

# The H-Pd (Hydrogen-Palladium) System

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## Equilibrium Diagram

The Pd-H system is the paradigm of metal hydrogen systems: the longest studied (since 1866 [1866Gra]), the easiest to activate for hydrogen absorption, and probably the richest in the number of physically interesting phenomena that have been observed in this type of system. In matters of the thermodynamics of hydrogen absorption, the details of phase diagram delineation, description and analysis of electronic properties and a number of other features, work on the Pd-H system has tended to provide leading developments that have subsequently been used in other metal-hydrogen systems.

The  $T$ - $X$  phase diagram (Fig. 1) assessed here for pressures\* above  $10^2$  Pa, consists of the  $\alpha$  and  $\alpha'$  phases, in both of which the H occupies, randomly, the interstitial octahedral sites of the fcc Pd lattice. Table 1 gives the crystal structure and the lattice parameters of the system.

The  $\alpha$  phase is the low-concentration phase of the system, separated from the high-concentration  $\alpha'$  phase by a mixed ( $\alpha + \alpha'$ ) phase region. The boundary of this mixed phase region was delineated by taking an average of the limiting  $T$ - $X$  values for the isotherm plateaus (see Fig. 2) determined by [64Wic], [73Fri], [83Las], [85Las], and [87Wic] from experimental  $P$ - $X$  isotherms shown in Fig. 3. Because hysteresis\*\* is observed in absorption and desorption isotherms for  $T < T_c$  [36Gil, 60Eve, 89Fla], it is possible to draw two different sets of boundaries for the mixed-phase region at each temperature. For clarity, only  $P$ - $X$  desorption isotherms reproduced from the available literature are displayed in Fig. 3. (See further discussion on locating coexistence boundaries below.)

At  $\sim 25$  °C, the maximum H solubility in the  $\alpha$  phase is  $X = 0.017$  (1.68 at.% H), whereas the single  $\alpha'$  phase exists for  $X > 0.60$  (37.6 at.% H). The two-phase region in Fig. 1 bounded by the coexistence curve closes at the critical point located at  $T =$

293 °C,  $X = 0.29$  (22.5 at.% H), and  $P = 20.15 \times 10^5$  Pa (see Table 2). There is no distinction between the  $\alpha$  and  $\alpha'$  phases above this critical temperature consistent with the applicability of the lattice gas model for the Pd-H system [60Hil, 69Ale, 76Man]. Table 2 compares critical point parameters reported for the Pd-H system. Values obtained by [78Pic] are not included because they lack the overall consistency of those quoted in Table 2, and there is no compelling reason to try to justify this. With the exception of the values from [74Rib1], the critical point parameters have all been observed from analysis of absorption/desorption isotherms only.

[37Lac1] used what amounted to a lattice gas calculation in the Bragg-Williams (i.e. mean field approximation [37Lac2]) to calculate the form of the Pd-H absorption isotherms and, using the Maxwell equal area rule, to determine the location of the  $\alpha/\alpha'$  coexistence curve. [37Lac1] used the experimentally determined location of the critical point (i.e.  $T_c$  and  $X_c$  [36Gil]) to fix the value of the attractive H-H interaction and the value he assumed for the maximum permitted H concentration. The [37Lac1] calculation, apart from giving the first statistical thermodynamic model for H absorption in Pd-H, provided a parametric relation for analyzing the absorption of H in Pd, which is useful today (see "Solubility"). However, the

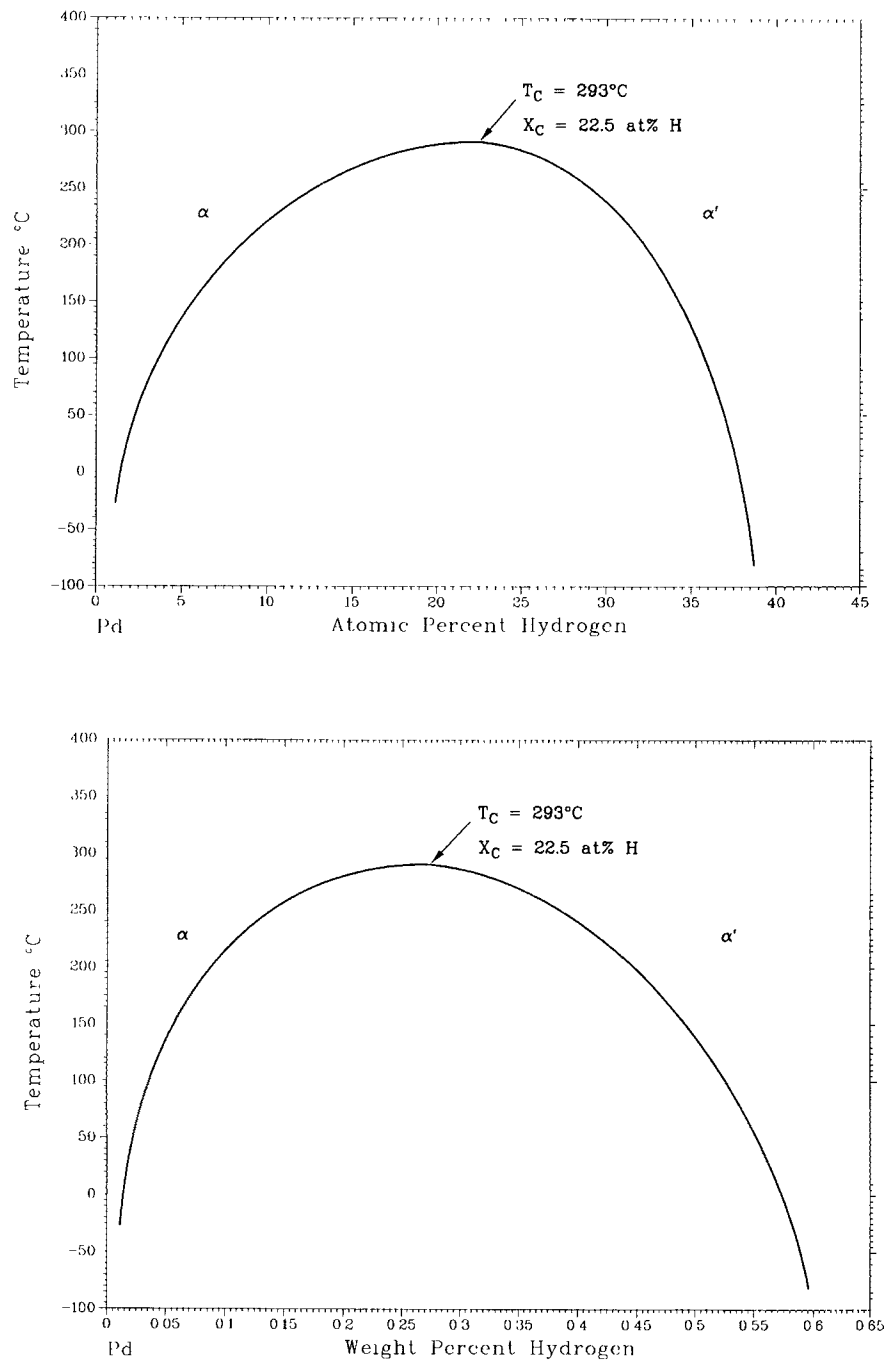
\*For H-in-metal systems, the equilibrium pressure of the H gas surrounding the metal is always a significant thermodynamic variable, in contrast to most situations involving metallic alloys. Thus, sections of the  $P$ - $X$ - $T$  surface in a  $T$ - $X$  plane and a  $P$ - $X$  plane are always necessary. In the presentation given here,  $P$  is the pressure in pascals,  $T$  is the temperature plotted in both K and °C, and  $X$  is the H concentration expressed either as atomic percent H or as  $X = \text{H/Pd}$ , the atomic ratio.

\*\*Hysteresis in metal-hydrogen systems with mixed phase regions, as in the  $\alpha/\alpha'$  regions of the Pd-H system, arises from plastic deformation due to a large volume change as one phase, e.g.  $\alpha$ , changes to the other, e.g.  $\alpha'$ , or vice versa (see [89Fla]).

Table 1 Pd-H Crystal Structure and Lattice Parameter Data

Phase	Composition, at.% H	Pearson symbol	Space group	Strukturbericht designation	Prototype	Lattice parameters, nm			Comments	Reference
						<i>a</i>	<i>b</i>	<i>c</i>		
Pd .....	0	<i>cF4</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	A1	Cu	0.38874	...	...	At 20 °C	[78Kin]
(Pd) .....	0 to ~2	<i>cF8</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	B1	NaCl	0.3895	...	...	At 25 °C	[64Mae]
$\alpha'$ .....	~37.6	<i>cF8</i>	<i>Fm</i> $\bar{3}$ <i>m</i>	B1	NaCl	0.4025(a)	...	...	At 25 °C	[64Axe,64Mae]
<b>Low-temperature ordered phases</b>										
A <sub>2</sub> B <sub>2</sub> .....	39.9 at.% D	<i>tI12</i> (b)	<i>I4</i> <sub>1</sub> / <i>amd</i>	<i>C</i> <sub>c</sub>	PdH <sub>0.5</sub>	0.402	0.805	1.207	At -230 °C	[78And2] (c)
A <sub>4</sub> B .....	43.2 at.% D	<i>tI10</i>	<i>I4</i> / <i>m</i>	<i>D1</i> <sub>a</sub>	Ni <sub>4</sub> Mo	0.639	0.639	0.404	At -203 °C (d)	[79Eil, 81Bla]

(a) In the literature this has often been referred to as the  $\beta^{\text{min}}$  value for the Pd-H lattice parameter [75Sch]. (b) This structure is an ordered arrangement of vacancies in the fcc H(D) lattice on interstitial octahedral sites in the Pd lattice. The Pearson symbol has been chosen to count both the vacancies and the interstitial H(D) corresponding to a structure that is stoichiometric at  $X = 0.5$  to maintain consistency with the usual listings of this symbol for tetragonal structures. (c) Values for lattice parameters of tetragonal cell estimated from [75Sch] with the help of [84Hem] for the  $X$  value and temperature given by [83Bon]. (d) As in (b), except that counting interstitials together with vacancies corresponds to a structure that is stoichiometric at  $X = 1$ . (e) Values for lattice parameters of tetragonal cell estimated from [75Sch] with the help of [84Hem] for the  $X$  value and temperature given by [79Eil]. The sets of tetragonal lattice parameters referred to in (c) and (e) are for PdD<sub>X</sub>.



**Fig. 1** Assessed Pd-H phase diagram.  $T$ - $X$  projection from a  $P$ - $X$ - $T$  surface onto a plane at  $P = 10^2$  Pa.

[37Lac1] model was not founded on an assessment of the basic mechanisms responsible for the attractive H-H interaction or on other basic physical features of the Pd-H system. Also using a lattice gas calculation [79Die] estimated values for  $T_C$  and  $X_C$  and the form of the coexistence curve, which were roughly comparable to those obtained from experiment. [79Die] used a

description of the elastic contribution to the H-H interaction, which was based on the earlier work of [74Wag] and [74Hor], and added to this an estimate of the electronic contribution to this interaction. To obtain numerical estimates, [79Die] used experimental data from independent measurements on several basic physical properties of the Pd-H system without reference