydroxide groups of the alumina support by potassium carbonate modifier produced aluminium-oxygen potassium groups which stabilise the rhodium/alumina catalysts against rhodium(I) formation.

The functionalisation could thus produce an effective practical method for the protection of environmental rhodium catalysts against loss of catalytic activity due to rhodium(0) degradation.