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A Review of the Thermodynamics and Phase Relationships in the Palladium-Hydrogen, Palladium-Deuterium and Palladium-Tritium Systems

R.P. Santandrea and R.G. Behrens

Materials Chemistry Group, Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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ABSTRACT

Thermodynamics and phase relationships in the Pd-H, Pd-D, and Pd-T systems have been reviewed and compiled into a comprehensive summary. Phase diagrams, crystal structures, pressure-composition-temperature (p-c-T) data, thermodynamic data, and diffusion and isotopic separation data are all discussed in this report. Thermodynamic data are collected and summarized in tabular form for easy reference and review.

1. INTRODUCTION

This report is a review of select physico-chemical properties of the palladium-hydrogen-deuterium and tritium systems. This report provides a survey of the scientific literature between 1900 and 1985. To facilitate compilation of results, and to gain a better understanding of the development of research in the scientific areas addressed here, the work in each area is reviewed and discussed in a loose chronological order.

Several reviews of the Pd-H (-D, -T) systems are available in the scientific literature and are referenced here for completeness /1-8/.

Section 2 of this report summarizes and describes the basic phase relationships within the Pd-H, -D and -T systems. This includes a general description of the phase diagram, phase boundaries, and critical point data for all three systems.

Crystal structures that have been reported for the Pd-H and Pd-D systems are discussed in Section 3. This section summarizes lattice parameter data for the well known α and β phases, and also includes discussions of other crystal structures that have been produced under novel conditions.

Pressure-composition-temperature (p-c-T) studies are reviewed in Section 4. When possible, a brief description of sample preparation and experimental technique is presented. Equations describing various p-c-T relationships, if available from the literature data, are also presented.

Reported thermodynamic data for the Pd-H, -D, and -T systems are summarized in Section 5. In addition to experimental data, theoretical calculations of the standard enthalpy of formation for palladium hydride are also described.

Diffusion and isotopic separation of hydrogen isotopes in palladium are described briefly in Section 6. Equations for the calculation of separation factors and diffusion coefficients are also presented in this section.

Appendices A and B summarize information on phase relationships and crystal structure, respectively. Appendix C is a collection of H_2, D_2 and T_2 pressures, calculated from equations given in the text, for the α, $\alpha+\beta$, and β phase regions of each system. Appendix D presents a summary of enthalpies and entropies of desorption and absorption.

2. PHASE RELATIONSHIPS

The basic features of the palladium-hydrogen phase diagram are well known. Figure 1, compiled

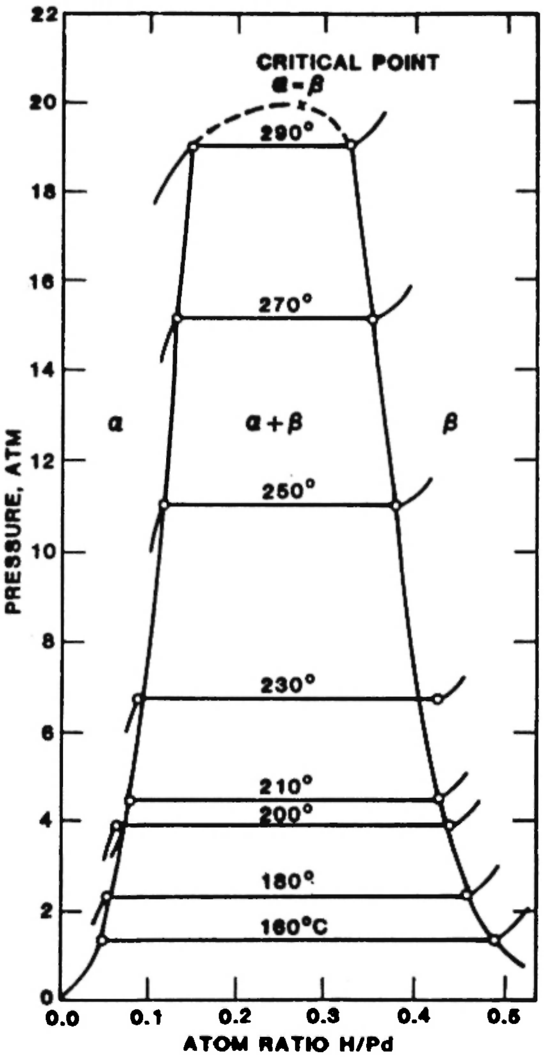

Fig. 1: Palladium-Hydrogen phase diagram compiled by Ref. 9.

by Hansen /9/, summarizes early results for $r \leqslant 0.5$ (r is the ratio of moles of H to moles of Pd in the solid phase). Three regions exist in the phase diagram: a solid solution (α) phase region at low hydrogen concentrations; a hydride (β) phase region at high hydrogen concentrations; and a broad two phase ($\alpha + \beta$) region. While Hansen /9/ gave only approximate values for phase boundaries, more recent studies /10-14/ give r values for phase boundaries as a function of temperature. Appendix A summarizes the concentration limits for pure α and pure β phases. Aside from these three regions, the Pd-H system exhibits other features. A critical point occurring at about 568 K, 19.87 atm H_2 and r = 0.27 was first reported by Gillespie and Gaulstaun /15/. Critical point values of $T_c = 564 \pm 2$ K, r = 0.250 and P_c and 19.7 ± 0.2 atm H_2 were also obtained from magnetic susceptibility measurements /11/. Calorimetry studies /14/ have produced critical point values of $T_c = 567$ K, r = 0.241 and $P_c = 19.35$ atm H_2. Critical point data are summarized in Appendix A, Table A-4. Nace and Aston /16/ have also described an anomaly in the heat capacity of Pd_2H at 55 K.

The palladium-deuterium and palladium-tritium systems are similar to the palladium-hydrogen system, forming analogous α and β phases with closely corresponding intervals of miscibility /10-13/. A similar critical point /17/ and heat capacity anomaly /18/ have also been observed in the Pd-D system.

3. CRYSTAL STRUCTURE

Both the α and β phases in these systems have a face centered cubic (fcc) crystal structure. The α phase of Pd-H has a lattice parameter of 0.3902 nm at the saturation limit of the single phase region /9/. This value is only slightly larger than the lattice parameter of 0.3891 nm for elemental palladium. In the α phase the hydrogen atoms are tetrahedrally arranged around random palladium atoms situated at corner sites in the Pd face centered cubic lattice /18, 19/.

Formation of the Pd-H β phase results in an abrupt expansion of the fcc lattice, producing a lattice parameter of 0.4026 nm at the boundary of the pure β phase /9/. The lattice parameter of the beta phase hydride increases with increasing hydrogen concentration and has been tabulated as a function of hydrogen pressure /20/ as well as hydrogen concentration /21/. To illustrate the magnitude of lattice expansion with increasing hydrogen or deuterium content, Schirber and Morosin /21/ extrapolated x-ray diffraction data measured over the concentration range $0.8 < r < 0.98$ to obtain lattice parameters for r = 1.0. They obtained values of 0.4090 nm and 0.4084 nm for PdHx and PdDx respectively. Electron diffraction studies /22/ have shown that the β hydride structure is one in which the hydrogen atoms are situated in the octahedral holes in the Pd lattice.

Other crystal structures have been reported for the Pd-H and Pd-D systems. Ordered phases of hydrides and deuterides, where r = 0.64 and r = 0.76, have been detected below the transition temperature of 50 K /23/ and after annealing at 70 K /24/. According to ref. /24/, deuterium atoms order on the interstitial fcc lattice with every fifth (4, 2, 0) plane vacant, corresponding to a Ni_4Mo structure.

Using palladium blacks with different crystallite sizes, Everett and Sermon /25/ determined lattice parameters for the α and β phases at 303 K and 333 K. Lattice parameters were found to be independent of crystallite size, changing only with the amount of absorbed hydrogen. On the basis of x-ray diffraction results obtained at 333 K, two additional face centered cubic hydride phases were identified. The phase labeled as δ by the authors has a lattice parameter of a = 0.3943 nm at the lower concentration limit of the $\alpha + \beta$ region. Similarly, the phase identified as γ has a lattice parameter of a 0.3960 nm at the lower $\alpha + \beta$ phase boundary. The lattices of these phases were found to expand when hydrogen is absorbed above the minimum concentration of the pure β phase.

Semiletov *et al.* /26/ described a superstoichiometric (r = 1.33) γ tetragonal hydride with lattice parameters of a = 0.2896 nm and c = 0.3330 nm. This structure was synthesized by either of two methods: bombardment of palladium films with hydrogen ions; or heating of Pd films to 873 K in 1 atm of hydrogen followed by rapid cooling. The same authors later reported a γ' primitive cubic phase with a = 0.2995 nm. This phase was obtained when the γ phase is heated in either a hydrogen atmosphere or in vacuo /27/. Structural data for the Pd-H and Pd-D systems are summarized in Appendix B.

4. PRESSURE-COMPOSITION-TEMPERATURE STUDIES

Pressure-composition-temperature (p-c-T) relationships in the palladium-hydrogen, palladium-deuterium, and palladium-tritium systems have been studied extensively. These investigations are discussed in chronological order in this section. A compendium of select calculated pressures is given in Appendix C.

Brüning and Sieverts /28/ studied the absorption of hydrogen on palladium wire in the range 160–310°C and up to 28 atm H_2 pressure using manometric techniques. Sievert's law, given by the equation

$$C = k \cdot \sqrt{P} \tag{1}$$

describes the dependence of the H/Pd ratio, C, as being proportional to the square root of the H_2 pressure, P, in the α phase region at a constant temperature. Hysteresis effects were observed upon measurement of desorption isotherms.

Gillespie *et al.* /15, 17, 29/ measured the absorption of hydrogen and deuterium in palladium manometrically. The Pd substrate was a "black" prepared by reducing palladosamine chloride with dry hydrogen. After achieving equilibrium hydrogen pressures, which were too low to be measured over the two-phase region at 0°C during the desorption cycle, Gillespie and Hall /29/ heated the sample to 200°C. Following this heat treatment, the equilibrium pressure was restored to a measurable, higher value at 0°C. A similar heat treatment was not applied by Gillespie and Gaulstaun /15/, who determined the critical point in the Pd-H system to be at 295°C, 19.87 atm and r = 0.27. For the $\alpha + \beta$ region, the equation

$$\log P(\text{atm}) = 4.6018 - 1877.22/T \tag{2}$$

was derived from their p-c-T data. The hydrogen pressures reported in ref. /29/ were low in comparison to those given by eq. (2). From their analysis of the phase diagram, Gillespie and Gaulstaun /15/ also identified the existence of the compounds Pd_8H, Pd_4H, Pd_3H and Pd_2H.

Lacher /30/ used a statistical mechanical treatment to generate isotherms which were in good agreement with the experimental results found in ref. /15/. The limiting Pd/H ratio is s = 0.59, according to Lacher. The equation

$$\log P(\text{atm}) = 2\log \frac{r}{s - r} + 4.61 - \frac{891 + 1973(r/s)}{T} \tag{3}$$

reported by Lacher, relates equilibrium hydrogen pressure to hydrogen concentration in the solid α phase and to temperature.

Deuterium absorption in palladium black was studied by Gillespie and Downs /17/. They observed that prior treatment of the metal greatly influenced the measured D_2 pressures. For example, the Pd sample initially used in this study was left standing in the reaction cell for nine months and had become "inactive", as evidenced by a discrepancy with H_2 isotherms obtained by Gillespie and Gaulstaun /15/ and Gillespie and Downs /17/. Freshly prepared palladium was used in subsequent experiments and reproducible results were obtained for H_2. Anomalous D_2 absorption isotherms were obtained when fresh samples of Pd, not previously exposed to hydrogen, were used. "Normal", reproducible D_2 absorption curves were obtained only after the so-called "virgin" palladium samples were first treated with H_2 at 250°C. This behavior, according to the authors, could be attributed to the reluctance of deuterium to form the α phase.

The critical solution temperature for the Pd-D system was found to be 276°C. This corresponds to a pressure of 35 ± 0.5 atm and a value of 0.25 for the D/Pd ratio. The temperature dependence of the D_2 pressure in the $\alpha + \beta$ region in this system is given by the equation

$$\log P(\text{atm}) = 4.6630 - 1696.11/T \tag{4}$$

A phase diagram for the Pd-D system, including pressure data gathered in the temperature range 200–300°C, is given in ref. /17/. The deuterium pressure observed above a given solid composition in the Pd-D system was greater than the H_2 pressure in the Pd-H system in equilibrium with a solid having the same composition. The ratio of deuterium to hydrogen pressure is given as a function of temperature by the expression

$$\log(P_{D_2}/P_{H_2}) = 0.0312 + 181.71/T \tag{5}$$

Perminov *et al.* /31/ studied high pressure (up to 1700 atm) behavior of the Pd-H_2 system over the temperature range −78°C to 100°C. Data for the β phase region up to an r value of 0.92 were reported. Three palladium samples – a 0.11 mm diameter wire; a powder prepared by reducing palladosamine chloride with hydrogen; and a powder prepared by reducing palladosamine with hydrazine – were used as substrates. Results obtained with the two powders were in agreement but solubility data collected with the palladium wire differed significantly from the results obtained using the powders. A linear relationship between P and r exists in the β phase region. Values of the coefficients a and b for the equation

$$\ln P(\mathrm{atm}) = a + br \qquad (6)$$

were derived from experimental measurements. Hydrogen pressures calculated from eq. (6) are listed in Appendix C. Electrochemical measurements also performed in the β phase region by Perminov *et al.* /31/ produced results which were consistent with their pressure measurements.

Moon /32/ summarized the results of refs. /15, 17/, and /28-31/ in an attempt to characterize the Pd-H alloys as normal homogeneous solutions. Data from these six sources were subjected to an analysis which was based on the fact that the logarithm of the activity coefficient of a dilute solute can be expressed as a power series in the concentration. Results reported by Bruning and Sieverts /28/ and Gillespie *et al.* /15, 17, 29/ were amenable to this analysis. Moon developed the expression

$$\log P^{1/2}(\mathrm{mm}) = \log r + 4.200 - 521.9/T - 926r/(T - 215) \qquad (7)$$

based upon the previously reported pressure-composition-temperature data mentioned above. Good agreement among eq. (7) and earlier experimental results, particularly those of refs. /15, 17/, and /29/ was reported by Moon.

In the first of a series of articles, Nace and Aston /33/ discussed the results of manometric experiments on a palladium hydride which was assigned the composition Pd_2H. The palladium black used to synthesize the hydride in these studies was "special grade" and supplied to the authors by a commercial firm. The palladium had a reported purity of 99.9% and was described as *very active.* The sample of palladium had a density of $0.6\ \mathrm{g\,cm^{-3}}$, in comparison to the density of bulk Pd, which is $12.0\ \mathrm{g\,cm^{-3}}$. An absorption isotherm was measured at 30°C and compared to the 30°C desorption isotherm reported in ref. /29/. The authors used the similarity between these two isotherms to imply that true equilibrium had been attained in the absorption measurements and attributed this result to the use of finely divided palladium as a substrate. The actual H_2 pressures measured by Nace and Aston /33/ at 30°C were about 1.5 mm below those reported in ref. /18/.

Ratchford and Castellan /34/ determined the H_2 saturation in the two phase $\alpha + \beta$ region using electrochemical techniques. Different types of palladium electrodes including wires, foils, and beads prepared by melting metal wires were studied. Based upon the experimental relationship between electrode potential and temperature, the expression

$$\log P(\mathrm{atm}) = 5.0968 - 2028.2/T \qquad (8)$$

for the H_2 saturation pressure above the two-phase region was derived.

Levine and Weale /35/ further extended the pressure and temperature ranges studied in the palladium-hydrogen system, using high pressure Bourdon gauges. Absorption isotherms over palladium rod (99.9% quoted purity) were determined up to 990 atm in the super critical region from 326°C to 477°C. A maximum value of 0.69 for the H/Pd ratio was obtained at 326°C and 990 atm. In contrast, a limiting value of 0.59 was previously suggested by Lacher /30/. Ref. /35/ also presents a Pd-H phase diagram covering the composition range $0.0 \leqslant r \leqslant 1.0$. This phase diagram, reproduced in Fig. 2, was compiled from isotherms reported by various investigators /15, 17, 29, 31, 35/. This provided a fairly complete summary of p-c-T studies up to this point.

Wicke and Nernst /10/ measured the solubility of hydrogen and deuterium in palladium over the temperature range −79°C to 50°C using elemental copper and uranium as transference catalysts. Volumetric measurements employed different types of palladium samples. Palladium "sheets" were used for studies of the α, $\alpha + \beta$ and β regions while Pd black was used for studies of the $\alpha + \beta$ and β regions. Absorption isotherms were measured in all three phase regions. The onset of β phase formation was impeded by carefully controlling addition of gas to the system. Pressures measured during absorption and desorption cycles in the pure α phase region were in agreement within the reported error limits of the measurements.

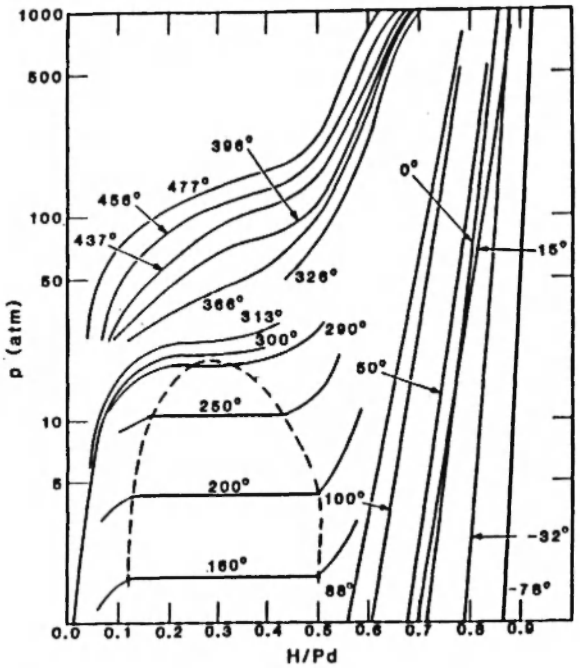

Fig. 2: Palladium-Hydrogen p-c-T data compiled by Ref. 35.

Wicke and Nernst also reported interesting observations regarding their experimental results. For a given value of r, the equilibrium D_2 pressure was three to five times greater than the corresponding H_2 pressure. Over the pure β phase, the desorption pressure was closest to the true equilibrium pressure. Less hysteresis was observed in the $\alpha + \beta$ region when Pd black was used as a substrate, although pressure equations, which were determined using different types of palladium, lie within experimental error limits. The use of different transference catalysts did not appear to affect experimental results.

Wicke and Nernst drew four major conclusions concerning the Pd–H and Pd–D systems. First, the onset of β hydride formation is hindered when "compact" palladium is used as a substrate. When this type of palladium is used, a maximum pressure is attained over the α phase just prior to β phase formation. The authors claimed that this behavior is analogous to a drop in potential observed in electrochemical measurements on the Pd–H system just before plateau voltages are reached /34/. No such effects were observed for the reverse β to α reaction.

Secondly, both absorption and desorption isotherms are truly horizontal when Pd black is used as a substrate. In the presence of "compact" palladium, the absorption isotherm passes through a minimum and then increases when the above mentioned hindrance of β phase formation is observed. If no hindrance of the α to β transition occurs, then the absorption isotherm above the compact metal is horizontal. Desorption isotherms above "compact" palladium were observed to always be horizontal.

Thirdly, the hydrogen pressure measured above compact palladium is greater than that measured above Pd black in the absorption branch of any given isotherm.

Finally, Wicke and Nernst noted that pre-treatment of the metal significantly influences the absorption pressure, while desorption isotherms are not as strongly dependent upon sample history. Cycling a "compact" palladium sample through repeated absorption and desorption reduces the amount of observed hysteresis. The lattice expansion that is required to transform the α phase to the β phase is more strongly opposed than the transition from the β to α form. The authors therefore concluded that "mechanical tension" plays a role in the α to β transition kinetics.

Because no observable effects on desorption isotherms in the $\alpha + \beta$ region due to pre-treatment or type of palladium were found, Wicke and Nernst /10/ stated that their desorption pressures represented a condition where the system was close to, if not at, equilibrium. The measured desorption hydrogen pressures were therefore used to determine enthalpies and entropies of desorption for the two-phase region. The temperature dependence of the H_2 desorption pressure in this region is given by the equation

$$\ln P_{H_2}\,(\text{atm}) = -4693/T + 10.97 \qquad (9)$$

The expression

$$\ln P_{D_2}\,(\text{atm}) = -4469/T + 11.78 \qquad (10)$$

describes the temperature dependence of the D_2 desorption pressure above the two-phase solid. The higher D_2 pressures which were observed were attributed to the higher entropy of desorption of D_2. No significant differences in desorption pressures were observed when either Pd black or compact Pd was used as the substrate. For the region where only the α phase exists, the equations describing the temperature and composition dependences of H_2 and D_2 are

$$\ln P_{H_2}\,(\text{atm}) = 12.9 + 2\ln\frac{r}{1-r} - \frac{r}{T}\left[\frac{2330}{r} + 4530 + \frac{2.017 \times 10^6}{T}\right] \quad (11)$$

and

$$\ln P_{D_2}\,(\text{atm}) = 12.8 + 2\ln\frac{r}{1-r} - \frac{r}{T}\left[4530 + \frac{1900}{r} + \frac{1.813 \times 10^6}{T}\right] \quad (12)$$

respectively. The respective H_2 and D_2 desorption pressures above the hydride (β) phase are given by the expressions

$$\ln P_{H_2}\,(\text{atm}) = 12.9 + 2\ln\frac{r}{1-r} - \frac{1}{T}(12070 - 10830r) \quad (13)$$

and

$$\ln P_{D_2}\,(\text{atm}) = 12.8 + 2\ln\frac{r}{1-r} - \frac{1}{T}(11490 - 10830r) \quad (14)$$

Wicke and Nernst /10/ extrapolated their pressure data to the critical region and found that their calculated pressures were in good agreement with the experimental results of Gillespie *et al.* /15, 17, 29/. In contrast, electrochemical experiments by Ratchford and Castellan /34/ gave H_2 pressures which are twice as high as those determined from the volumetric measurements reported in ref. /10/ and ref. /15/. This discrepancy has been attributed to continuous "loading" of the palladium wire submerged in solution used in the studies of ref. /34/.

Ref. /10/ lists phase boundary concentrations in the Pd–H and Pd–D systems for the temperature range –78°C to 75°C. The highest H/Pd and D/Pd ratios reported in this work are 0.84 and 0.78, respectively.

Baranowski /36/ suggested that the solubility of hydrogen in metals can be increased by treatment of a palladium metal substrate with thermodynamically active hydrogen. While so-called kinetic methods for the production of active hydrogen species such as H^+ and H may give rise to situations where significant deviations from thermodynamic equilibrium occur, static techniques, particularly at very high pressure, do not present such problems. In addition, hydrogen deviates considerably from ideal gas behavior at high pressures and is therefore more thermodynamically active than expected under these conditions. The fugacity of H_2 may in fact be several orders of magnitude greater than the corresponding hydrostatic pressure.

Tkacz and Baranowski /37/ performed *in situ* high pressure studies of hydrogen absorption by palladium over the pressure range 1–12 kbar at 25°C, 45°C, and 65°C. Compositions within the range $0.85 \leqslant r \leqslant 1.0$ were investigated. The H/Pd ratio did not exceed unity – a condition where the number of hydrogen atoms in the solid exceeds the number of octahedral sites within the palladium lattice. Assuming that the hydrogen concentration in the solid varied with H_2 pressure according to eq. (6), the authors used values of a and b reported in ref. /10/ to calculate concentrations for the low pressure segments of the experimentally obtained isotherms. In general, this analysis yielded higher hydrogen concentrations than those actually observed. Two opposite effects are produced by high H_2 pressures, according to ref. /37/. The increased H_2 pressure results in an increase in the thermodynamic activity of hydrogen, which in turn results in higher solubility of hydrogen in the metal. At the same time, an increase in the hydrostatic pressure reduces the hydrogen concentration in the solid due to the positive partial molar volume change in the solid.

Tritium solubility in bulk palladium was measured in the pure α phase by Schmidt and Sicking /38/. These authors used copper as a transference catalyst and measured tritium pressures manometrically. Tritium pressures were varied from 0.0013 to 0.05 atm and desorption isotherms were obtained over the temperature range 25°C to 70°C. Experimental results were expressed in terms of Sievert's Law /28/ (eq. 1).

Picard *et al.* /14/ recorded desorption and absorption isotherms at 245°C during calorimetry experiments where palladium foil was used as a substrate. The equilibrium H_2 pressure measured during absorption in the two phase region was found to be 10.15 atm. The desorption pressure was 8.90 atm.

The effect of palladium grain size upon absorption and desorption was studied using simultaneous sorption and x-ray diffraction techniques /25/. Crystallite size was varied from 0.007 to 0.140 microns. In order to avoid sintering of the finely divided palladium, measurements were limited to the 195 K to 333 K temperature range. The authors analyzed their results by considering the amount of hydrogen absorbed internally within the solid. That is, by determining the number of palladium atoms on the surface of the material, the number of adsorbed hydrogen atoms as well as the amount of hydrogen absorbed within the bulk of the powder can be determined.

Based upon this analysis, the amount of hydrogen absorbed should depend upon crystallite size. The absorption isotherms show the smaller the particle size, the smaller the hysteresis loops that are present. At low temperatures, the observed hysteresis loops approach the vertical loops reported in ref. /10/. The smaller hysteresis loop area is caused by decreasing absorption and increasing desorption pressure which accompany a decrease in Pd crystallite size. A decrease in particle size also causes a corresponding increase in the concentration limit of the pure α phase as well as a decrease in the β phase boundary. Most of these trends occurred within the particle surface area range 0–20 m^2/g. This corresponds to a reduction in particle size to 0.020 microns. Below this particle size adsorption and desorption properties remained essentially constant. The authors state that hysteresis would not eventually disappear with a further reduction in crystallite size. This is based on the observation that hysteresis still persists when 0.007 micron powder is used as a substrate.

Tritium solubility data were extended by Lasser and Klatt /12/ to include the $\alpha+\beta$ and β regions of the phase diagram. Pressure-composition-temperature measurements were performed over the pressure range 0.1–2 atm; over the composition range $0.2 \leqslant r \leqslant 0.65$; and over the temperature range 35°C to 125°C. Absorption and desorption isotherms were measured in the hydrogen-palladium and deuterium-palladium systems, while only the desorption isotherms in the tritium-palladium system were investigated. Results obtained for the Pd-H and Pd-D systems were in good agreement with those reported in ref. /10/. Concentrations for the β phase boundaries for different temperatures for all three systems and coefficients in eq. (6) for the Pd-H, Pd-D, and Pd-T systems are given in ref. /12/. The authors report that, under all experimental conditions, solubility decreases from H to D to T at equal temperature and pressure. Similarly, at equal concentrations and temperature, $P_{T_2} > P_{D_2} > P_{H_2}$.

Sicking /39/ used isotope separation data to determine the desorption pressure of the pure β tritide in the concentration range $0.650 \leqslant r \leqslant 0.775$. He supplemented his results with data from ref. /10/ to estimate the attractive energy of tritium atoms within the palladium lattice. The expression

$$\ln P_{T_2}\,(\mathrm{atm}) = 12.4 + 2\ln\frac{r}{1-r} - \frac{1}{T}(11099 - 10820r) \qquad (15)$$

describing the T_2 pressure above the β phase, was obtained using eq. (14), which is found in ref. /10/.

Absorption of hydrogen onto thin Pd films has been investigated by Bakker *et al.* /40/. Palladium films were evaporated onto both gold and quartz substrates and absorption and desorption isotherms were measured using a microbalance. The gold substrates were found to alloy with the palladium film, as indicated by a decrease in plateau widths for measured isotherms in the 400 K region. Pressure-composition absorption isotherms for a 122 nm thick Pd film on a quartz substrate revealed that the critical temperature and pressure of the Pd-H system had been lowered to 470 K and about 3.1 atm. Desorption isotherms produced a critical temperature of 450 ± 10 K. The critical concentration (H/Pd) was found to be 0.26. Plots of ln P vs 1/T obtained from absorption and desorption pressures showed that heats of absorption and desorption for Pd films did not significantly differ from those for bulk palladium. Although the binding energy of a H atom to an interstitial site is more negative in Pd films than in a bulk sample, the H-H interactions are less attractive in thin films due to boundary conditions imposed by the substrate. The variation of binding energies from palladium films to bulk samples is therefore compensated in each case. Both absorption and desorption enthalpies should not differ from one state to another.

Additional experiments were performed in the 300 K to 500 K temperature range by the same group of researchers /41/. To avoid interdiffusion of the gold or silver backing into the palladium films, Pd was evaporated directly onto quartz substrates. All hydrogen isotherms obtained for thin films deviated markedly from those of bulk material. In addition to lowering of the critical point, as described in ref. /40/, the $\alpha + \beta$ region was considerably narrower for the thin films. Absorption and desorption pressures above the thin films were approximately the same as those reported for bulk samples. It should be added that the palladium samples were "activated" by exposing them to 10 to 20 absorption-desorption cycles prior to the measurement of the isotherms.

The rate of hydrogen desorption from palladium foil, powder and wire has recently been investigated using thermal desorption spectroscopy /42/. This tehcnique measures the rate of desorption into a volume with a pressure which is lower than the equilibrium pressure while the temperature is increased linearly with time. The desorption of hydrogen consists of two steps, either of which may be rate limiting. Hydrogen atoms first must diffuse from the bulk to the surface and then pass through a surface layer, where they then combine to form H_2. Experimental results show that, due to shorter diffusion paths, desorption from palladium powder and foil is surface limited. In contrast, desorption from Pd wire is diffusion limited, as analyses of desorption rates indicate that hydrogen concentration gradients exist within the sample. Based upon threshold temperatures and desorption peaks, hydrogen desorption from palladium foil exhibits a rate-limiting step which is intermediate between wire and powder samples.

Additional desorption spectroscopy measurements /43/ provided information on the rate of hydrogen desorption from palladium powder with a particle size of about 2 μm. In this study, spectra were taken for various initial concentrations ($0.89 \geqslant r \geqslant 0.04$) as well as for different sample heating rates. All samples exhibited a desorption peak whose onset was apparently independent of initial hydrogen concentration. This corresponded to desorption from a two phase solid. When $r \geqslant 0.6$, a peak was observed at lower temperatures, indicating desorption from the β phase. The threshold temperature for β phase desorption decreased with increasing initial hydrogen concentration.

The onset of desorption for $0.89 \geqslant r \geqslant 0.60$ as well as the onset of desorption from the two phase solid can be described by an Arrhenius-type expression, thereby enabling the determination of activation energies. For β phase desorption, the activation energy varied with initial hydrogen concentration and ranged from 1037 cal/mol H_2 for $r = 0.60$ to 595 cal/mol H_2 for $r = 0.89$. An average value of 1291 cal/mol H_2 was obtained for the activation energy of desorption in the $\alpha + \beta$ region. The authors concluded that, since the observed desorption rates corresponded to low diffusion coefficients, the rates must be determined by either phase transformations or surface processes. Since both α and β phases are explicitly in equilibrium with each other, desorption must be limited by a surface process – namely, the recombination of hydrogen atoms to form H_2.

The same authors also performed temperature programmed absorption studies of hydrogen in palladium powder over the 80 K to 480 K temperature range /44/. This technique measures the amount of hydrogen absorbed by the metal as the temperature is linearly increased with time. The initial absorption was found to be an Arrhenius-type process, with an average activation energy of 3.80 kcal/mol H_2. The concentration region over which this behavior was observed was $0.001 \leqslant r \leqslant 0.01$. The difference between this activation energy and that reported in ref. /43/ for desorption is due to the higher hydrogen concentrations studied in the earlier paper.

Pressure-concentration-temperature isotherms for thin palladium-hydrogen films were measured volumetrically as well as with a quartz crystal microbalance /45/. Four palladium film thicknesses 98.0, 67.0, 49.0 and 31.0 nm, were prepared and p-c-T data for each were collected at 300 K. The experimental results show that the character of the p-c-T relationship is essentially the same as that observed for bulk palladium. Both pure α and β phase regions have steep slopes whereas the two phase region has a negligible slope. The onset of the pure β phase region, however, occurs at much lower hydrogen concentrations. For films having thicknesses of 98.0 and 67.0 nm, the minimum H/Pd ratio for the pure β phase is 0.50. This decreases to 0.46 for 4.90 nm films and 0.38 for 31.0 nm films. This trend, according to the authors, suggests that there is a threshold film thickness between 50.0 and 65.0 nm below which hydrogen absorption properties change.

No numerical values are given in ref. /45/ for either absorption or desorption pressure. In the two phase region, an absorption pressure of 0.013

atm (10 torr) and desorption pressure of 6.6×10^{-3} atm (5 torr) have been estimated from the plotted data.

Areas of hysteresis loops were plotted as a function of film thickness. Loop area decreases with decreasing film thickness, and the authors of ref. /45/ claim that this effect parallels that observed for palladium black having different grain sizes /25/.

The dependence of the p-c-T curves upon the number of adsorption/desorption cycles was also studied in ref. /45/. The curve for the as-deposited film was very rounded, having no clear plateau region. With increased cycling, the characteristic shape of the Pd-H p-c-T curve developed. About fifteen cycles were required to produce a sharp p-c-T diagram.

Whereas alloying of a gold substrate with palladium films affected earlier p-c-T measurements /40/, the extent of such interaction upon the results reported in ref. /45/ were assumed to be negligible, as the films in this case were not annealed and data were collected shortly after the metal films were deposited. Slight discrepancies exist between p-c-T results obtained from volumetric data and those obtained from microbalance data /45/. Microbalance isotherms were more rounded and the maximum concentration of the pure α phase was significantly higher. The authors suggested that this may not be an artifact of the microbalance data, but offered no further explanation for the observed differences.

5. THERMODYNAMICS

Thermodynamic studies of the palladium-hydrogen system have usually been presented as an integral part of most p-c-T studies. Many of the investigations described in the previous section have also included isosteric measurements of absorption and desorption enthalpies. In addition, other works have reported thermodynamic data obtained from electrochemical /34/, calorimetric /14, 16, 18/ and x-ray diffraction /20/ measurements. The thermodynamics of the Pd–H, Pd–D, and Pd–T systems will be discussed in this section. The collected results of the studies discussed in this section are summarized in Appendix D.

As with the previous section, thermodynamic results will be presented in chronological order rather than grouped together by isotopic system. Many authors have discussed thermodynamic results for the Pd-H and Pd-D systems, and, in at least one case, all three isotopic systems were discussed either in the same work or in a series of publications. Describing the results in chronological order, therefore, allows the results reported for different isotopes to be better examined for consistency.

Gillespie *et al.* /17, 29/ measured isosteric heats of solution for the Pd-H and Pd-D systems. The enthalpy for the solution process increases with hydrogen content, from a value of −6000 cal at low hydrogen concentrations (pure α phase) to −8860 cal along the horizontal absorption isotherms $(\alpha + \beta)$, to −9740 cal for higher hydrogen concentrations (pure β phase). These results were integrated by Gillespie and Hall /29/ to give heats of solution of −8780, −8700 and −8450 cal/mol H_2 at 0°C, 30°C and 80°C, respectively. A later p-c-T study by Gillespie and Downs /17/ on the Pd-D system also indicated an increase in heat of solution with increasing D_2 concentration. The enthalpy of solution, or, the heat per mole required for conversion from the α to the β phase, was reported to be 7760 cal/mol.

Isosteric heats of desorption and absorption of hydrogen were reported by Nace and Aston /33/. Pressure measurements made while the sample was heated from 45°C to 75°C yield a heat of desorption of 8870 cal/mol H_2. This value is in good agreement with that reported in ref. /29/. Measurements made while decreasing the temperature, however, produced an enthalpy of desorption of 9440.8 cal/mol H_2. Heats of desorption of 9330, 9440 (after the Pd black sample had stood for two months, having been subjected to temperatures from 15 K to 300 K) and 10,300 cal/mol H_2 were obtained from pressure measurements made during calorimetry experiments. The discrepancies existing among these values and previous results were attributed to a lack of internal equilibrium in the calorimetric studies.

An evaluation of heats of absorption and desorption was also presented in ref. /33/. The average enthalpy of absorption at 30°C was −9605 cal/mol H_2 in the $\alpha + \beta$ region. Combination of the above value with the single absorption enthalpy value of −8948 cal/mol determined for the α phase /33/ yielded an enthalpy of −9440 ± 45 cal/mol for the reaction

$$4Pd(s) + H_2(g) = 2Pd_2H(s) \qquad (16)$$

Nace and Aston /33/ report that poor agreement was obtained between measured heats of desorption and adsorption due to the absence of equilibrium during desorption. The authors also reported an entropy change of −23.50 ± 0.19 cal/deg · mol for the above reaction at 30°C.

The zero point entropy of Pd_2H was determined using adiabatic calorimetry /16/. Heat capacities of elemental palladium and palladium hydride having a (H/Pd) ratio of 0.487 were measured from 16 K to 303 K. At 0 K, the entropy of Pd_2H approaches a value of 0.59 ± 0.18 cal/deg · mol, and $S^{\circ}_{303.2} - S^{\circ}_0$ is 6.66 ± 0.16 cal/deg · mol. A heat capacity anomaly occurring at 55 K reported in ref. /16/ is attributed to the onset of molecular rotation within the solid. The authors also assert that the non-zero entropy of palladium hydride at 0 K is due to some degree of randomness in the arrangement of hydrogen atoms within the palladium matrix.

Using the same type of active palladium and calorimeter as in the study of ref. /16/, Nace and Aston /18/ studied the absorption of deuterium in Pd. In the $\alpha + \beta$ region, an enthalpy of absorption of −8379 cal/mol D_2 was determined at 30°C. The isosteric heat over the 0°C–33°C range for a D/Pd ratio of 0.479 is −8635 cal/mol D_2.

The heat capacity of Pd_2D was measured over the 15 K to 152 K and 279 K to 301 K temperature ranges, respectively. A heat capacity anomaly for Pd_2D was observed at 57.5 K, shifting upward from the transition temperature of 55 K for Pd_2H /16/.

Thermodynamic data were obtained by Ratchford and Castellan /34/ by measuring palladium electrode potentials over the 25°C to 60°C temperature range. A standard heat of solution of −9280 ± 100 cal/mol H_2 was obtained for the two phase region. For comparison with their results, these authors also list a number of other enthalpy values, dating back to the year 1873.

Studies in the super critical region of the Pd-H system (326°C–477°C) have been used to calculate isosteric heats of solution from the H_2 fugacity and temperature /35/. The resulting enthalpies of absorption are listed as a function of the (H/Pd) ratio in Table 1.

The x-ray diffraction study of the Pd-H system described in ref. /20/ also yielded a heat of absorption. From plateau pressures, i.e. the pressure over the $\alpha + \beta$ region, an absorption enthalpy of −9.5 kcal/mol was obtained.

Enthalpies of desorption in all three regions (α, $\alpha + \beta$, β) of the Pd-H and Pd-D systems were determined by Wicke and Nernst /10/. In the α region, the respective desorption enthalpies for H_2 and D_2 were found to be temperature dependent and are given by the equations

$$\Delta H^{\circ}_{H_2}\ (\mathrm{cal/mol}) = 4620 + 9000(1 + 445/T)r \tag{17}$$

and

$$\Delta H^{\circ}_{D_2}\ (\mathrm{cal/mol}) = 3770 + 9000(1 + 400/T)r \tag{18}$$

TABLE 1. Isosteric Heats of Absorption of H_2 on Palladium vs. H/Pd Ratio as Reported by Levine and Weale /35/

H/Pd	$-\Delta H^{\circ}$ (kcal/mol H_2)
0.225	11.0
0.3	10.2
0.35	9.4
0.4	8.2
0.45	7.2
0.5	6.8
0.55	5.4
0.6	3.2
0.65	2.8

Eqs. (17) and (18) were used to derive eqs. (11) and (12), respectively, which describe the pressure above the α phase in both systems.

The desorption enthalpies and entropies for the $\alpha + \beta$ region of the Pd-H and Pd-D systems were reported in ref. /10/ to be independent of temperature. Values of ΔH° = 9325 ± 100 cal/mol and ΔS° = 21.8 ± 0.2 cal/deg · mol were obtained for the palladium-hydrogen system. The enthalpy and entropy of desorption of D_2 were found to be ΔH° = 8880 ± 100 cal/mol and ΔS° = 23.4 ± 0.2 cal/deg · mol. The higher entropy for D_2 desorption accounts for the higher D_2 pressures which are actually observed.

Wicke and Nernst /10/ also provide desorption enthalpies for the β, or hydride, phase. The respective heats of desorption of H_2 and D_2 in this region are given by the equations

$$\Delta H^{\circ}_{H_2}\ (\mathrm{cal/mol}) = 23970 - 21500r \tag{19}$$

and

$$\Delta H^{\circ}_{D_2}\,(\text{cal/mol}) = 22820 - 21500r \qquad (20)$$

The desorption enthalpies and entropies obtained by ref. /10/ for the two-phase region may be compared to the values reported by other authors /15, 17, 34/. Gillespie *et al.* /15, 17/ list somewhat smaller values of ΔH° and ΔS°. Ref. /34/ reports a value of 9280 cal/mol for the heat of solution of H_2 in Pd, in good agreement with results reported by Wicke and Nernst /10/. An entropy of 23.6 cal/deg · mol H_2 obtained from electrochemical measurements /34/ is somewhat larger, however. Differences in entropies have been attributed by the authors of ref. /10/ to continuous "loading" of the palladium wire submerged in solution /34/.

In situ high pressure studies /37/ over the concentration range $0.85 \leqslant r \leqslant 1.0$ yielded molar free energies, from which enthalpies and entropies were determined. The thermodynamic quantities are strongly dependent on the hydrogen concentration when $r > 0.90$. For example, the value of ΔH°, taken from the plot of enthalpy vs. composition presented in ref. /37/, varies from −5 kcal/mol at $r \cong 0.90$ to −10 kcal/mol at $r \cong 0.95$.

Calorimetric studies /14/ at 245°C yielded a heat of solution of −4.6 kcal/mol H in the $\alpha + \beta$ region. This corresponds to a value of −9.2 kcal/mol H_2. The enthalpy values obtained are found to be independent of hysteresis effects.

Enthalpies and entropies at 303 K were calculated from data obtained using palladium blacks having different crystallite size /25/. The effect of crystallite size upon ΔH° and ΔS° is small. Results are presented graphically, and a value of 5.0 kcal/mol H for the heat of absorption in the two phase region is estimated from the plotted data found in ref. /25/. Similarly, ΔS°_{303} is estimated to be 12 cal/deg · mol H.

Isotopic separation experiments /39/ also yielded thermodynamic data for the palladium-tritium system over the concentration range $0.650 \leqslant r \leqslant 0.775$. Using eq. (15), the entropy and enthalpy of desorption of $T_2(g)$ from the β phase tritide are obtained. The expression

$$\Delta H^{\circ}(\text{cal/mol } T_2) = 22053 - 21500r \qquad (21)$$

relates enthalpy to hydrogen composition. The value of ΔS° is determined to be 25.4 cal/deg · mol.

Thermodynamic data for T_2 desorption from the α phase were determined from the temperature dependence of Sievert's constant /38/, K_s, given by

$$K_s = -832/T + 6.243 \qquad (22)$$

The entropy and enthalpy of desorption of tritium from palladium were found to be 24.81 cal/deg · mol T_2 and 3305 cal/mol T_2, respectively. These values, when compared with the results reported for H_2 and D_2 in ref. /10/, show that hydrogen solubility in palladium is lowered with increasing isotope mass. This confirms the inverse isotope effect. Schmidt and Sicking /38/ have attributed this effect to the difference between zero point vibrational energies in both gaseous and solid states which decreases with increasing isotopic mass. This results in a corresponding decrease in desorption enthalpy.

Thermodynamic properties of the $\alpha + \beta$ region in the palladium-tritium system as well as the respective $\alpha + \beta$ regions of the Pd-H and Pd-D systems were determined from desorption data by the authors of ref. /12/. An enthalpy and entropy of desorption of 9321 cal/mol H_2 and 22.1 cal/deg · mol H_2 were reported for hydrogen. For desorption of D_2, an enthalpy of 8461 cal/mol D_2 and an entropy of 22.34 cal/deg · mol D_2 were obtained. For the Pd-T system, the entropy and enthalpy of desorption in the $\alpha + \beta$ region are reported to be 7959 cal/mol T_2 and 21.92 cal/deg · mol T_2, respectively.

Harada /46/ measured heats of desorption of hydrogen from different palladium-hydrogen alloys using differential scanning calorimetry (DSC). The differential heat of desorption was determined from the amount of heat absorbed by the solid and the amount of H_2 desorbed. Heats of reaction were then plotted as a function of r. Although the author reports the dissociation of palladium hydride to be endothermic, the values are graphically presented as being exothermic. Values of the desorption enthalpy taken from the plot found in ref. /46/ range from about 4.3 kcal/mol H_2 at approximately $r = 0.1$ to 13 kcal/mol H_2 at about $r = 0.7$. The absolute value of the heat of desorption decreases when the hydrogen concentration in the solid exceeds 0.7, indicating (according to the author) that hydride formation becomes unstable.

Differential scanning calorimetry and pressure differential scanning calorimetry were also used by Wagner /47/ to study hydrogen and deuterium absorption in palladium powder. Exchange reactions and the effects of hydrogen or deuterium pressure changes were also investigated. In these experiments, the metal was first hydrided or deuterided and then exposed to either a higher pressure of the same isotope or to another hydrogen isotope. Heats of reaction for these processes were measured from endothermic and exothermic calorimeter peaks. The enthalpies for absorption of deuterium at ambient pressure were reported as -11.4 ± 0.7 kcal/mol D_2 for DSC measurements and -12.7 ± 0.8 kcal/mol D_2 for pressure DSC results, respectively. Similarly, a heat of absorption of H_2 at ambient pressure of $--13.7$ kcal/mol H_2 was obtained from the DSC measurements. In determining the molar enthalpy of absorption, the final product was assumed to have a H(D)/Pd ratio of 0.62. The value obtained for D_2 desorption is described as "comparable" to that of -8.38 kcal/mol D_2 reported by ref. /18/ for D/Pd = 0.48 at 303 K, although it is not readily clear to us as to how or why these values should agree. No other attempt is made by the author of ref. /47/ to correlate his experimental results with data in the literature.

Some general observations concerning enthalpies of reaction are also described in ref. /47/. Enthalpies of exchange reactions, for example, have values of about 10% of the heat of absorption initially measured for each sample. When the gas pressure is increased above ambient pressure, a more exothermic heat of absorption was observed, indicating that the hydrogen content of the solid was increased. Anomalous peaks were observed during the exchange reactions when the gas pressure was increased. The author attributed this effect to an oversaturation of hydrogen atoms in the metal during the exchange. This would in turn cause a release of hydrogen atoms or deuterium atoms by the metal in order to achieve thermodynamic equilibrium. An endotherm would therefore be observed.

It is interesting to note that no mention of a specific temperature at which the above experiments are carried out is made in the entire text of ref. /47/

Several attempts to model and estimate the enthalpies of formation of transition metal hydrides have also been made. Gelatt *et al.* /48/ considered the complex energy bands of non-stoichiometric hydrides, such as those formed in the Pd-H system, and correlated the band structure with enthalpies of formation of various transition metal hydrides. Three principle contributions to the total enthalpy of formation were considered in the estimation procedure. First, a metal-hydrogen bonding band is formed. Second, the d bands in the transition metal are shifted downward in energy. Third, the extra electron associated with the hydrogen atom is situated at the Fermi energy. Corrections for Coulombic repulsion associated with the possibility of more than one electron being located at a hydrogen site were then added to the model. Using this model the authors estimate an enthalpy of formation of 2.5 kcal/mol H_2 for PdH. It must be remembered, however, the principle goal of this work was to identify the principal factors causing periodic trends in enthalpies of formation of metal hydrides rather than to obtain quantitative values.

An empirical model for calculating enthalpies of formation of binary hydrides of transition metals was formulated by Bouten and Miedema /49/ based on earlier work concerning the formation of alloys of transition metals /50, 51/. The model described in refs. /50/ and /51/ allows estimates of enthalpies of formation which are based on three factors. The first contribution to $\Delta \bar{H}_f$ is due to charge transfer between atoms. This quantity is proportional to the differences in chemical potential of electrons of the different elemental constituents. Secondly, the discontinuity in electron density between dissimilar elements must be smoothed. Thirdly, a contribution to the enthalpy is included which reflects more effective bonding when a transition metal forms a compound with a p-type chemical element. Problems with this model arise, however, when a non-metal either has an anomalous electronic structure (such as silicon or phosphorus) or is gaseous in its standard state (as is the case with nitrogen and hydrogen). For these cases an extra energy term must be considered to account for the "metallization" of such elements. For hydrogen, this extra term represents the enthalpy of reaction for the hypothetical process

$$\tfrac{1}{2}H_2\,(g) = H\,(\text{metal}) \qquad (23)$$

Other parameters must also be estimated for "metallic" hydrogen, including electronegativity, electron density, hybridization energy and molar volume. In ref. /49/ these parameters were estimated and used to calculate enthalpies of formation for specific compositions in different transition metal-hydrogen systems. Predictions were made regarding maximum hydrogen concentrations and stabilities in various binary hydride systems. For $Pd_{0.67}H_{0.33}$, a heat of formation of 1.7 kcal/g-atom H was estimated. The endothermicity of this value is due to the fact that the zero point energy of hydrogen in palladium is considerably lower than that assumed in ref. /49/ for an average metal used in the calculations.

A cluster-Bethe lattice approximation was used by Anagostaras and Lowther /52, 53/ to estimate the enthalpies of formation of non-stoichiometric palladium hydrides. The enthalpy of formation for palladium hydride, for example, is dependent upon several factors: the electron band energies of the solid hydride and palladium metal; the dissociation energy of H_2 (g); the shift in palladium bands as hydrogen is added; and the elastic strain energy due to the inclusion of hydrogen atoms in the metal lattice. The enthalpy of formation for Pd-H was calculated for $0 \leqslant r \leqslant 1.0$ in both refs. /52/ and /53/ and compared to calorimetry data presented by Harada /46/.

The existence of systems which were assumed to contain only a single hydride phase was considered in ref. /52/. When no interaction between hydrogen atoms was considered in the model, qualitative agreement was achieved between estimated and experimental values when $r \geqslant 0.58$. The authors attributed this to their assumption that hydrogen atoms were randomly dispersed throughout the crystal lattice. Breakdown of the model was attributed to the formation of hydrogen clusters within the solid.

In ref. /53/, Anagostaras and Lowther considered the existence of two different solid hydride phases, again employing the cluster-Bethe formalism. The total electron band energy of the solid hydride which is used in this model is a weighted sum of the energies calculated for the two individual hydride phases. Heats of formation of different compositions were calculated using the two phase model and graphically compared with the results reported in refs. /46/ and /53/. Whereas the single phase treatment produced qualitative agreement with experimental data at high hydrogen concentrations, the two-phase model produces a smoother ΔH vs. r curve which is closer in shape to the experimentally obtained curve. Enthalpies of formation obtained from the two-phase model are negative through most of the concentration range.

The combined results of refs. /52/ and /53/ show that the $\alpha + \beta$ region of the Pd-H system can be microscopically characterized as a non-homogeneous distribution of hydrogen, consisting of segregated regions of α and β phases. Agreement between the single phase model and experimental data taken from ref. /46/ when $r \geqslant 0.58$ is consistent, as only the β phase exists in this concentration range.

6. DIFFUSION AND ISOTOPIC SEPARATION

Separation of hydrogen isotopes can conceivably be accomplished by allowing a mixture of isotopes to diffuse into and through a palladium barrier. Each isotope will pass through the metal at a different rate, causing the relative concentrations of each isotope in both solid and vapor to change with time. This section summarizes work dealing with isotopic separation factors, diffusion of deuterium and tritium in the presence of hydrogen and diffusion of pure isotopes in the Pd-H β phase.

Separation factors over the 50°C–78.5°C range were reported in ref. /10/ for hydrogen-palladium mixtures and for the β hydride. The separation factor α is defined by the expression

$$\alpha = \frac{X_D^g / X_H^g}{X_D^s / X_H^s} \tag{24}$$

where X_D^g, X_D^s, X_H^g, and X_H^s denote mole fractions of deuterium and hydrogen in the gas and solid phases, respectively. The equation

$$\ln\alpha = \frac{245}{T} - 0.055 \tag{25}$$

represents the temperature dependence of α. The separation factor α, which has a value of 2.40 at 25°C, is essentially independent of total pressure of the system.

Tracer diffusion of deuterium and tritium in β palladium hydride was studied in ref. /54/. The mobility of deuterium atoms in the solid hydride indicated the presence of correlation effects. In the mixed isotope system, mutual exchange of surface sites between different isotopes does not occur. Hence, deuterium mobility is reduced when the D atoms are replaced by H atoms in the hydride matrix. Tritium mobility in the β hydride is the slowest of the three isotopes. Since no data concerning tritium mobility in β-PdT_n is available, it was assumed by the authors that tritium is as mobile in the β hydride as in the β tritide.

Separation factors for liquid-solid and solid-gas systems were determined from electrode potentials by Sicking /55/. In the case of the solid-gas system, the separation factor is almost independent of total pressure and hydrogen concentration in the solid. At "normal" temperatures, a value of $\alpha = 2.45$ was calculated from H_2 and D_2 isotherms. The author re-wrote eq. (25), given by ref. /10/, to yield

$$\alpha = 1.057 \exp(\frac{486}{RT} \text{ cal/mol}) \qquad (26)$$

and cites a similar expression for tritium separation,

$$\alpha = 0.927 \exp(\frac{636}{RT} \text{ cal/mol}) \qquad (27)$$

found in an earlier paper /56/. Diffusional separation factors (S_D) for deuterium and tritium in the β hydride were also calculated from diffusion measurements and equilibrium distribution experiments. This parameter, which is dependent upon both mobility and solubility, is proportional to the ratio of diffusion coefficients (e.g. D_D/D_H for deuterium-hydrogen) and α. The temperature dependence of diffusional separation factors for deuterium and tritium in β-PdH_n are given by the expressions:

Deuterium:

$$S_D = 1.62 \exp(\frac{36 \text{ cal/mol}}{RT}) \qquad (28)$$

yielding a value of $S_D = 1.73$ at 25°C, and tritium:

$$S_D = 0.37 \exp(\frac{1236 \text{ cal/mol}}{RT}) \qquad (29)$$

which yields a value of $S_D = 3.00$ at 25°C. The author attributes the difference in temperature dependence of S_D for these isotopes to the anomalous nature of tritium diffusion.

Birnbaum and Wert /57/ summarized bulk diffusion studies of hydrogen and its isotopes in palladium. Information regarding hydrogen diffusion, obtained from numerous sources, was described as being remarkably consistent, yielding the expression

$$D = 4.5 \times 10^{-3} \exp(\frac{5750 \text{ cal/mol}}{RT}) \qquad (30)$$

for the diffusion coefficient of hydrogen in palladium.

Reported values for the diffusion coefficient of deuterium in palladium are listed in ref. /57/, but no equation for the temperature dependence of D is given. A single value for the diffusion coefficient of tritium in palladium, D = 10.25, is cited. While the diffusion coefficients for both hydrogen and deuterium decrease with temperature, that for tritium appears to increase. The result is that the isotopes diffuse in the order $H > D > T$ at low temperatures. Extrapolation of D for the different isotopes to higher temperatures suggests that the above order would be reversed.

The distribution of tritium in the gas phase and β palladium hydride was measured in ref. /39/. The temperature dependence of the separation factor α is given by the equation:

$$\ln\alpha = \frac{636 \text{ cal/mol}}{RT} - 0.075 \qquad (31)$$

APPENDIX A

Phase Boundaries and Critical Point Data for the Pd-H, Pd-D, and Pd-T Systems

TABLE A-1. Phase Boundaries for the Pd-H System

T	r_α (maximum)			
(°C)	Ref. /10/	Ref. /11/	Ref. /13/	Ref. /14/
0	0.0055	–	–	–
50	0.0120	–	–	–
60	0.0135	–	0.0133	–
70	–	0.017	0.0158	–
120	–	0.030	0.0313	–
200	–	0.075	–	–
243	–	0.117	–	–
245	–	–	–	0.131

T	r_β (minimum)			
(°C)	Ref. /10/	Ref. /11/	Ref. /12/	Ref. /14/
-30	0.629	–	–	–
0	0.615	–	–	–
50	0.599	–	0.602	–
70	–	0.575	0.590	–
120	–	0.540	0.555	–
200	–	0.459	–	–
243	–	0.399	–	–
245	–	–	–	0.362

TABLE A-2. Phase Boundaries for the Pd-D System

T	r_α (maximum)	
(°C)	Ref. /10/	Ref. /13/
0	0.0065	–
30	0.0103	–
50	0.0150	–
60	0.0155	0.0154
70	–	0.0184
75	0.0190	–
90	–	0.0250
100	–	0.0283
110	–	0.0316

T	r_β (minimum)	
(°C)	Ref. /10/	Ref. /13/
-30	0.616	–
0	0.609	–
30	0.600	–
50	0.587	0.591
70	–	0.573
90	–	0.562
110	–	0.550
120	–	0.544

TABLE A-3. Phase Boundaries for the Pd-T System

T	r_α (maximum)
(°C)	Ref. /13/
50	0.0135
60	0.0168
70	0.0202
80	0.0237
90	0.0274

T	r_β (minimum)
(°C)	Ref. /12/
50	0.582
60	0.575
70	0.567
80	0.560
90	0.548

TABLE A-4. Critical Point Data for the Pd-H and Pd-D Systems

	T_c (°C)	P_c (atm)	r_c (Pd/H)	Ref.
(Pd-H)	564	19.7	0.250	/11/
	568	19.7	0.27	/15/
	567	19.35	0.241	/14/
(Pd-D)	543	35	0.25	/17/

APPENDIX B

Crystal Structure Data for the Pd-H and Pd-D Systems

TABLE B-1. The Pd-H System

Phase	Structure	Lattice parameters (nm)	Ref.
Pd metal	fcc	0.3891	/9/
Pd metal	fcc	0.3886	/25/
α	fcc	0.3902	/9/
α	fcc	0.3891	/25/
β	fcc	0.4026	/9/
		0.4022	/25/
β*	fcc	0.4090	/21/
δ	fcc	0.3943	/25/
γ	fcc	0.3960	/25/
γ	tetragonal	a = 0.2896, c = 0.3330	/26/
γ'	primitive cubic	0.2995	/27/

* Extrapolated to $r = 1$ from data obtained for $0.8 < r < 0.98$.

TABLE B-2. The Pd-D System

Phase	Structure	Lattice parameters (nm)	Ref.
β*	fcc	0.4084	/21/
γ	tetragonal, ordered	none given	/23/

* Extrapolated to r = 1 from data obtained for $0.8 < r < 0.98$.

TABLE B-3. Isothermal Variation of α and β Phase Lattice Parameters with H_2 Pressure /20/

T = 206°C

Pressure (atm)	Lattice parameters (nm) α phase	β phase
0	0.3903	–
1.7	0.3909	0.4013
3.8	0.3916	0.4013
5.1	**	0.4022
13.3	–	0.4040
22.3	–	0.4043

T = 258°C

Pressure (atm)	Lattice parameters (nm) α phase	β phase
2.0	0.3912	–
4.4	0.3916	–
7.1	0.3926	–
9.4	**	0.4016
11.8	–	0.4022
23.3	–	0.4035

** Author reports faint reflections for α phase but does not provide lattice parameter.

APPENDIX C

Hydrogen, Deuterium, and Tritium Pressures Calculated from Select Pressure-Composition-Temperature Equations for the Palladium Hydrogen Systems

TABLE C-1. The α Phase Region

T (K)	Pressure (atm) for r = 0.010 H_2 [Eq. (11)	 D_2 [Eq. (12)	 T_2 [Eq. (1)
273	5.284×10^{-3}	–	5.979×10^{-2}
293	9.905×10^{-3}	–	9.063×10^{-2}
303	1.303×10^{-2}	4.990×10^{-2}	0.1093
323	2.189×10^{-2}	7.599×10^{-2}	0.1535
343	3.342×10^{-2}	0.1100	0.2073
393	8.612×10^{-2}	0.2346	0.3842
433	0.1538	0.5613	0.5680

TABLE C-3. The $\alpha + \beta$ Two Phase Region for the Pd-D System

T (K)	D_2 Pressure (atm) Eq. (4)	 Eq. (10),	 Eq. (6)
273	2.819×10^{-2}	1.015×10^{-2}	–
293	7.846×10^{-2}	3.104×10^{-2}	–
303	0.1162	5.135×10^{-2}	–
323	0.2582	0.1280	0.1480
343	0.7543	0.2867	0.3119
393	2.224	1.505	1.493
433	5.570	4.302	–

TABLE C-2. The $\alpha + \beta$ Two Phase Region for Pd-H

T (K)	Eq. (9)	Eq. (2)	Eq. (8)	Eq. (3)**	Ref. /29/***	Eq. (6)
273	1.988×10^{-3}	5.315×10^{-3}*	4.650×10^{-3}	4.900×10^{-3}	5.296×10^{-3}	–
293	6.428×10^{-3}	1.566×10^{-2}*	1.495×10^{-2}	1.462×10^{-2}	1.523×10^{-2}	–
303	1.091×10^{-2}	2.542×10^{-2}*	2.530×10^{-2}	2.384×10^{-2}	2.452×10^{-2}	–
323	2.846×10^{-2}	6.166×10^{-2}*	6.569×10^{-2}	5.893×10^{-2}	5.816×10^{-2}	–
343	6.639×10^{-2}	0.1341	0.1526	0.1283	0.1247	7.90×10^{-2}
393	0.3785	0.6686	0.8629	0.6442	0.5981	0.436
433	1.141	1.847	2.587	1.796	1.615	1.353

* Extrapolated value.

** Calculated for r = 0.30.

*** $\log P\,\mathrm{mm} = 7.3278 - 1835.4/T$.

TABLE C-4. The $\alpha + \beta$ Two Phase Region for the Pd-T System

T (K)	T_2 Pressure (atm) Eq. (6)
303	0.1984
323	0.2941
343	0.4392
373	0.733
393	1.699

TABLE C-5. The β Phase Region for the Pd-H System

T	H_2 Pressure (atm)					
	Eq. (13)		Eq. (6)		Eq. (6)	
(K)	r = 0.65	0.75	r = 0.65	0.75	r = 0.65	0.75
273	1.372×10^{-2}	1.892	3.196×10^{-2}	5.078	–	
290	4.042×10^{-2}	4.416	0.1423	15.643	–	
293	4.287×10^{-2}	5.076	–		–	
303	8.507×10^{-2}	7.918	–		–	
323	0.2378	17.74	–		0.3471	24.83
343	0.590	36.18	–		3.479	26.76
373	–		6.959	200.3	–	

TABLE C-6. The β Phase Region for the Pd-D System

T	D_2 Pressure (atm)		
	Eq. (14)		Eq. (6)
(K)	r = 0.65	0.75	r = 0.65
273	0.1039	14.33	
293	0.3162	33.25	
303	0.5220	48.59	
323	1.296	96.69	1.359
343	2.895	177.58	2.476

TABLE C-7. The β Phase Region for the Pd-T System

T	T_2 Pressure (atm)		
	Eq. (15)		Eq. (6)
(K)	r = 0.65	0.75	r = 0.65
273	0.2849	39.13	
293	0.7874	82.51	
303	1.245	115.47	
323	2.857	212.48	2.552
343	5.953	364.13	3.479

APPENDIX D

Select Thermodynamic Data for the Palladium-Hydrogen Systems

TABLE D-1. The α Phase Region for the Pd-H System

ΔH° (cal/mol H_2)		Ref.	Remarks	ΔS° (cal/deg · · mol H_2)	Ref.
6000	~~/29/~~	/29/			
–8948	~~/33/~~	/33/	absorption		
4732* (r = 0.005, T = 298 K)		/10/		25.6	/10/
4822* (r = 0.009, T = 298 K)		/10/			

* $\Delta \hat{H} = 4620 + 9000\,(1 + 445/T)\,r$

TABLE D-2. The α Phase Region for the Pd-D System

ΔH° (cal/mol D_2)	Ref.	ΔS° (cal/deg · mol D_2)	Ref.
3875* (r = 0.005, T = 298 K)	/10/	25.4	/10/
3980* (r = 0.009, T = 298 K)	/10/		

* $\Delta \hat{H} = 3770 + 9000\,(1 + 400/T)\,r$

TABLE D-3. The α Phase Region for the Pd-T System

ΔH° (cal/mol T_2)	Ref.	ΔS° (cal/deg · mol T_2)	Ref.
3305	/38/	24.809	/38/

TABLE D-4. The $\alpha + \beta$ Two Phase Region for the Pd-H System

ΔH° (cal/mol H_2)	Ref.	Remarks	ΔS° (cal/deg · mol)	Ref.
-8860	/29/	(absorption)		
8870	/33/	(desorption, increasing T)		
9441	/33/	(desorption, decreasing T)		
9330	/33/	(desorption, calorimetry)		
9440	/33/	(desorption, calorimetry)		
10300	/33/	(desorption, calorimetry)		
-9605	/33/	(absorption)	23.50	/33/
-9440	/33/	[ΔH for the reaction: $4Pd(s) + H_2(g) = Pd_2H(s)$]		
-9280	/34/	(heat of solution, electrochemical measurements)		
-9500	/20/	(absorption, x-ray diffraction measurements)		
9325	/10/		21.8	/10/
9321	/12/		22.1	/12/
8590	/15/			

TABLE D-5. The $\alpha + \beta$ Two Phase Region for the Pd-D System

ΔH° (cal/mol D_2)	Ref.	Remarks	ΔS° (cal/deg · mol D_2)	Ref.
-8379	/18/	(absorption, calorimetric)		
-8635	/18/	(absorption, isosteric)		
7760	/17/	(heat required for conversion from α to β phase)		
8880	/10/		23.4	/10/
8461	/12/		22.34	/12/

TABLE D-6. The $\alpha + \beta$ Two Phase Region for the Pd-T System

ΔH° (cal/mol T_2)	Ref.	ΔS° (cal/deg · mol T_2)	Ref.
7959	/12/	21.92	/12/

TABLE D-7. The β Phase Region for the Pd-H System

ΔH° (cal/mol H_2)	Ref.	Remarks	ΔS° (cal/deg · mol H_2)	Ref.
9995	/10/ (Eq. 19)	r = 0.65	No data available	
8920	/10/	r = 0.70		
6770	/10/	r = 0.80		
9740	/29/			
-10000	/37/	(estimated from graph in paper, r ≅ 0.95)		

TABLE D-8. The β Phase Region for the Pd-D System

ΔH° (cal/mol D_2)	Ref.	Remarks	ΔS° (cal/deg · mol D_2)	Ref.
8845	/10/ (eq. 20)	r = 0.65	No data available	
7770		r = 0.70		
5620		r = 0.80		

TABLE D-9. The β Phase Region for the Pd-T System

ΔH° (cal/mol T_2)	Ref.	Remarks	ΔS° (cal/deg · mol T_2)	Ref.
8078	/39/ (eq. 21)	r = 0.65	25.4	/39/
7003		r = 0.70		
4853		r = 0.80		

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