

Palladium-Hydrogen System

STRUCTURES NEAR PHASE TRANSITION AND CRITICAL POINTS

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A wide ranging survey is presented updating information and opinions on the correlations which occur between structural change and hydrogen pressure-hydrogen content-temperature (p - c (n)- T) relationships in the palladium-hydrogen and other related systems. Particular attention is directed to problems of the estimation and definition of the limits of composition over the $\alpha \leftrightarrow \beta$ phase transition region and near to designated critical points.

The representation of temperature dependent forms of the families of hydrogen pressure-composition (p - c (n)) isotherms of the palladium-hydrogen system is still quite commonly shown by the diagram in Figure 1(a), which is a result of important and gradual systematic development of relevant information obtained by Sieverts and colleagues (1). In a sense, this Figure is a consolidating point in the development of such diagrammatic representations, after a period of improvements in basically similar outlines (2–5). The outlines were produced quite soon after the initial observations of the substantial absorption (occlusion) of hydrogen by palladium, without it destroying the essentially metallic characteristics of the face centred cubic (f.c.c.) palladium matrix (2–6).

The p - c (n)- T Diagram: Experimental Advantages and Developments

The quite comprehensive form of the relationship shown in Figure 1(a) often appears in textbooks as a representation of the palladium-hydrogen system and of other systems which exhibit non-stoichiometric characteristics (7).

The preferential development of relative comprehensiveness for the particular case of the palladium-hydrogen system, Figure 1(a), probably results from the conveniently accessible experimental ranges of temperature (~ 160 to 310°C) and hydrogen pressures (~ 1 to 35 atmospheres) needed to cover the whole of the data

in the Figure. Also experimentally attractive were the generally quite reasonable times required to reach equilibria under various hydrogen pressures. Ready equilibration resulted from high values for the coefficients of hydrogen diffusion (2–12) combined with acceptable efficiencies for the surface catalysis at comparatively low temperatures.

However, during the ensuing time interval up to the present, there have been considerable extensions to the range of data in Figure 1(a) in regard to higher and lower ranges of both temperature and equilibrium hydrogen pressure. For general descriptive convenience, however, the diagrammatic representation of p - c (n) relationships shown in Figure 1(a) has continued to be a commonly utilised background illustration (2–7).

Amplification of Information on the p - c (n)- T and Allied Relationships

In addition to accompanying the general improvement in experimental techniques, the extended scope of the p - c (n)- T relationships has been increasingly co-ordinated with complementary measurements of other physical and structural parameters and with information on specimen characteristics: including geometric forms, surface:volume ratios and surface catalytic activities.

Significant consolidation has been made with compatible results of the p - c (n) relationships, derived from thermodynamically equivalent

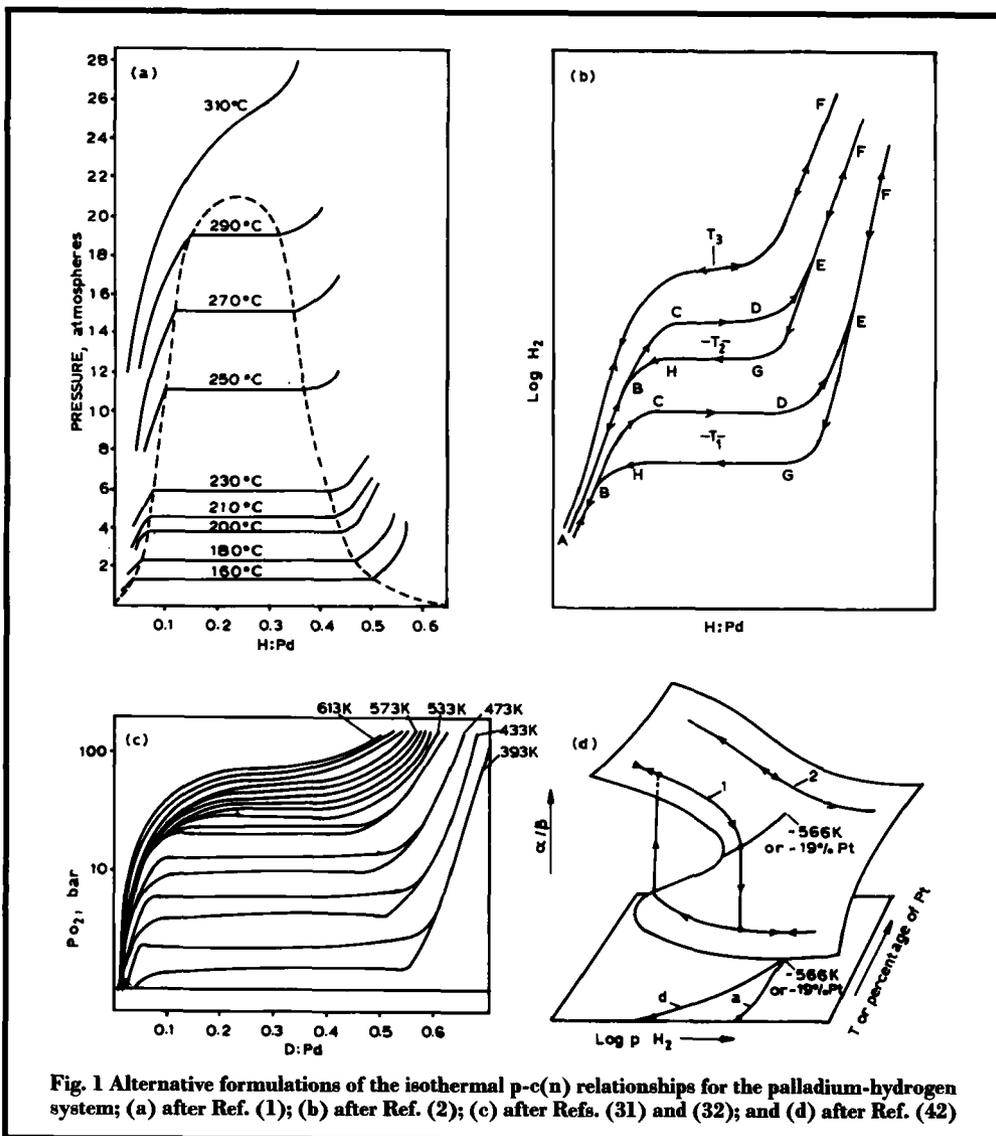


Fig. 1 Alternative formulations of the isothermal p-c(n) relationships for the palladium-hydrogen system; (a) after Ref. (1); (b) after Ref. (2); (c) after Refs. (31) and (32); and (d) after Ref. (42)

components found from potentials measured by electrodes (2, 5). Hydrogen contents have continued to be represented in various ways; but they seem most unambiguous when denoted by the atomic ratio hydrogen:palladium, generally synonymous with the commonly used symbols, n (2, 3, 13) or the alternatives r (14, 15), ρ (15, 16) or c (17, 18).

A generalising factor of structural importance has been acceptance of the findings, from neutron scattering (19) and channelling (20) tech-

niques, that the hydrogen entities which expand the lattice, occupy preferentially the octahedral interstices of the f.c.c. palladium lattice.

Hysteresis

A central and basic elaboration to the p-c(n) relationship of Figure 1(a) has been the early observed discovery (1-6) that, at temperatures below about 310°C, plots of the results form a "hysteresis loop". The shape of the loops, shown in Figure 1(b), is dependent upon whether the

respective measurements have been made by a succession of increases (absorption) in, or decreases (desorption) in, hydrogen content. Such regions of hysteresis are paralleled by analogous hysteretic differences in plots of hydrogen content and lattice parameters (2, 21), and also hydrogen content and various physical parameters, such as electrical resistivity (2, 22, 23) and magnetic susceptibility (2, 3, 24).

As Figure 1(b) indicates, the extent of the hysteretic differences formally decreases in magnitude with increasing isothermal temperature. This is shown by sequence: $T_1 \rightarrow T_2 \rightarrow T_3$, where T_3 represents a formally denoted critical temperature $T_c(\alpha, \beta)$ above which absorption and desorption relationships involving pressure or other parameters ostensibly seem to be coincident.

Comments on Figures 1(a) and 1(b)

In commonly accepted correlations of the main features in Figures 1(a) and 1(b) the initial "reversible" lower hydrogen content p-c(n) regions, such as **AB** in Figure 1(b), are regarded as corresponding to areas where the solid solution of hydrogen occupies octahedral interstitial positions in the f.c.c. lattice (for example References 1–10, and 13–22). The ranges of hysteretic irreversibility diagrammatically represented by **BCDEFGH** in Figure 1(b), have generally been associated with regions of coexistence (transition) of α -phase and β (α') phase hydride structures.

Finally, formally reversible p-c(n) regions, such as **EF** in Figure 1(b), (with higher hydrogen contents than those where the hysteresis loops are closed, at points such as **E**) have been associated with regions where the solid solution of hydrogen occupies the residual octahedral interstices (which could be regarded as in a defective sodium chloride lattice) up to values of $n \sim 1.0$ that may be attained (at 25°C) in equilibrium with very high hydrogen pressures (2, 25).

Phase Regions of Apparent Reversibility of p-c(n) Relationships

If it may be assumed that the influence of sub-surface hydrides and lattice defects (2, 3, 5) can be neglected and if bulk lattice palladium

hydride is regarded as a point of reference, then regions such as **AB** in Figure 1(b) may be broadly defined as ranges where Sieverts' Law applies:

$$n = \text{constant} \times \sqrt{p}$$

Extrapolations of this form of relationship have been employed to estimate upper limits of these regions, which are conventionally defined as α_{max} (2, 3).

Up to these formal α -phase limits a measure of effective overall reversibility in the physical properties of the specimens, over numerous hydrogen absorption and desorption cycles, has been shown in the course of work on electrolytic hydrogen isotope diffusion, separation and exchange (2, 9, 26).

Interpretations of Hysteresis

Since the early recognition of such hysteresis phenomena (1, 2, 3–5, 14, 27–29) there has been substantial additional information (2, 3, 5, 30–32) about the limits of the hysteresis loops, about estimates of values of the associated critical temperatures and about variations in the geometric and particulate forms of the palladium sample.

There have also been ongoing discussions as to whether measurements taken during a hysteresis loop have corresponded to conditions of thermodynamic equilibrium.

In principle, when both α - and β -phase hydrides are present the corresponding hydrogen pressure during the phase transition is expected to remain invariant, from consideration of the Gibbs Phase Rule in the form:

$$F = C + 2 - P$$

corresponding to only one permitted degree of freedom, F, in conditions of 2 components C and 3 phases P.

Universal Thermodynamic Equilibrium Viewpoint

Nevertheless, Ubbelohde argued quite early on (33), after considering the available relevant experimental results (1, 2), that from a thermodynamic standpoint it was justified to regard the hysteresis phenomena in palladium-hydrogen

and allied condensed phase systems by a modified form of the Phase Rule:

$$F = C + 2 - P + \Sigma n$$

where Σn represents a thermodynamically permitted inclusion of terms appropriate to involved factors, such as elastic strain conditions and particle size. Such an extension of the Phase Rule would allow possibilities for establishing true thermodynamic equilibrium within a wide range of experimental conditions, including each section of the hysteresis loops.

This extended perspective is consistent, for example, with measurements of electrode potential E , hydrogen pressure p and relative electrical resistance R/R_0 , recorded together during formulations of p - $c(n)$ (1-3, 22-30, 27, 30-32), E - n (2, 22, 23, 34) and of important associated R/R_0 - n relationships, being independent of the length of the equilibration times. These interrelationships all can exhibit substantial hysteretic differences between the absorption and desorption data, including the strikingly clear findings of "hydrogen content shut-in" effects (34).

Statistical Thermodynamic Approach

Explanation based on an extended Phase Rule have since, however, been largely discounted, in preference to the arguments of a statistical thermodynamical analysis (14, 27) in which both absorption and desorption p - $c(n)$ isotherms have been regarded as representing conditions of merely quasi-equilibrium. Limitations to establishing effective states of thermodynamic equilibria for either the absorption or desorption isotherms also seem to have been accepted in analyses of recent hysteresis studies where it has been broadly advanced that the hysteretic differences are largely associated with irreversible processes of fissuring and deformation resulting from the generation of complex dislocation networks (5, 28).

Current Interest in Hysteresis Energetics

Irreversible dissipation of energy is certainly involved in the deformation and fissuring of specimens. This factor does, however, repre-

sent a different effective variable from the more elastically reversible factors, such as those associated with the structure differences between regions with the same total hydrogen content but different combinations of precise structural compositions (22).

A quite recent appreciation of Ubbelohde's approach to the problem by Baranowski has seemed, however, to provide an initiative for a more quantitative form of analysis (29), based on associating hysteresis with calculations of energetic differences which complement the stresses produced by the hydrogen.

Gorsky Effect Involvements in Hydrogen Systems

This more recent energetically-centred approach (29) has encouraged a rather similar explanation, based on a strain gradient difference factor, which is related to interpretations of Uphill Effect studies of hydrogen permeation along lines of strain, that involve the interstitial diffusion mechanism introduced earlier by Gorsky (35).

Thus, for absorption isotherms during the course of the $\alpha \rightarrow \beta$ phase transitions, supplementary energy components may be necessary to override the addition of stress energy equivalents to strain gradients between α -phase regions of low hydrogen content and substantially more expanded β -phase regions (2-5).

Hysteretic differences which have been found for the p - $c(n)$ desorption isotherms may then be attributed to a reduced influence from the strain gradient in the $\beta \rightarrow \alpha$ phase transition region, and lower desorption hydrogen content in the β -phase component domains during the desorption cycle, at the same overall hydrogen content (22).

Substantial experimental evidence of the influence and complex operation of strain gradient participation, has recently been obtained from hydrogen diffusion processes occurring within α and $\alpha + \beta$ phase hydride compositions of palladium membranes (10, 26-39).

The increasing interest and quite quantitative information now available on stress and strain factor participation in hydrogen interstitial

thermodynamics (10, 29, 35–39) has appeared to support Ubbelohde's essential hypothesis that, in principle, all sections of hysteresis loops can represent points of establishment of thermodynamic equilibrium (33).

Relationships "Supercritical" to Apparent Hysteresis Elimination

Over latter years, Wicke and colleagues have presented several series of reports of detailed absorption and desorption p - $c(n)$ isothermal relationships of both the palladium-hydrogen and palladium-deuterium systems (3, 24, 30–32). Detailed measurements of the dependence of magnetic susceptibility on the hydrogen and deuterium contents have been reported in conjunction (3, 24, 31–32).

The example illustrated in Figure 1(c), for the palladium-deuterium system (31, 32) provides a clear demonstration of the gradual reductions, with increasing isothermal temperature, of the extent of the p - $c(n)$ hysteresis loops. However, Figure 1(c) also illustrates the strong persistence of very similar s-shaped forms of the relationship over a substantial range of temperatures, extending above a cited critical temperature $T_c(\alpha, \beta)$ of 556 K (283°C), that has been associated with an apparent total elimination of hysteresis (31, 32).

Somewhat analogous extended temperature ranges of p - $c(n)$ isotherm plots bearing close similarity to critical forms have also been recorded in the p - $c(n)$ relationship of several palladium alloy hydrogen systems. In these cases, the range of supercritical temperatures of isotherms exhibiting pronounced stretches of s-shaped plots has been so prolonged as to suggest their alternative descriptions as regions of "quasi two-phase" or "ghost-two-phase" coexistence (2, 22, 25).

Other attention has been drawn to an essentially analogous pattern of high temperature p - $c(n)$ relationships in the palladium-hydrogen system, which had been considered in conjunction with the shape of the electrical resistivity hydrogen content (R/R_0 - n) relationships. These latter relationships were indicated to be only gradually modified from the forms char-

acteristic of well designated regions of $\alpha \leftrightarrow \beta$ phase transitions at lower temperatures (2, 25, 40). Such combined evidences for extended supercritical p - $c(n)$ region retentions of indications of domain or quasi β -phase structures also would seem to fit in with current interpretations of the dependence of elastic energy dissipation (Q^{-1}) peaks on hydrogen content, in palladium-silver alloys, and of interpretations of similar trends in the R/R_0 - n relationships with alloy composition for both the palladium-silver-hydrogen and the palladium-gold-hydrogen systems (40, 41).

Catastrophe Theory Representations

It has been suggested (2, 42) that the retention at higher temperatures of s-shaped regions above $T_c(\alpha, \beta)$, in combination with the hysteretic differences between absorption and desorption p - $c(n)$ isotherms at lower temperatures, may be suitably accommodated and represented by a cusp catastrophe type of format, as illustrated in Figure 1(d).

In Figure 1(d) the ratio α/β , of contributions from the α - and β -phase hydride structures, has been adopted as the composition variable for which finite values continue to persist (curve 2) at temperatures higher than $T_c(\alpha, \beta)$, ~ 566 K, for p - T relationships in the palladium-hydrogen system, and also in comparison with an analogous critical percentage at 25°C of approximately 19 per cent platinum in the hydrogen pressure-percentage of platinum relationship of the palladium-platinum-hydrogen system (42).

Extensions of Limits of Hysteresis Loops

It was also established early (1, 22, 25) that boundaries of p - $c(n)$ hysteresis loops, such as **DEG** and **CBH** in Figure 1(b), extended beyond the limits of the more horizontally linear sections of the loops, as for example the **CD** and **HG** regions in the same Figure.

Further confirmation of the continuation of the loops (for instance the **CBH** region in Figure 1(b)) has been provided by evidence, from X-ray lattice parameters, of the appearance of β -phase structures at hydrogen contents and pressures

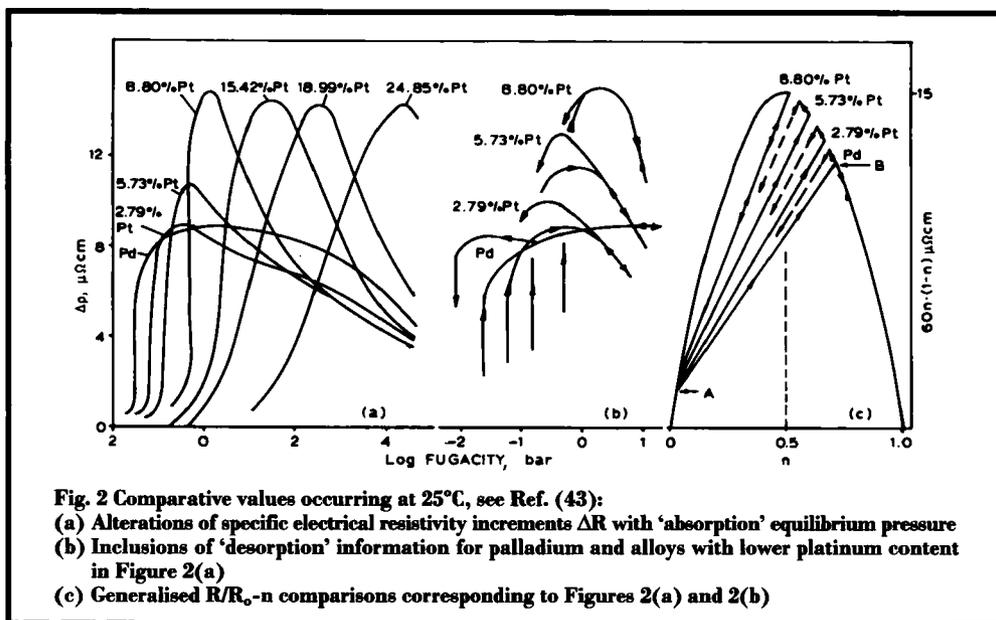


Fig. 2 Comparative values occurring at 25°C, see Ref. (43):
 (a) Alterations of specific electrical resistivity increments ΔR with 'absorption' equilibrium pressure
 (b) Inclusions of 'desorption' information for palladium and alloys with lower platinum content in Figure 2(a)
 (c) Generalised R/R_0 -n comparisons corresponding to Figures 2(a) and 2(b)

in advance of their anticipated appearances (2, 21) over the main $\alpha \leftrightarrow \beta$ phase transition region (for example **CD** in Figure 1(b)).

Complementary evidence was also obtained of α -phase spectral line appearances within regions (such as **EG** in Figure 1(b)) of higher hydrogen content and pressure than over the main linear regions of the $\beta \leftrightarrow \alpha$ phase transition, for example **GH** in Figure 1(b) (21). These phase relationship and crystallographic indications of regions of hysteresis loop extensions also have appeared to be paralleled by seemingly analogous findings from electrical resistance measurements (22, 23, 34). Here features of desorption R/R_0 -n relationships indicative of the nucleative emergence of α -phase regions have interconsistently appeared at hydrogen contents corresponding again to ranges of n (such as **EG** in Figure 1(b)) higher than those of the main (for example **GH** in Figure 1(b)) regions of the desorption transition.

Extension into Regions of Seeming Reversibility

The importance of continuing the hysteretic differences into the more obviously extended regions of the hysteretic loops (represented by

regions **CBH** and **DEG** in Figure 1(b)) has been further endorsed by an analysis of an extensive study of the phase relationships for the palladium-platinum-hydrogen system (25, 42). For this system, patterns of changes in the p-c(n) and the R/R_0 (ΔR)-n relationships with the content of platinum are partly illustrated in Figures 2(a) and 2(b).

An extension of the arguments, which are based upon the information represented in the diagram shown as Figure 1(d), have recently produced explanations for the obvious hysteretic features that are illustrated in Figure 2(b) (43).

In addition a computational analysis, which is based upon the proposition of extensions to the regions of coexistence of the α -phase and β -phase domain structures beyond the more generally accepted hysteresis limits, (and focused on the outline models of the catastrophe theory that are shown in Figure 1(d)), has been used to account for the p-c(n) relationships of the palladium-hydrogen system, and then also to complementarily explain the forms of the relationships of the palladium-platinum-hydrogen system, which are illustrated in Figures 2(a) to 2(c) (43).

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Dispersion Strengthened Platinum-Based Alloys

Mechanical Properties of Metallic Composites, Materials Engineering 7

EDITED BY S. OCHIAI, Marcel Dekker, New York, 1994, 808 pages,

ISBN 0-8247-9116-9, U.S. \$195

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