

The Form of the Interaction between Palladium and Hydrogen

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The high diffusibility of hydrogen in solid phases of the palladium-hydrogen system allows thermodynamic equilibrium to be established over a wide range of experimental conditions. Evidence has long existed that, in the hydride phases formed, the hydrogen:palladium ratio is not simple and is a function of equilibrium pressure and of temperature. Theoretical models of the system have often centred on modifications of the palladium electron band structure due to hydrogen absorption but increasing attention has been paid to the consequences of lattice strain. The position is now reviewed in the light of recent work.

In the course of the last ten years a number of general reviews (1-6) have appeared concerning the palladium-hydrogen system. Within this same period also has occurred (and been marked by a compilation of review articles (7)) the centenary of Thomas Graham's initial observation (8) of the absorption or "occlusion" of considerable volumes of hydrogen by a palladium membrane or "septum"—prepared for his use by George Matthey.

Some thirty years after Graham's original observations isothermal studies in the temperature range 10 to 250°C of the variation of the composition of the hydrided solid as a function of the pressure of hydrogen gas in steady-state equilibrium with it had sug-

gested that these relationships were likely to be represented by a family of plots of the form shown in Fig. 1. These studies (9) by Roozeboom and Hoitsema might well be claimed to be the first examples of evidence for the non-stoichiometric and temperature-dependent composition of the solid phases represented in such diagrams.

The plots in Fig. 1—which represent results subsequently obtained (6, 10, 11) over a wider range of temperature and pressure than those presented by Hoitsema—are clearly representative of a system subject to the existence of critical phenomena. In terms of a physically descriptive correlation in this particular instance, individual isotherms may

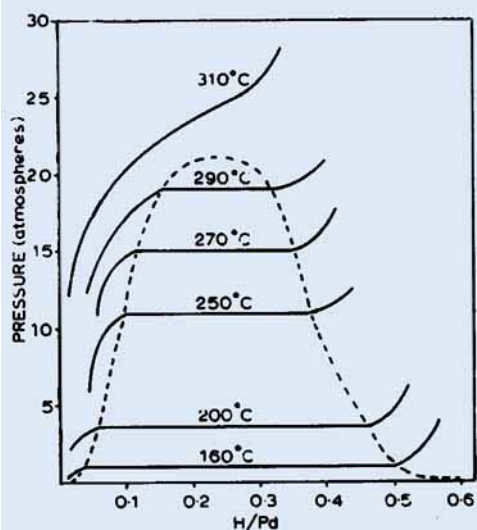


Fig. 1 A family of pressure-composition isotherms for the palladium-hydrogen system

be described, or defined, as supercritical, critical or subcritical with respect to the possibility of the co-existence within the solid of two hydride phases (the α - and β -phases), which for the cases of the subcritical isotherms can exist together in varying proportions over the ranges of composition corresponding to the horizontal "plateau" regions—the actual composition of each phase over these horizontal pressure-invariant regions corresponding with the break points of the isotherms at the beginning and end of the plateaus.

The subcritical isotherms exhibit a "hysteresis" of pressure-composition (p-c) relationships over the pressure invariant and adjacent regions, in that, for a given hydrogen content, the steady-state "equilibrium" pressures are higher when hydrogen contents are being steadily increased by the admission of successive doses of gas into the equilibrating system rather than decreased by the successive removal of incremental volumes of gas.

Theoretical Models

Clearly it is a central requirement of any theoretical model of the palladium-hydrogen system that it should be possible to be correlated with, and to account for the form of the pressure-composition relationships. In this context there are two main features of these solubility relationships which require an explanation. These are firstly the occurrence of critical isothermal behaviour, and secondly the tendency for palladium to have a limiting solubility for hydrogen at a composition which is considerably less than that which would be expected from purely geometrical considerations. This limiting solubility condition is manifested as a rapid rise in equilibrium hydrogen pressure for small changes in hydrogen content above about H/Pd = 0.60 at room temperature.

In general the interpretation of critical phenomena has been based on the early postulate of Fowler (12, 13) that an attractive interaction must occur between neighbouring absorbed species, thus resulting in the heat

of solution of hydrogen having a negative dependence on concentration (i.e., the heat of solution becomes more negative as the concentration of dissolved hydrogen is increased).

The first significant attempt to apply these concepts to the palladium-hydrogen system was made by Lacher (12, 14) in 1937 using a statistical thermodynamic approach which formed an extension of an allied treatment (13) of the problem of absorption of hydrogen by transition metals such as iron and platinum in which it is only sparingly soluble.

Recently it has been pointed out (15) that critical behaviour only requires that the heat of solution should become more negative as the hydrogen content is increased and that this does not necessarily require so specific an interaction as that between neighbouring atoms. In this case (15) the decreasing heat of solution of hydrogen is taken to be a reflection of the continuous filling of the palladium 4d-band by electrons from hydrogen atoms.

Within the more general framework of the Fowler/Smithells (13) concept of pairwise interactions the nature of this interaction has been considered by various authors (16, 17, 18, 19). This interaction has been attributed to the occurrence of electronic coupling of the screening electrons surrounding each proton (17) or more generally to be a consequence of the lower strain energy associated with paired as distinct from monoatomic species in an elastic matrix (16, 17, 18, 19). Recently, by considering the volume expansion produced in the palladium lattice due to the absorption of hydrogen, Burch (20) has derived a value for this pairwise interaction energy. The derived value is in good agreement with the experimental data which would seem to support the general view that the critical phenomena occur as a consequence of the release of strain energy associated with the clustering of dissolved hydrogen atoms.

The tendency towards a limiting solubility at about H/Pd = 0.59 led Lacher to postulate that this limit corresponded to a completely filled 4d-band and therefore that

this represented the maximum hydrogen content which would be possible without some change in mechanism. Consequently his theoretical equation contained a term such that the derived isotherm unavoidably reached a solubility limit at this composition.

The equation derived by Lacher (14) was of the form:

$$\log p^{\frac{1}{2}} = \log \left(\frac{\theta}{1-\theta} \right) - \frac{k_1 \theta}{RT} + k_2 \quad (1)$$

where $\theta = n/s$ is the ratio of the number of hydrogen atoms "n" to the maximum number of absorption sites "s" where Lacher took a value for "s" of 0.59. Lacher's apparent success in achieving a good correlation between this theoretical equation and a significant body of the experimental data led to a widespread acceptance of the general correctness of the physical model for the system which he had employed.

Important limitations of the agreement between p-c relationships derived from Lacher's theoretical equations and those obtained experimentally, especially when the artificial condition whereby "s" is put equal to 0.59 is removed, are revealed by detailed analysis of the existing data. Subsequently, however, attempts have been made to improve the agreement by extending the Lacher model while still assuming a limited number of absorption sites (21, 22, 23, 24). Modified equations have been derived from models which have variously taken account of the effects of lattice expansion (21, 22), made allowance for the occurrence of hysteresis of the subcritical isotherms (23), or considered the pairwise interaction not only of hydrogen atoms but also of vacancies and vacancy-hydrogen atom pairs (24). In all these cases, however, the limiting solubility was explained on the basis of a limited number of absorption sites.

Recently attempts have been made (15, 16, 18, 25, 26) to relate the solubility limit to variations in the energy associated with the donation of electrons by hydrogen to the 4d and 5s bands of palladium. There is as yet still some disagreement as to whether or not

the gradual filling of the 4d-band is paralleled by an endothermic (16, 18) or exothermic (15) electron donation energy term. In all cases, however, it has been assumed that, at higher hydrogen contents when the 4d-band is full, the energy required to transfer an electron from hydrogen to the 5s-band of palladium is greater than the energy which would be required, at low hydrogen contents, for a similar electron transfer to the 4d-band.

The resulting theoretical equation is of the generalised form:

$$\log p^{\frac{1}{2}} = \log \left(\frac{n}{1-n} \right) - \frac{k_1 n}{RT} + k_2 + E(n) \quad (2)$$

where $E(n)$ is a positive electronic energy term which is a function of the hydrogen content "n".

The electronic term in equation (2) has the effect of increasing the equilibrium hydrogen pressure very rapidly at hydrogen contents greater than about H/Pd = 0.6, in agreement with experiment. Only Simons and Flanagan (18) have attempted to evaluate $E(n)$ from basic principles. Using the rigid band model they have derived, from the density of states curve for palladium, an energy relationship which is of the correct form to predict a limit in the solubility at moderate pressures. A detailed analysis of these various "protonic" models has been presented elsewhere (17) and attention has also been drawn (27) to shortcomings in this model when applied to the absorption of hydrogen by palladium alloys.

The Elastic Model

Recently Burch (20) has developed the concepts of the elastic model, which had already been invoked to explain the existence of critical absorption isotherms, to account for the main features of the observed solubility behaviour. In view of the experimental observation that occupation of an interstitial site by a hydrogen atom causes expansion of the palladium lattice and consequently a displacement of adjacent palladium atoms, it was suggested that vacant sites surrounding the occupied site would be modified to varying

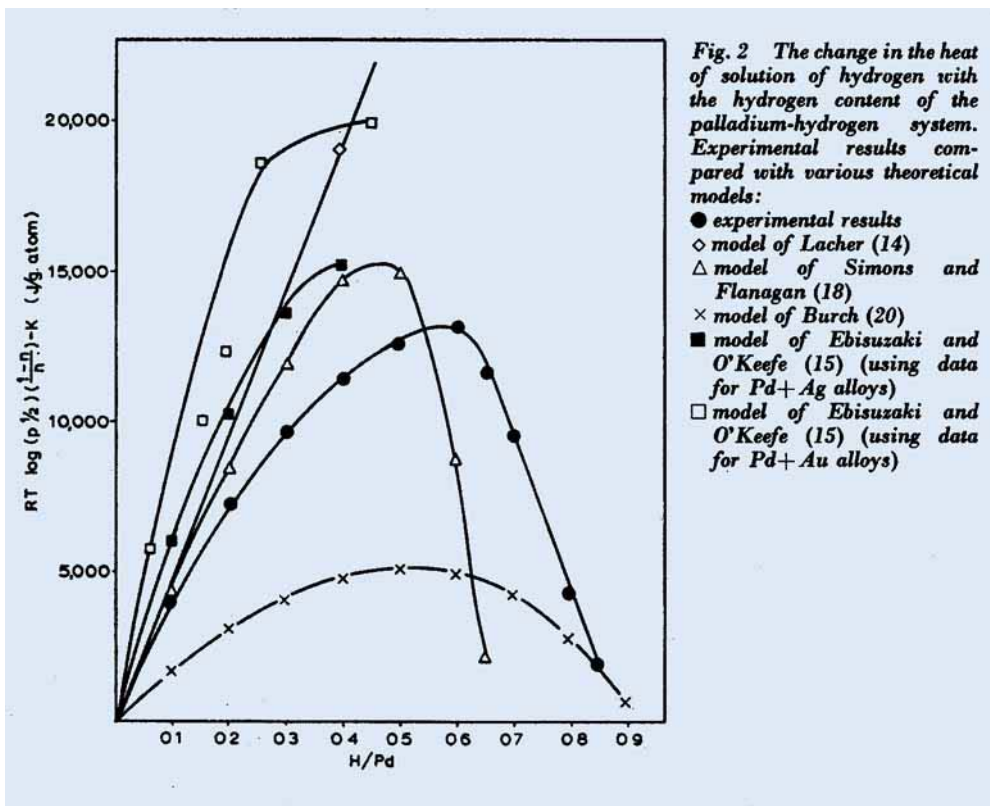


Fig. 2 The change in the heat of solution of hydrogen with the hydrogen content of the palladium-hydrogen system. Experimental results compared with various theoretical models:

- experimental results
- ◇ model of Lacher (14)
- △ model of Simons and Flanagan (18)
- × model of Burch (20)
- model of Ebisuzaki and O'Keefe (15) (using data for Pd+Ag alloys)
- model of Ebisuzaki and O'Keefe (15) (using data for Pd+Au alloys)

extents by this localised expansion. Subsequently by relating the energy required to place further hydrogen atoms in partially blocked sites to the volume change of each modified site, it was found possible to derive an equation relating the equilibrium hydrogen pressure to the hydrogen content. An error in the original equation (20) has been pointed out by Dr W. A. Oates. A corrected form of the equation is as follows:

$$RT \log \left(p^{1/2} \frac{1-n}{n} \right) - K = zW_{HH}n + \frac{2}{3}GN \left(\frac{(\Delta V + n\Delta V')^2}{(V_0 - n\Delta V')} - \frac{\Delta V^2}{V_0} \right) \quad (3)$$

where W_{HH} represents the attractive interaction between pairs of atoms, G is the modulus of rigidity of the metal, V_0 is the initial volume of an interstitial site (assumed spherical), ΔV is the increase in volume of the site after occupation by a hydrogen atom, and $\Delta V'$ is the reduction in volume of a modified site. In this model the limiting

hydrogen solubility occurs as a consequence of the increasing difficulty associated with the occupation of sites which have been modified by the presence of hydrogen atoms in adjacent, and especially next nearest neighbour, sites.

As compared to the earlier 'protonic' models this latter model has the advantage of a more general applicability to an interpretation of the behaviour of other transition metals towards hydrogen. In addition the phenomena of hysteresis of the isotherms and the peculiar absorption behaviour of palladium-nickel alloys can more readily be explained using the elastic strain model rather than the electronic model. A comparative summary of the various models is presented in Fig. 2.

It is clear that even after a hundred years of research the absorption of hydrogen by palladium still produces considerable controversy. It is probable that the isothermal relationships obtained experimentally reflect

a balance between electronic and physical effects. Thus, while there is fairly general agreement that hydrogen donates its electrons to a collective metallic electron band there is still dispute as to the effect that this can have on the energetics of hydrogen absorption. It will be of future interest to see which of the physical or electronic factors have most relevance not only in the palladium-hydrogen system but in all transition metal-hydrogen systems.

References

- 1 F. A. Lewis, *Platinum Metals Rev.*, 1960, **4**, 132; 1961, **5**, 21
- 2 G. G. Libowitz, *Binary Metals Hydrides*; W. A. Benjamin: New York, 1965
- 3 K. M. Mackay, *Hydrogen Compounds of the Metallic Elements*, Spon: London, 1966
- 4 A. Macland and T. B. Flanagan, *Platinum Metals Rev.*, 1966, **10**, 20
- 5 H. J. Goldschmidt, *Interstitial Alloys*, Butterworth: London, 1967
- 6 F. A. Lewis, *The Palladium Hydrogen System*, Academic Press, London and New York, 1967
- 7 *Engelhard Industries Tech. Bull.*, 1966, **7**, (1) and (2)
- 8 T. Graham, *Phil. Trans. Roy. Soc.*, 1866, **156**, 415
- 9 C. Hoitsema, *Z. Phys. Chem. Leipzig*, 1895, **17**, 1
- 10 P. L. Levine and K. E. Weale, *Trans. Faraday Soc.*, 1960, **56**, 357
- 11 E. Wicke and G. Nernst, *Ber. Bunsen. Phys. Chem.*, 1964, **68**, 224
- 12 R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge Univ. Press, 1939
- 13 R. H. Fowler and C. J. Smithells, *Proc. Roy. Soc.*, 1937, **160A**, 37
- 14 J. R. Lacher, *Proc. Roy. Soc.*, 1937, **161A**, 525
- 15 Y. Ebisuzaki and M. O'Keefe, *J. Phys. Chem.*, 1968, **72**, 4695
- 16 H. Brodowsky, *Z. Phys. Chem.*, 1965, **44**, 129
- 17 R. Burch, *Trans. Faraday Soc.*, 1970, **66**, 736
- 18 J. W. Simons and T. B. Flanagan, *Can. J. Chem.*, 1965, **43**, 1665
- 19 M. von Stackelberg and P. Ludwig, *Z. Naturforsch.*, 1964, **19a**, 93
- 20 R. Burch, *Trans. Faraday Soc.*, 1970, **66**, 749
- 21 A. Harashima, T. Tanaka and K. Sakaoku, *J. Phys. Soc. Japan*, 1948, **3**, 208
- 22 T. Tanaka, K. Sakaoku and A. Harashima, *Ibid.*, 213
- 23 D. H. Everett and P. Nordon, *Proc. Roy. Soc.*, 1960, **259A**, 341
- 24 R. V. Bucur and M. Crisan, *J. Phys. Chem. Solids*, 1967, **28**, 905
- 25 H. Brodowsky and E. Poeschel, *Z. Phys. Chem.*, 1965, **44**, 143
- 26 H. Brodowsky and H. Husemann, *Ber. Bunsen. Phys. Chem.*, 1966, **70**, 626
- 27 R. Burch and F. A. Lewis, *Trans. Faraday Soc.*, 1970, **66**, 727

Cubane-type Platinum Metal Complexes

Recent X-ray diffraction studies have shown that the two platinum metal complexes $[(C_2H_5)_3PtCl]_4$ and $[(CO)_3OsO]_4$ have cubane-type structure. The eight carbon atoms of cubane, C_8H_8 , are situated at the corners of a cube. The structure of $[(C_2H_5)_3PtCl]_4$ is shown in the diagram to resemble cubane and that of the osmium compound is similar, the four osmium and four oxygen atoms being at alternate corners of a cube with the osmium atoms each bound to three terminal carbonyl groups.

In a joint communication Professor Sir Ronald Nyholm and Professor Mary R. Truter (University College, London) and C. W. Bradford (Johnson

Matthey Research Laboratories) point out (*Nature*, 1970, **228**, (5272, November 14), 648-651) that Pt(IV) and Os(II) are iso-electronic and that similar structures might be expected for other iso-electronic metals, e.g. W(O), Re(I) and Ir(III). In fact

$[(CO)_2(NO)Mo(OH)]_4$ is formally of this type with one NO and two CO groups on each Mo(O) atom, OH being the negative group. The NO group is assumed to act as a uni-positive radical. Furthermore Re(I) and Mn(I) form compounds $[(CO)_3M(SR)]_4$, which have structures with cubic symmetry. So far, however, no compounds of this type have been reported for the triad Co(III), Rh(III) and Ir(III).

