The Hydrides of Palladium and Palladium Alloys

A REVIEW OF RECENT RESEARCHES

By F. A. Lewis, Ph.D.

Department of Chemistry, The Queen's University of Belfast

In this article, to be published in two parts, some recent findings are included in a review of the pressure-concentration temperature (P–C–T) relationships of the palladium/hydrogen and palladium/deuterium systems. A brief account is given of experimental information concerning the structure of, and diffusion of hydrogen in, the solids which are the products of the absorption of hydrogen by palladium. Attention is paid to considering errors of interpretation of experimental results that can arise when true thermodynamic equilibrium does not exist between the solids and hydrogen molecules—both in the presence and absence of aqueous solution

Since the initial investigations of Graham (1) it has been fairly clearly established that, under almost all conditions of temperature and hydrogen gas pressures, the amount of hydrogen which can be *ab*sorbed* by palladium greatly exceeds the amount *ab*sorbed by any other element from Group VIII of the periodic table and compares (2) with the amounts absorbed by the electropositive metals of Groups I to V; for example, at temperatures of about 25°C, the atomic ratio (H/Pd) of hydrogen to palladium can readily be made to exceed 0.5. Moreover, in contrast to what is found for the remainder of Group VIII, *ab*sorption of hydrogen by palladium is an exothermic process (3) albeit with a fairly low heat of reaction of about 9.5 Kcal/mole H_2 at around 25°C. (*Ad*sorption of hydrogen on to a clean surface is, however, an exothermic process for all Group VIII metals (4).)

The original volume of a palladium specimen expands by about 10 per cent when H/Pd attains a value of about 0.5 but, in contrast to the other transition metals which *ab*sorb large volumes of hydrogen (i.e. titanium, zirconium and hafnium in Group IV and vanadium, niobium and tantalum in Group V), there is virtually no macro-disruption of palladium specimens which undergo this expansion although roughening of the surface and complex slip line structures are observed (5) as a result.

It has been claimed (6) that at temperatures of about 25°C hydrogen may subsequently be desorbed from palladium hydrides without the specimen contracting to its original dimensions, but more recent work (7, 8, 9, 10) does not confirm these findings. Certainly there is no dispute that on removal of hydrogen by heating at about 300°C, either in air or in vacuo, the original dimensions of a palladium specimen are almost completely restored, although they may eventually be markedly altered when a large number of cycles of absorption and violent expulsion of hydrogen

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*Graham described the *ab*sorption of gas as 'occlusion'. In some subsequent publications it is not however always clear that 'occlusion' does not refer to *ad*sorption as well as *ab*sorption.

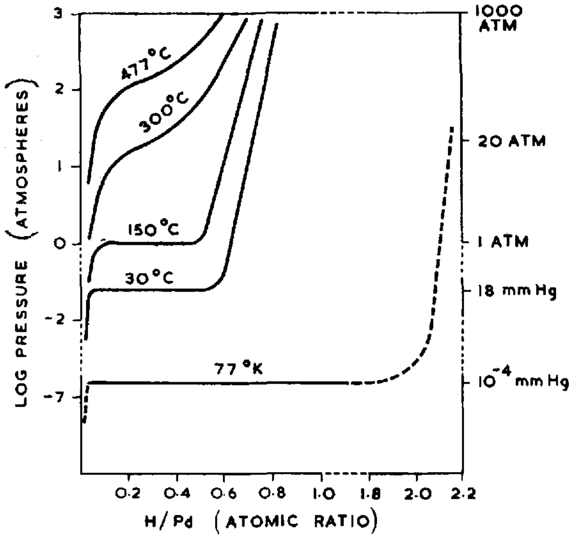

Fig. 1 Pressure-concentration isotherms of the palladium/hydrogen system

have been undergone. The possibility of dimensional changes has to be carefully considered when palladium is used as a diffusion membrane to separate hydrogen from other gases: this problem has been discussed in a previous issue of this review (11).

Hydrogen Pressure-Hydrogen Content-Temperature (P-C-T) Relationships of the Palladium/Hydrogen System

Conditions have been attained by several investigators in which the concentration of hydrogen absorbed by palladium is in almost true dynamic equilibrium with molecular hydrogen in the gas phase. Particularly detailed and accurate P-C-T relationships at temperatures from 0°C–350°C and at hydrogen pressures up to about 30 atmospheres have been compiled by the research groups of Gillespie and Sieverts (12). More recently P-C-T data have also been obtained at higher pressures (13, 14) and at higher and lower temperatures (14, 15).

Below a critical temperature, T_c, of about 300°C (critical pressure, P_c, $\sim$20 atm) there are regions over which the hydrogen pressure is invariant with change of hydrogen content indicating the coexistence of two solid phases, α and β. The ratio of hydrogen to palladium in both these phases is generally non-stoichiometric; just below the critical temperature $(H/Pd)_\alpha \simeq (HPd)_\beta \simeq 0.27$ but over the range of contents where α and β phases coexist at 30°C, $(H/Pd)_\alpha \simeq 0.03$ and $(H/Pd)_\beta \simeq 0.57$. It seems that at even lower temperatures (77°K) the maximum hydrogen content of the α phase is very low indeed while in β-phase $H/Pd \sim 2$. A composite diagram is shown in Fig. 1.

P-C-T Data and Electrode Potentials

The palladium/hydrogen system also lends itself to quite convenient derivation of P-C-T data from electrode potential measurements (10) by use of the relationships between pressure P, chemical potential μ, and electrode potential E, i.e. $RT\ln P = \mu = 2FE$ where R is the gas constant and F is Faraday's constant.

The advantages to be gained from the storage of hydrogen by palladium electrodes are under examination in connection with electrochemical cells (16) and electrophoresis studies (17).

Crystallographic Investigation

The several X-ray studies (2) that have been reported have generally been carried out at about 25°C.

The weight of evidence indicates that over α-phase concentrations there is a small but continuous increase of the cell constant a_0 of the face-centred cubic palladium lattice from 3.88Å to attain a value of 3.89Å when H/Pd = 0.03.

On further increasing the hydrogen content a new set of X-ray reflections are observed which are characteristic of the β-phase hydride. The palladium atoms in this phase retain f.c.c. symmetry, but the cell constant increases to about 4.02Å. The β-phase reflections (they exhibit considerable line broadening (18)) increase in intensity as the total hydrogen content increases over the region where α and β phases coexist. The expansion of a_0 to 4.02Å parallels the 10 per cent expansion of the macrovolume observed when the $\alpha \rightarrow \beta$ transformation is completed (H/Pd ~0.57). Results indicate that still further absorption of hydrogen then causes an additional continuous increase of the β-phase cell constant. Neutron diffraction studies on completely transformed β-phase hydride (H/Pd ~ 0.65) have also been reported (19).

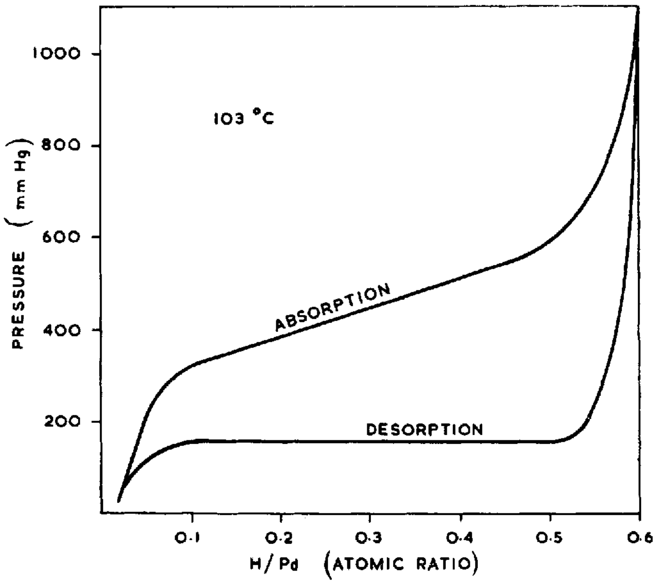

Fig. 2 Pressure hysteresis between 'absorption' and 'desorption' isotherms. Data obtained with palladium sponge at 103°C (Reference 20)

Hysteresis of Isotherms

Fig. 1 does not indicate that over regions of α and β phase coexistence the 'equilibrium' pressures measured when the hydrogen content is being successively increased (absorption isotherms) often exceed (Fig. 2) the 'equilibrium' pressures when hydrogen is successively removed between measurements (desorption isotherms).

By using finely particulated palladium and by heating to 360°C between measurements, Gillespie and his co-workers (12) obtained isotherms in which this 'hysteresis effect' was eliminated: the pressures measured in the two-phase region were generally intermediate between the absorption and desorption pressures obtained with more massive specimens (3). Furthermore, early work in Sieverts' laboratory (12) with finely divided palladium black at 111°C, indicated that the absorption and desorption pressures approached a common mean on standing. However, during further recent work (3) with palladium blacks at 30°C, hysteresis was again observed; neither absorption nor desorption pressures altered appreciably on standing at this low temperature, and here it was suggested that it was the absorption isotherm which represented true equilibrium conditions.

Nucleation of β-phase Hydride

There is still disagreement as to whether β-phase first forms a layer on the surface of the solid or whether growth generally develops from nucleation centres in the interior.

The inward migration of a β-phase layer, with a concentration gradient extending from a hydrogen rich surface to the α-β phase boundary, has been invoked (3, 10) to explain the slight increase (20) (see Fig. 2) of equilibrium pressures often observed during absorption over the region of α and β phase coexistence. (A similar effect can also be produced by a temperature gradient along the sample but in these circumstances sloping isotherms should be observed during both absorption and desorption (21).

A corollary to this picture is that during desorption the α-β phase boundary retreats inwards from the surface and over the two-phase region the measured pressure is that in equilibrium with a surface consisting solely of α-phase (3).

The Palladium-Deuterium Equilibria

Reliable P-C-T data for the Pd/D system have also been obtained by Sieverts and Gillespie (12). When the data are plotted as isotherms these are found to have a similar appearance to those of the Pd/H system. The critical temperature, T_c, for α and β-phase coexistence is about 276°C which is only slightly lower than T_c for the Pd/H system but P_c is $\sim$ 35 atm for Pd/D which is almost twice the corresponding critical pressure for Pd/H. Furthermore, in regions where α and β phases coexist below T_c, the equilibrium pressure for the Pd/D system markedly exceeds the corresponding pressure for the Pd/H system at the same temperature; for example, at 30°C, when α and β phases coexist $P_{D_2} \sim 80$ mm while $P_{H_2} \sim 18$ mm. Methods for the separation of hydrogen from palladium have been designed (22) to take advantage of these differences, which are perhaps best illustrated by plotting the P-C-T data in the form of isobars. Characteristic 'absorption' isobars in Fig. 3 show that the pressure of D_2 in equilibrium with β-phase deuteride attains a pressure of one atmosphere at $\sim$110°C while the pressure of hydrogen over β-phase hydride only attains one atmosphere at $\sim$150°C. These features are in line with the fact that deuterium is less strongly absorbed by palladium than is hydrogen; the heat of absorption (3) of D_2 (ca. 8.5 Kcal/mole) being about 1 Kcal/mole lower than the value for H_2 (compared over regions of α and β-phase coexistence at 30°C).

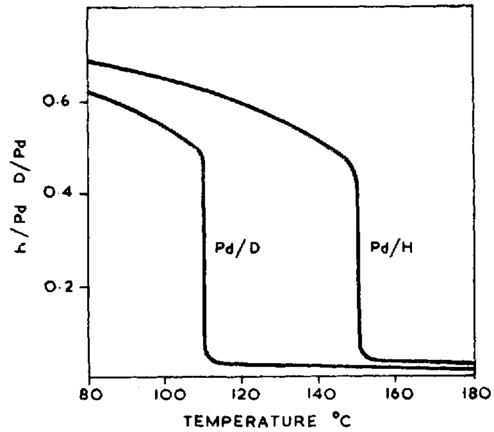

Fig. 3 Comparison of absorption by palladium of hydrogen and deuterium under a pressure of one atmosphere as a function of temperature

Factors governing the electrolytic separation of hydrogen from deuterium on a palladium cathode have been discussed (23).

Diffusion of Hydrogen in Palladium Hydride

When interpreting experimental results related to the diffusion of hydrogen in palladium hydride the possible contribution of the following processes must be considered:

(1) Diffusion in the α-phase
(2) Diffusion of the α-β phase boundary
(3) Diffusion in β phase after completion of the α → β transformation

Methods of analysing experimental results where these alternative possibilities exist have been outlined (24).

The high mobility of hydrogen in palladium hydride has been indicated from nuclear magnetic resonance experiments (25), and it is known empirically that processes (1) and (3) proceed extremely rapidly even at room temperature (10). It is, however, only for diffusion of hydrogen in the α-phase that detailed experiments have been carried out and the activation energy for this process has been reported as about 5 Kcal/mole H_2. However, in spite of recent claims (26) to the contrary it does not appear to be finally established that this activation energy refers to a diffusion process in the solid and not to processes of molecular dissociation and association at the entrant and emergent surfaces.

With reference to the phase boundary permeation, experiments have been carried out in which palladium wires were only partly immersed in electrolyte and then charged with hydrogen by electrolysis. Macro-expansion of the section immersed in electrolyte results in the formation of quite a sharp boundary between this part of the wire and the part not directly charged with hydrogen; for wires of convenient diameter, say 32 SWG, this boundary can be quite readily seen under low power magnification (Fig. 4) and as a first approximation may be taken as separating regions of α and β phase. Rates of advance of the boundary into the part of the wire not immersed in electrolyte have been calculated (27) to be about 0.2 mm/hour at about 30°C.

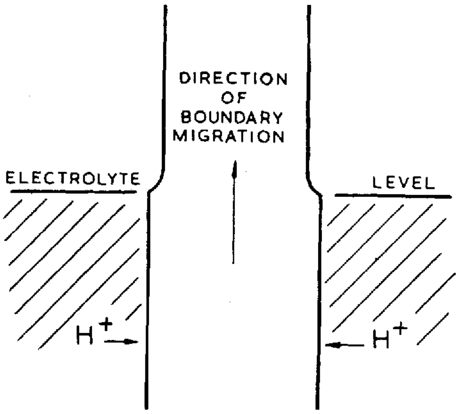

Fig. 4 Upward diffusion, from a gas-electrolyte interface, of β-phase hydride formed by electrolysis

Phase boundary migration rates of a similar order of magnitude are also suggested from experiments (28, 29) in which wires were again charged over part of their lengths but the time dependent changes of hydrogen content were measured after their removal from electrolyte.

Inhibition of Equilibria in the Palladium-Hydrogen System

There is much evidence (2) that, without very careful preactivation of the palladium sample, P-C-T data, under equilibrium conditions, below temperatures of about 200°C can only be conveniently derived in the gas phase if the sample has a very large surface-to-volume ratio such as in the case of finely divided palladium blacks or evaporated metal films: for example, when used as diffusion membranes, palladium tubes are generally impermeable to hydrogen gas at about 25°C. Even when there is incomplete inhibition of the absorption of molecular hydrogen by more massive specimens the kinetics are generally irreproducible (12).

Since the rates of absorption of hydrogen can be varied by annealing and by cold working the palladium, it has been advanced (12) that both inhibition and irreproducibility of absorption rates are related to defects present in the solid. However, a likely alternative solution of these effects is that there is inhibition of surface reaction steps (10, 30), the most likely of which is the dissociation of hydrogen molecules.

Inhibition of Equilibria in Aqueous Solution

Although more massive specimens of palladium may be very slow to absorb molecular hydrogen from the gas phase at room temperature, they are often found to absorb hydrogen readily when they form the cathode of an electrolytic cell (2). For this reason, electrolytic methods have very often been employed to introduce hydrogen: the amount absorbed can be estimated by using a voltameter placed above the cathode combined with a coulombmeter in series with the cell (31). However, it is only quite recently (9, 10, 32, 33, 34) that systematic investigation has been made of the equilibrium between palladium hydride and molecular hydrogen dissolved in solution. Results indicate (9, 10, 34) that this equilibrium is relatively easily poisoned and that in the absence of electrode potential measurements it is difficult to draw conclusions as to the ability or inability of the surfaces in many earlier electrolysis studies to equilibrate in this way.

It is important to realise that especially if the surface step $\underset{*}{\mathrm{H}} + \underset{*}{\mathrm{H}} \rightleftharpoons H_2$ is inhibited the electrolytic discharge of hydrogen ions can be equivalent to very high pressures of hydrogen gas (18, 35). Again, it must be noted that once having entered the metal, hydrogen cannot be readily released if the surface recombination step is poisoned. Although at about 20 to 30°C (where the majority of electrolytic studies have been carried out) the hydrogen content of palladium is not strikingly increased by pressures exceeding one atmosphere, the amounts of hydrogen absorbed after prolonged electrolysis at high current densities, and retained after its cessation, have been of sufficient significance to have encouraged suggestions (12) that palladium hydrides formed by electrolysis may in some respects differ from those formed by absorption of initially molecular hydrogen from the gas phase. The more recent measurements do not support such a difference (10, 34). They have stressed that, regardless of the method of introduction of hydrogen, comparisons of hydrogen content can only be made with reference to pressure, either directly or by electrode potential measurements, and that when comparisons are made there must be no inhibition of any intermediate stage of the absorption equilibria.

It may be noted that the hydrogen contents of certain palladium alloys can be increased by orders of magnitude by increasing the pressure above one atmosphere, and in such cases hydrogen contents obtained from electrolytic studies can be grossly misleading (34) if quoted without the pressure reference provided by electrode potential measurements.

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The concluding part of Dr Lewis's article will be published in the January issue of 'Platinum Metals Review'.