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## THE ROLE OF ELECTRON DONATION TO METALLIC BANDS OF PALLADIUM AND ITS ALLOYS IN THE ABSORPTION OF HYDROGEN

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### Abstract

Recent experimental and theoretical advances dealing with the absorption of hydrogen by palladium and its alloys are reviewed. A discussion is given of quantitative interpretations of data in terms of specific electronic models in which the electrons from the hydrogen are donated to the combined *s-d* bands of palladium and its alloys. The experimental dependence of the heat of absorption upon hydrogen content is given and related to the theoretical dependence of the contribution due to band filling. Finally the possible relevance of these absorption data to chemisorption and catalysis is considered.

### Introduction

This anniversary issue of the Journal provides an opportune time in which to point out some recent developments in the experimental and theoretical aspects of the absorption of hydrogen by palladium and its alloys. These results should be of interest to workers in the field of heterogeneous catalysis. The phenomenon of absorption of hydrogen by palladium and its alloys has been reviewed in detail<sup>1)</sup> and in addition a special review has been devoted to the more recent developments in this field.<sup>2)</sup> The present article has been written primarily with research workers in heterogeneous catalysis in mind because this work explores the possible relevance of the latest developments in absorption to chemisorption.

Several factors have provoked renewed interest in the study of absorption of hydrogen and deuterium by palladium and its alloys. For example, it has been found that certain palladium alloys have advantages as hydrogen purification membranes as compared to pure palladium.<sup>1)</sup> Palladium alloys are also finding applications in fuel cell technology.<sup>1)</sup>

The pioneering researches by SIEVERTS and his coworkers on the absorption

T. B. FLANAGAN

of hydrogen by palladium-rich alloys were conducted at relatively elevated temperatures,  $\geq 138^{\circ}\text{C}$ , where palladium-rich alloys with relatively large added metal contents absorb but little hydrogen.<sup>3)</sup> The behavior of such alloys towards hydrogen absorption is of special interest because in the region of high added metal contents the theories of absorption are particularly subject to testing. Prior to about 1960 absorption studies on palladium and its alloys were not, in general, carried out below about  $120^{\circ}\text{C}$  because there was found to be an inhibition of the equilibration process at the surface (A notable exception is the work of NACE and ASTON<sup>4)</sup>).

### Recent Experimental Advances

It is relevant here to discuss some of the recent experimental methods utilized for the study of absorption of hydrogen by palladium and its alloys. Electrochemical approaches have been particularly useful in supplementing the early high temperature gas-phase data. The former have the advantage that the specimen can be readily activated in solution either by deposition of a fine coating of palladium onto its surface or by prior anodic treatment. The activity of the surface towards absorption is maintained in solution for long periods of time.

The electrochemical approaches can be subdivided into two broad categories. The first category utilizes electrolytic charging or discharging of the specimen. Many of the earlier studies with this technique are of doubtful validity because they were unaccompanied by simultaneous electrode potential measurements and therefore, for example, "final hydrogen contents" do not represent any well-defined thermodynamic state.<sup>5)</sup> More recently TVERDOVSKII and his coworkers<sup>6-10)</sup> have used this technique with electrolytically deposited alloys utilizing electrode potential measurements to determine the absorption isotherms of a series of palladium-rich alloys. In the second category, developed principally by LEWIS and his coworkers,<sup>11-14)</sup> hydrogen is absorbed spontaneously from hydrogen-stirred solutions. The course of absorption is followed by simultaneous changes in the electrode potential and resistivity of the specimen. (This technique is electrochemical only in the sense that the pressure of the hydrogen within the surface layers of the specimen is determined by electrode potential measurements but absorption itself takes place *via* molecular hydrogen as in the gas phase techniques).

It can be stated with regard to these recent electrochemical studies that, in general, they have proven to be extremely useful for the establishment of the general features of the absorption behavior of alloys. For example such features of the absorption as the general shape of the isotherms, the final

*The Role of Electron Donation to Metallic Bands*

hydrogen content at 1 atm., *etc.*, can be established conveniently and rapidly. Because of the nature of this technique, *i. e.*, it is a dynamic technique, there is no assurance that the hydrogen content within the specimen is uniform and therefore the derived isotherms must be regarded with some reservations with regard to the validity of detailed thermodynamic data obtained from them. It can be stated however that values derived from two-phase electrode potential measurements appear valid<sup>1)</sup> and LEWIS and coworkers have recently shown that their data for hydrogen absorption by silver/palladium alloys using the electrochemical technique described above agree reasonably well, particularly at hydrogen contents greater than about  $H/M=0.1$ , with gas phase data obtained by BRODOWSKY and POESCHEL.<sup>15)</sup> It is likely that data obtained in the  $\beta$ -phase by this technique may be valid because the diffusion coefficient is greater in this region,<sup>16)</sup> however, detailed quantitative arguments based on diffusion measurements have not been given as yet. By contrast, in the  $\alpha$ -phase of the hydrogen/palladium system absorption from hydrogen-stirred solutions at 1 atm. pressure can lead to errors in thermodynamic data arising from nonuniform distribution of hydrogen within the specimen.<sup>17)</sup>

SIMONS and FLANAGAN<sup>17)</sup> have utilized a variant of the technique employed by LEWIS and coworkers.<sup>11-14)</sup> They employed mixtures of hydrogen and helium in order to slow down the rate of absorption to allow sufficient time for diffusion within the metal to occur. Some of their data were, in fact, taken after equilibration for many hours with a given, extremely low hydrogen pressure; this technique therefore closely resembles a gas-phase technique. This hydrogen-dilution technique has been recently extended to the low hydrogen content region of a series of gold/palladium<sup>18)</sup> and lead/palladium<sup>19)</sup> alloys.

About the same time that the electrochemical techniques were becoming sophisticated enough to yield useful data, a novel gas-phase technique was being developed by WICKE and coworkers.<sup>20)</sup> This is based on "hydrogen transfer" catalysts, *i. e.*,  $UH_3$  or copper powder, in intimate contact with the palladium or palladium alloy. This technique has allowed the determination of equilibrium data at temperatures as low as  $-78^\circ C$ .<sup>21)</sup> In the same laboratory BRODOWSKY and his coworkers<sup>15,22)</sup> have utilized this technique for a series of palladium-rich alloys. This hydrogen-transfer catalyst technique has the advantage compared to the electrochemical techniques that its temperature range is not so limited.

### Recent Theoretical Advances

The experimental approaches described above have allowed the determi-

nation of equilibrium data on the absorption of hydrogen and deuterium by a number of palladium-rich alloys. These data have been analyzed in terms of the model in which hydrogen and the added metal (in the case of an alloy in which the added metal has a filled  $d$ -band and extra electrons in its  $s$ -band) donate electrons to the combined  $s$ - $d$  bands of palladium.<sup>15,17,22-24)</sup> There have been several recent observations which lend strong support to this electron donation theory which was originally postulated by MOTT.<sup>25)</sup> (This theory has been modified slightly in the sense that it is considered that the electrons are donated to both the  $s$  and  $d$ -bands of palladium.<sup>21b,23,24)</sup>

The observation of SCHINDLER and coworkers<sup>26)</sup> that the electronic specific heat of pure palladium decreases as hydrogen is absorbed constitutes perhaps the strongest evidence in favor of the electron donation model. The extensive data obtained by BRODOWSKY and coworkers<sup>15,22)</sup> on the absorption by palladium alloys which is self-consistent when analyzed on the basis of the electron donation model, *e. g.*, tin is about four times\*) as effective as hydrogen or silver in filling in the bands of palladium with reference to hydrogen absorption also lends strong support to this model.

The band-filling effect also accounts for the relationship  $\ln p^{1/2} = -A(T) + B(T)n$ ,<sup>21,27,28)</sup> where  $n$  is the ratio of hydrogen to metal, which occurs for high values of  $n$ . (This relationship was first derived by NAKHUTIN.<sup>29)</sup> He employed several assumptions, the most important being that all of the electrons go into a parabolic  $s$ -band when this relationship obtains,  $n \geq 0.6$ . At about the same time NERNST<sup>21b)</sup> qualitatively pointed out that hydrogen donates its electrons to both the  $s$ - and  $d$ -bands of palladium and when the  $d$ -band becomes filled the logarithmic relationship obtains as then the Fermi energy of the  $5s$ -band shifts linearly as hydrogen is added. FLANAGAN and SIMONS<sup>30)</sup> later rederived this relationship independently and more generally using the experimentally derived  $s$ - $d$ -bands from the work of HOARE and coworkers<sup>31)</sup>).

Two alternate approaches, which are both within the framework of the electron donation model, have been employed for the analysis of absorption results by palladium and palladium-rich alloys. The approach of SIMONS and FLANAGAN and coworkers<sup>18,23)</sup> has been to use an approximate density-of-states relationship based on the data of HOARE *et al.*<sup>31)</sup> (and the rigid-band model) and to apply this within the LACHER approach<sup>32)</sup> with the removal of the artificial assumption of LACHER that the total number of interstitial sites is 0.6 (expressed as  $n$ ). (This artificial assumption of 0.6 as a limiting value was earlier removed by WAGNER<sup>33)</sup> and WICKE and NERNST<sup>21)</sup> and JOST<sup>34)</sup>

\*) More exactly this factor is 3.85.<sup>22)</sup>

*The Role of Electron Donation to Metallic Bands*

has pointed out its artificiality). This approach has been extended to absorption by a series of gold/palladium alloys<sup>18)</sup> considering that both gold and hydrogen fill the combined *s-d* bands of palladium.

The other approach has been based upon an earlier treatment of WAGNER<sup>33)</sup> and extended by WICKE and BRODOWSKY and their coworkers<sup>35)</sup> to include the effect of variable energy of electron donation. BRODOWSKY,<sup>15,22)</sup> in contrast to FLANAGAN *et al.* has utilized experimental absorption data to obtain the density-of-states relationships, *i. e.*, the hydrogen has been used as an experimental probe for the determination of the density-of-states relationships. An important improvement in BRODOWSKY's treatment has been to employ the quasi-chemical approximation rather than the less precise BRAGG-WILLIAMS method.

Evidence has been accumulated which indicates that the hydrogen-interaction, which must be included in the statistical model to account for the initial increase in the heat of absorption with hydrogen content and two-phase formation below the critical temperature for pure palladium and alloys with relatively low added metal content, arises from the lowering of strain energy when protons are in adjacent octahedral interstitial positions in the lattice. This suggestion of von STACKELBERG and LUDWIG<sup>36)</sup> has been developed both theoretically and experimentally by BRODOWSKY and coworkers.<sup>15,22,24,37)</sup>

Although the two treatments discussed above differ in detail, both are based upon the idea of electron donation to the empty holes in the bands of palladium or the alloy. It is believed that the results from either approach must be judged to be successful because they explain the general features of absorption behavior. It is likely that the model will be improved by, for example, the incorporation of the shifting *s*-band proposed by DUGDALE and GUÉNAULT<sup>38)</sup> into the statistical model of hydrogen absorption. It is possible that alternative models could be proposed to account for the absorption behavior but it is believed that the electron donation model explains *a priori* the many facets of the absorption behavior of palladium and its alloys, *e. g.*, either tin or lead are approximately four times as effective as silver or hydrogen in reducing absorption capacity of the metal,<sup>22)</sup> whereas an alternate model would require many *ad hoc* assumptions.

### Possible Relationship of Absorption to Chemisorption

Since some aspects of chemisorption can be considered to be two-dimensional counterparts to absorption, it is tempting to try to relate these recent advances in absorption in a very speculative way to chemisorption. Because of the difficulties in obtaining absorption data below 120°C as described above

T. B. FLANAGAN

and because of the earlier comparative lack of technological interest in absorption, greater efforts have been expended in the literature to the role of the electronic effect in chemisorption and catalysis rather than to a quantitative extension of the ideas of MOTT to absorption of hydrogen by transition metals. It is fortunate that this situation has now changed somewhat for inherently the chance of a successful treatment of absorption in terms of a quantitative electronic model is much greater than for its two-dimensional counterpart because in contrast to chemisorption, bulk properties of the metal may be used for the interpretation of absorption. It is the opinion of the author that since absorption has now been treated relatively successfully by an electronic band model, it is now worthwhile reexamining chemisorption in the light of these results. In recent years it seems fair to say that workers in catalysis have become disenchanted with models involving electronic bands of the metal catalyst.<sup>39,40)</sup>

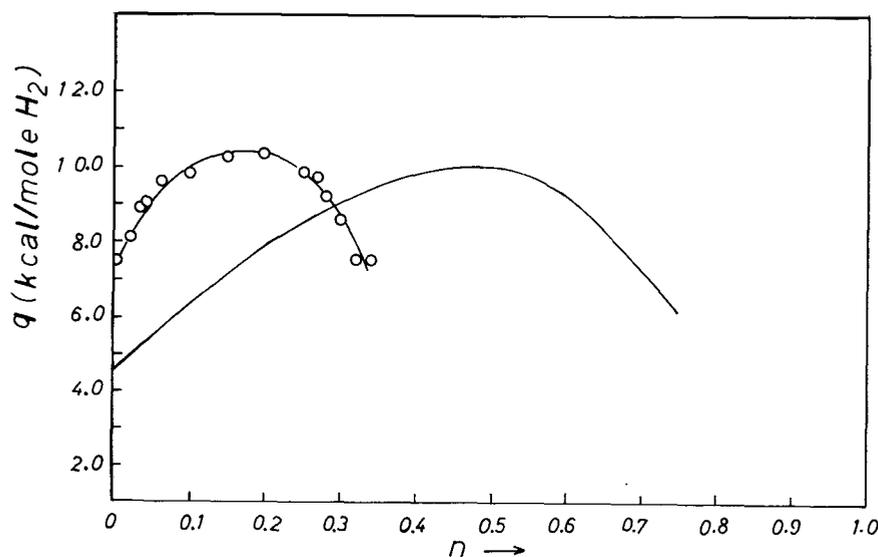
It has been postulated by TEMPKIN<sup>41)</sup> and others<sup>42)</sup> that a two-dimensional band exists at the surface of a metal analogously to the three-dimensional band in the interior of the metal and that this band may take part in chemisorption and catalysis. Electron donation to empty holes in this band or alternatively a withdrawal of electrons from a band would lead to a progressive decline in the heat of adsorption (More probably an intermediate situation would exist, *i.e.*, a localized surface band involving both protons and surface metal atoms). Now this simple picture has been criticized on several grounds<sup>43~45)</sup>—the most often repeated criticism, and the one that concerns us here, is that there is no progressive decrease in heat when hydrogen is absorbed by transition metals. With regard to the “classical” system of hydrogen absorption by a transition metal, namely hydrogen/palladium, the situation with regard to the behavior the heat of absorption (isosteric) has been clarified by the recent investigations.

It is now clear that the isosteric heat of absorption cannot be expected (except in special cases, see below) to show a progressive decline with hydrogen content such as found for adsorption. Three possibilities present themselves for the dependence of the heat of absorption upon hydrogen content for palladium and its alloys in which the added metal is an electron donor. First of all, many metal/hydrogen systems form two phases and throughout the two-phase range the heat of absorption must remain constant. (This elementary consideration has been often disregarded in the case of palladium/hydrogen, for example, the linear decrease in the magnetic susceptibility along the two-phase region frequently has been misinterpreted as has been recently pointed out by GIBB<sup>46)</sup>). Consequently for the case of an alloy in which two phases are

*The Role of Electron Donation to Metallic Bands*

formed or for pure palladium ( $<310^{\circ}\text{C}$ ), the decrease in the heat of absorption expected to arise from band filling can be observed only after the two-phase region is traversed. This is what has been observed.<sup>22,28)</sup>

For certain palladium-rich alloys the critical temperature is below room temperature so that a region of constant heat of absorption is not expected at or above room temperature. However even in the absence of two-phase formation, there is an attractive interaction between the protons.<sup>32,24)</sup> For an alloy in which the attractive interaction predominates over the effect of filling in the *s-d*-bands, the heat of absorption initially shows an increase with hydrogen content and only after the bands are filled considerably does the heat decrease. This leads to maxima in the heat of absorption with hydrogen content; such behavior is shown in Fig. 1, where an 18.8% gold/palladium alloy is compared to data for pure palladium near its critical temperature. (This latter data was kindly supplied by Professor E. WICKE and is derived from experimental data obtained at lower temperatures<sup>21)</sup>). It may be seen from Fig. 1 that the presence of gold shifts the position of the maximum to lower values of  $n$ . This is the anticipated trend if both gold and hydrogen donate electrons to the unfilled bands of palladium. Alloys which can be expected to show maxima are those in which the added metal content is



**Fig. 1.** The relationship between the isosteric heat of absorption and hydrogen content,  $n(=H/M)$ .  $\circ$ , experimental data for 18.8% atomic percent gold/palladium; solid curve, pure palladium ( $300^{\circ}\text{C}$ ) as calculated from results given in reference 21.

T. B. FLANAGAN

low compared to the number of holes in the d-band but high enough so that two phases are not formed at and above room temperature, *e.g.*, see refs. 15 and 18.

The final possibility, which does indeed lead to a progressive decrease in the heat of absorption, is the case of an alloy with a high enough added metal content so that the effect of filling in the *s-d* bands predominates over the attractive interaction. This has been observed with, for example a 44.4% gold/palladium alloy.<sup>18)</sup>

It can be concluded therefore that the predictions of the electron donation model with regard to the behavior of the heat of absorption with hydrogen content are verified experimentally in all of these cases.

It is of interest to compare the magnitude of the decline in the heats of adsorption and absorption. This comparison will be restricted to pure palladium where the heats of adsorption and absorption have been determined. For adsorption of hydrogen on palladium at  $\theta=0$ , BEECK<sup>47)</sup> has given  $q=27,500$  cal/mole  $H_2$  and the value for  $q$  for absorption at  $n=0$  is only 4,600 cal/mole  $H_2$ <sup>17,21)</sup> but this latter value includes a large contribution due to lattice strain which is presumably not present in the former value. BRODOWSKY<sup>24,35)</sup> has estimated this strain to be 8,400 cal/mole  $H_2$  (at  $n=0$ ) so that the heat of absorption in the absence of strain would be 13,000 cal/mole  $H_2$ . At  $n=0.8$  the experimental heat of absorption is 6,770 cal/mole  $H_2$ <sup>21)</sup> but again this value can be corrected to a strain-free value of 3,450 cal/mole  $H_2$ . (In keeping with the quasi-chemical approximation as applied to the hydrogen/palladium system at  $n>0.5$  the contribution due to strain to the isosteric heat is in the opposite sense to values at  $n<0.5$ <sup>24)</sup>). The only data in the literature reporting the fall in the heat of adsorption of hydrogen on palladium are those determined electrochemically by VERT and coworkers.<sup>48)</sup> There is no reason to question the validity of these data especially since they agree with BEECK's gas-phase value at  $\theta=0$ . (Indeed for the special case of hydrogen on palladium electrochemical techniques may be superior to conventional techniques because adsorption can be more readily distinguished from absorption). At  $\theta=0.8$  the heat for adsorption can be estimated from a graphical presentation of their data to be 15,000 cal/mole  $H_2$ .

Thus, the magnitudes of the decrease in the heats are 9,600 (abs.) and 12,500 (abs.). Since these decreases are of the same order of magnitude, they both may have their origins in electronic band-filling effects. Admittedly a similarity in the shape of the hypothetical two-dimensional band and the bulk band has not been demonstrated here. It is not the intention of this work to suggest that the idea of a two-dimensional band is necessarily valid.

*The Role of Electron Donation to Metallic Bands*

The motive is rather to point out that the principal extant objection to the idea has been removed and therefore a careful reappraisal seems to be in order.

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