Measurement for Palladium Hydride and Palladium Deuteride Isotherms Between 130 K and 393 K

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Palladium is a unique hydride-forming metal that finds applications in next-generation target-filling systems and isotope separation systems. The uniqueness of palladium among hydride-forming metals stems from the ability to generate significantly higher hydrogen pressures than other hydriding metals.[1] In a next-generation target-filling design, a single palladium bed could replace the existing diaphragm compressor and condensation cell. Replacing these components with a single palladium bed allows for a smaller, simpler system with fewer moving parts. The high pressures achieved using the compressor can be achieved with a palladium bed by loading the bed at low temperature and subsequently raising the temperature to release the absorbed gas. In addition to next-generation target-filling systems, palladium is currently used in the isotope separator, which is deployed in the tritium laboratory. It has been extensively demonstrated that palladium has an affinity for lower mass hydrogen isotopes. The isotope separation system at LLE exploits this affinity to separate protium (H), deuterium (D), and tritium (T) in the fuel supply, allowing for specific DT mixtures to be made.

Currently in the literature, the pressure–composition–temperature (PCT) phase diagrams for the palladium hydride system extend only to 273 K. Measurement of the PCT diagram to cryogenic temperatures is necessary for the development of next-generation systems, which intend to employ palladium as a hydriding material. The focus of the current work is to measure the PCT curves at low temperatures for both protium and deuterium.

To measure the PCT curves for palladium hydride, a small getter bed containing 2.5 g of palladium powder was utilized. This bed is connected to a manifold of calibrated volumes, which can be charged with H_2 or D_2. Absorption isotherms were measured by sequentially adding gas onto the bed from the charge volume. Hydrogen absorption onto palladium is rapid for all temperatures investigated. The data show that 99% of the gas is absorbed within 6 min.

To achieve temperatures between 130 and 240 K, a cryogenic cooler ("Q-Drive") was purchased from Chart Industries. The Q-Drive operates using an acoustically driven Stirling cycle to remove heat from a cold head. The cold head of the Q-Drive was indirectly coupled to the exterior of the Pd bed through a multilam. This multilam was in contact with a stainless-steel rod that was in direct contact with the bottom of the Pd bed. Such a design protects the cold head during high-temperature excursions, while still maintaining the capability of subambient temperatures. Temperatures greater than ambient were set by using a heater that was wrapped around the exterior of the Pd bed.

Using the above procedure and experimental setup, the PCT curves were measured for protium and deuterium from 130 to 393 K. High-temperature ($\geq$20°C) data were measured to compare with previously reported PCT curves, while low-temperature data have not been previously reported in the literature. The measured PCT curves are shown in Fig. 1 for (a) protium and (b) deuterium. In each panel, the equilibrium pressure of each isotope is plotted against the hydrogen-to-metal (HM) ratio for an array of temperatures. The measured PCT curves display the expected three-region trend with increasing hydrogen content: the pressure initially increases rapidly (α phase), followed by a region of relatively little change in pressure (mixed α–β phase), and a second region of rapid pressure increases (β phase). The α and the β phases correspond to hydrogen diffusion into either palladium or palladium hydride, respectively. In between the α and β phases, the mixed phase exists. Here, an increasing quantity of palladium hydride is formed with an increasing hydrogen-to-palladium ratio. In general, the maximum hydrogen-to-metal ratio increases as the temperature decreases. For temperatures ≤20°C, this maximum ratio is ~0.75. The onset of the mixed α–β phase begins at HM ~ 0.08 for high-temperature isotherms and decreases to ~0.03 at ambient temperatures before increasing again at very low temperatures to ratios between 0.1 and 0.2.

A van't Hoff plot for the current data set was constructed by using the equilibrium pressures and temperatures from the measured PCT curves shown in Fig. 1. The resulting van't Hoff plot is shown in Fig. 2, which includes the protium and deuterium results from this study, along with several data sets reported in the literature.[2–4] Finally, straight-line fits to each of the data

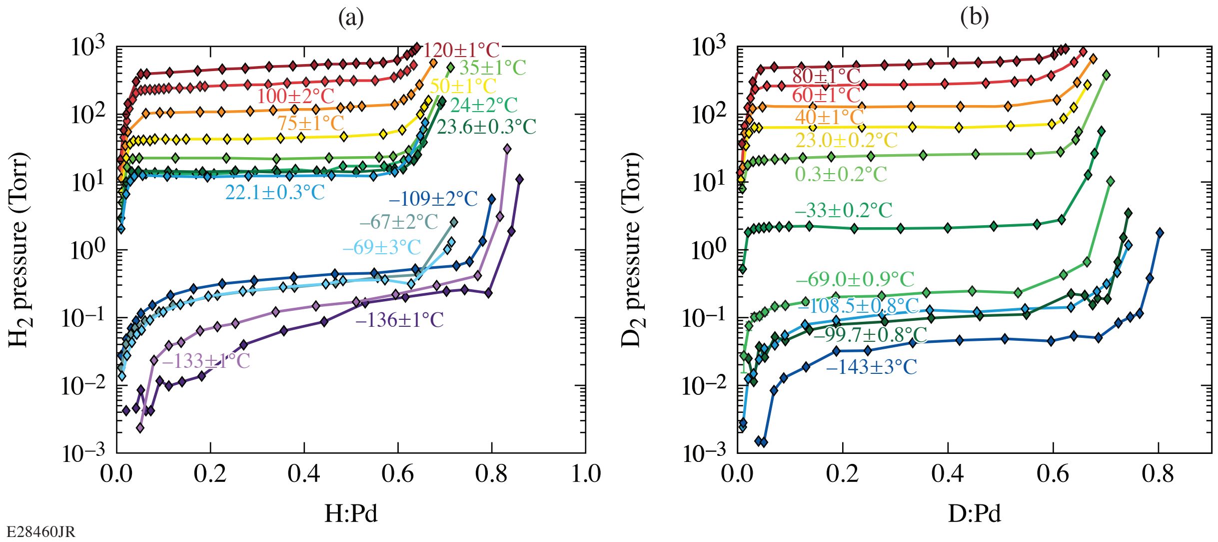

Figure 1
Pressure–composition–temperature isotherms measured using (a) hydrogen at temperatures between 296 K and 393 K and (b) deuterium at temperatures between 130 K and 353 K.

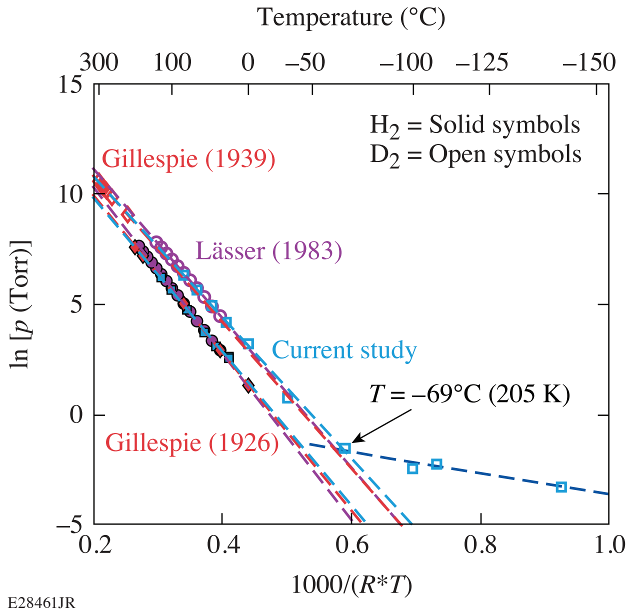

Figure 2
A van't Hoff diagram generated using equilibrium hydrogen (solid symbols) and deuterium (open symbols) pressures in the mixed region.

sets are shown as the dashed lines. The low-temperature data collected from the current work show a deviation from the high-temperature data; therefore, separate lines were fit to the low- and high-temperature data.

At low temperatures, palladium may absorb hydrogen by a mixed mechanism of hydride formation and physical adsorption. From the van't Hoff diagram (Fig. 2), a hydride forms until ~205 K. Assuming no further hydride formation occurs with lower temperature, additional pressure reductions may be due to physical adsorption of hydrogen onto palladium. The expected hydride formation and physical adsorption regions are illustrated in Fig. 3. Here, the van't Hoff diagram is reproduced with data from the present work. The shaded areas show the expectation of where a hydride forms and where physical adsorption occurs.

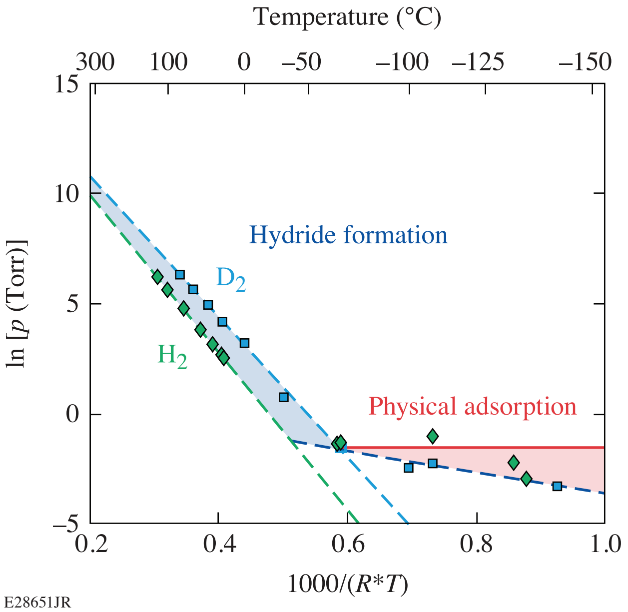

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Figure 3
This van't Hoff diagram shows the different mechanisms for hydrogen absorption by palladium. The upper blue region corresponds to the pressures and temperatures at which palladium will form a hydride. The lower red region corresponds to the pressures and temperatures where hydrogen will physically adsorb onto the palladium surface.

This combination of mechanism and lower temperatures is justified by two observations: First, hydrogen and deuterium show similar equilibrium pressures at low temperatures. Similar pressures are not a result of the formation of a hydride since palladium has a greater affinity for less-massive isotopes. However, similar pressures may be a result of physical adsorption since the quantity of adsorbed gas depends primarily on the adsorbate and substrate sizes. Second, we estimate that all hydrogen loaded onto the palladium at low temperatures can be physically adsorbed into approximately six monolayers. For this estimation, it was assumed that a hydride is formed until 205 K. Below 205 K, any observed pressure reduction below the equilibrium pressure at 205 K represents hydrogen adsorbing onto the palladium's surface. Taking the "worst" case scenario, the difference between the equilibrium pressures at 205 K and 130 K is 0.174 Torr, which corresponds to 1.9×10^{-7} mol of H_2 or D_2. Assuming the specific surface area is 2 m^2/g, the total surface area is 5 m^2. The number of H_2 molecules per monolayer is given by

$$\frac{1\,\mathrm{H}_2}{\pi r^2} = 3.4 \times 10^{-5}\,\frac{\mathrm{mol\ H}_2}{m^2 * \mathrm{ML}}, \tag{1}$$

where r is the radius of a hydrogen molecule. Using the results of Eq. (1), the total surface area, and the total number of moles of adsorbed hydrogen, the number of monolayers is estimated to be 10^{-3}. Such a small number of monolayers is reasonable at these low temperatures.

In summary, the palladium hydride and palladium deuteride isotherms have been measured from 130 K to 393 K. The data collected for temperatures below 273 K are the first to be reported in the literature. The measured isotherms show that an increasing quantity of palladium hydride is formed with decreasing temperatures, with a maximum hydrogen-to-metal ratio of 0.75.

These data are consistent with the literature, where the temperatures overlap. The van't Hoff diagram shows a deviation from high-temperature behavior for temperatures of less than 205 K. The data suggest that palladium can form a hydride until 205 K. Below this critical temperature, any further reduction in equilibrium pressure occurs due to physical adsorption onto the surface.

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