Measuring Isotherms of the Hydrogen-Palladium System

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Abstract:

Palladium is a metal that absorbs and reacts with hydrogen and its isotopes to form palladium hydride at temperatures below 610 K. Palladium absorbs a significant amount of hydrogen within its crystal lattice and can act as a storage medium for hydrogen. The equilibrium residual hydrogen pressure over palladium was measured as a function of the hydrogen-to-palladium atom ratio (H:Pd) at fixed temperatures, producing isotherm curves. In the present work, equilibrium pressures have been measured for H:Pd ratios between 0.0 and 0.8 and temperatures between 293 K and 393 K. The van't Hoff plot of the present data shows consistency with literature data, regarding the standard enthalpy change ΔH and the standard entropy change ΔS. The ΔH was measured to be -36.8 kJ/mol and the ΔS was measured to be -143.9 J/mol*K. This experiment validates prior data on the hydrogen-palladium system.

1. Introduction:

Palladium has long been used as a means of storing hydrogen and its isotopes. Prior to this work, the data known for palladium hydride was spread out across a wide temperature range and there was inconsistency in the literature. This paper's data fills in temperature gaps in that range, thus creating a denser and more filled in series of isotherms, which are curves relating pressure and H:Pd atom ratio at various temperatures.

The study of the behavior of palladium hydride and palladium deuteride is important to the Laboratory for Laser Energetics (LLE) because of its mission to study inertial confinement fusion reactions. A typical test involves filling a cryogenic target with deuterium and tritium in order to establish the fuel density necessary for fusion conditions. In order to do this, a stock of gaseous deuterium and tritium is required for charging. A palladium sponge would make the targets' fuel delivery method involve simply alternating the temperature of the palladium, which is a simpler and cheaper alternative to the current approach. Precise measurements of pressure over palladium hydride are important to ensure that the delicate targets are not crushed due to a rapid pressure excursion. The purpose of creating these isotherms is to study the vapor pressure of hydrogen and deuterium above the palladium bed during the hydriding process. The focus of the current work is on the formation of palladium hydride at modest temperatures.

2. Theory:

Palladium is part of a special group of metals called getters, which chemically combine with gas molecules upon contact. Getters are used in vacuum systems to remove gas from evacuated space in order to complete and maintain the vacuum. Palladium is non-reactive with oxygen at standard temperatures, and therefore does not tarnish in air. As a hydrogen getter, palladium is able to absorb and react with hydrogen, motivating further study of palladium's viability as a storage medium for hydrogen and its isotopes. The formation of palladium hydride is a reversible reaction, given by:

$$\frac{x}{2} H_2(g) + Pd(s) \rightleftarrows H_x Pd(s) \tag{1}$$

where g indicates the gaseous state, s indicates the solid state, and x indicates the moles of hydrogen contained in palladium hydride.

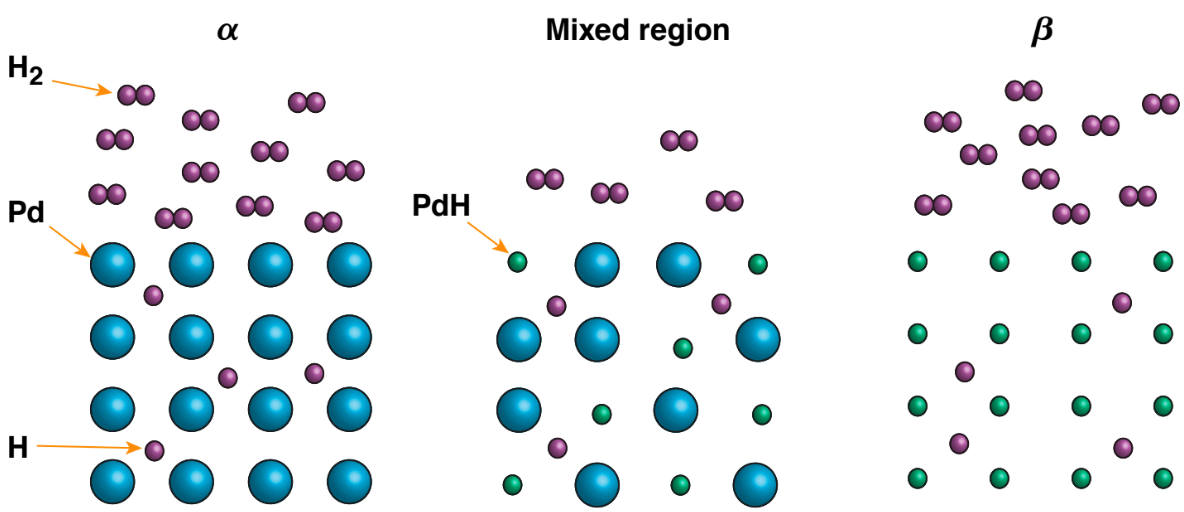

Figure 1: Visual representation of the alpha, mixed, and beta regions on an atomic level. Each region demonstrates unique interactions between hydrogen and palladium.

Palladium absorbs hydrogen atoms in the three stages shown in figure 1. The first stage is the alpha region, where hydrogen molecules dissociate on the palladium surface and the hydrogen atoms are absorbed into the palladium matrix.

As seen in figure 2, the hydrogen vapor pressure at a constant temperature increases rapidly over the palladium as more hydrogen is added to the system. In this stage, hydrogen atoms occupy interstitial locations between palladium atoms in the palladium lattice but have not chemically bonded to palladium atoms. The second stage is the mixed region (alpha and beta region) where a fraction of the hydrogen atoms continue to be absorbed interstitially in the palladium, and the remaining fraction begins to chemically bond to palladium atoms within the crystal lattice. Hydrogen pressure above the palladium remains relatively constant with increasing H:Pd ratio in this stage. Hydrogen pressure above the palladium bed will increase in the mixed region as metal temperature increases. The third stage is the beta region where all possible hydrogen-palladium bonds have formed. As a result, the pressure increases significantly with increasing hydrogen-to-metal ratios. High pressures are required to insert gas in the beta region because additional hydrogen atoms are no longer bonding to palladium, but rather occupying the interstitial locations within the crystal lattice of the new material: palladium hydride.

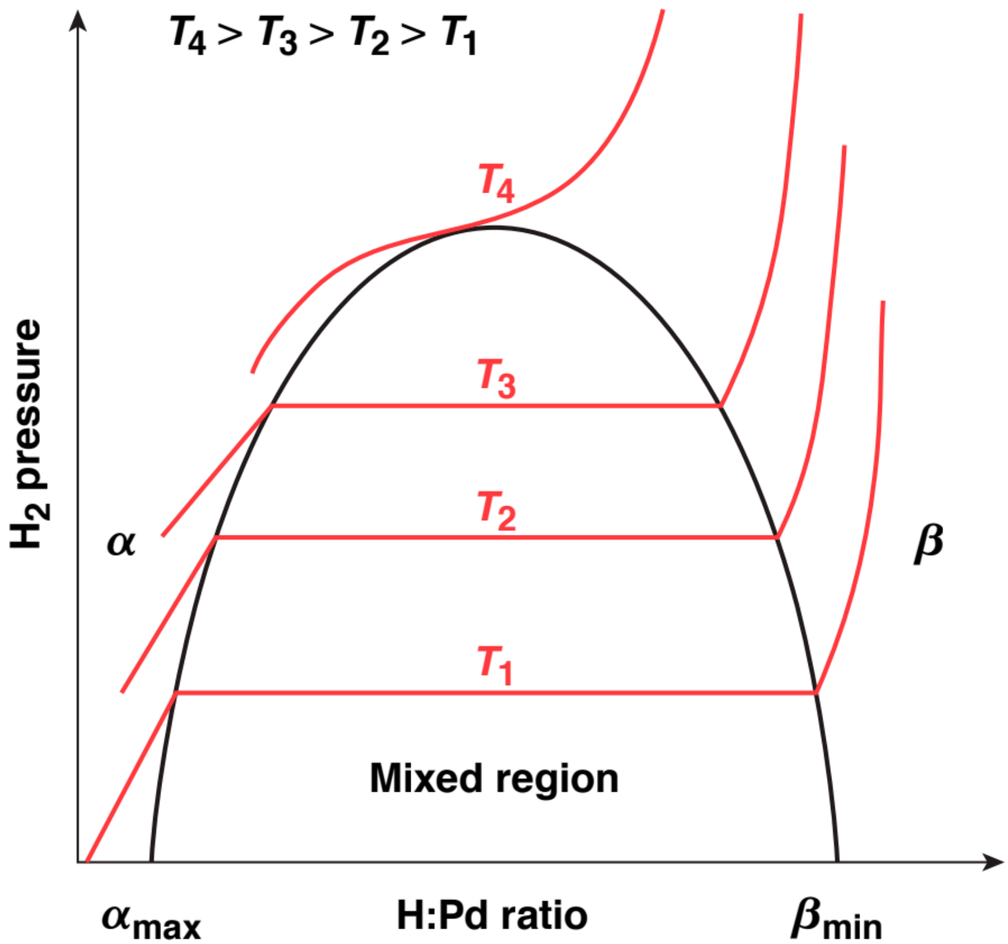

Figure 2: Isotherms indicating the relationship between pressure and composition at increasing temperatures, T_1-T_4. The parabola serves to show the three regions of palladium hydride: left of the parabola represents the alpha region, under the parabola represents the mixed region, and right of the parabola represents the beta region. Alpha max represents the part of the parabola that separates the alpha region of the isotherm from the mixed region. Beta min is the part of the parabola that separates the mixed region of the isotherm from the beginning of the beta region. (from Ref. 1)

Higher temperature isotherms have higher pressures and smaller mixed regions. This indicates that the hydriding reaction is exothermic, where H_2 (g) is favored at higher temperatures.

At standard temperature, a metal hydride can store 5.7 millimoles of gaseous hydrogen per cubic centimeter of metal at 0.5 atm. To store the same number of moles of hydrogen in a cubic centimeter container, the gas would have to be at a pressure of 130 atm. Using a metal getter as a storage mechanism and pump for hydrogen requires substantially less space, pressure, and money than using gaseous containers. Storing hydrogen in getters rather than containers also eliminates many dangers associated with pressurized hydrogen gas, such as laboratory fires or injuries caused by improper use of pressurized gas.

The mixed region of the isotherms can be used to perform van't Hoff analysis. The van't Hoff equation is used to determine the enthalpy and entropy of reaction. The van't Hoff equation can be used to predict the pressure required to obtain a given H:Pd ratio at a given temperature. The van't Hoff equation is given by:

$$\ln(p_{H_2}) = \frac{2\Delta H^\circ}{xRT} - \frac{2\Delta S^\circ}{xR} \tag{2}$$

where P_{H2} (also referred to as P_{eq}) indicates residual hydrogen pressure over palladium, R indicates the ideal gas constant, T indicates temperature, x indicates the number of moles of hydrogen contained in palladium hydride, ΔH° indicates enthalpy of formation, and $\Delta S°$ indicates entropy of formation. Enthalpy is the total heat content of the system and entropy is the degree of disorder of the system.

Using van't Hoff analysis, one can plot $\ln(P_{eq})$ vs. 1/RT and obtain the enthalpy and entropy of formation. To plot the van't Hoff curve, one data point from each isotherm must be chosen at a set H:Pd ratio. This plot should be linear. The slope of the plot represents the enthalpy of formation. The intercept of the line is proportional to the entropy of formation.

3. Experimental Setup:

The experimental setup was designed for the purpose of studying the formation of palladium hydride and palladium deuteride at temperatures between 293 K and 393 K, as well as cryogenic temperatures. The system (figures 3 and 4) introduces hydrogen or deuterium into an evacuated bed containing palladium powder. The experimental setup comprises a palladium bed, a hydrogen or deuterium tank, a reference volume ($V_{\mathbf{Ref}}$), an MKS pressure gauge, a Hastings pressure gauge, an ion gauge, a turbo vacuum pump, a scroll vacuum pump, and a series of valves connected by stainless steel pipes and Swagelok fittings. The valves are abbreviated as follows: hydrogen/deuterium valve ($V_{\mathbf{H/D}}$), palladium valve ($V_{\mathbf{Pd}}$), pressure valve ($V_{\mathbf{P}}$), reference volume valve ($V_{\mathbf{Ref}}$), vacuum valve ($V_{\mathbf{Vac}}$), helium valve ($V_{\mathbf{He}}$), air valve ($V_{\mathbf{Air}}$). Temperature, pressure, and volume calibrations were performed to reduce systematic errors in the data.

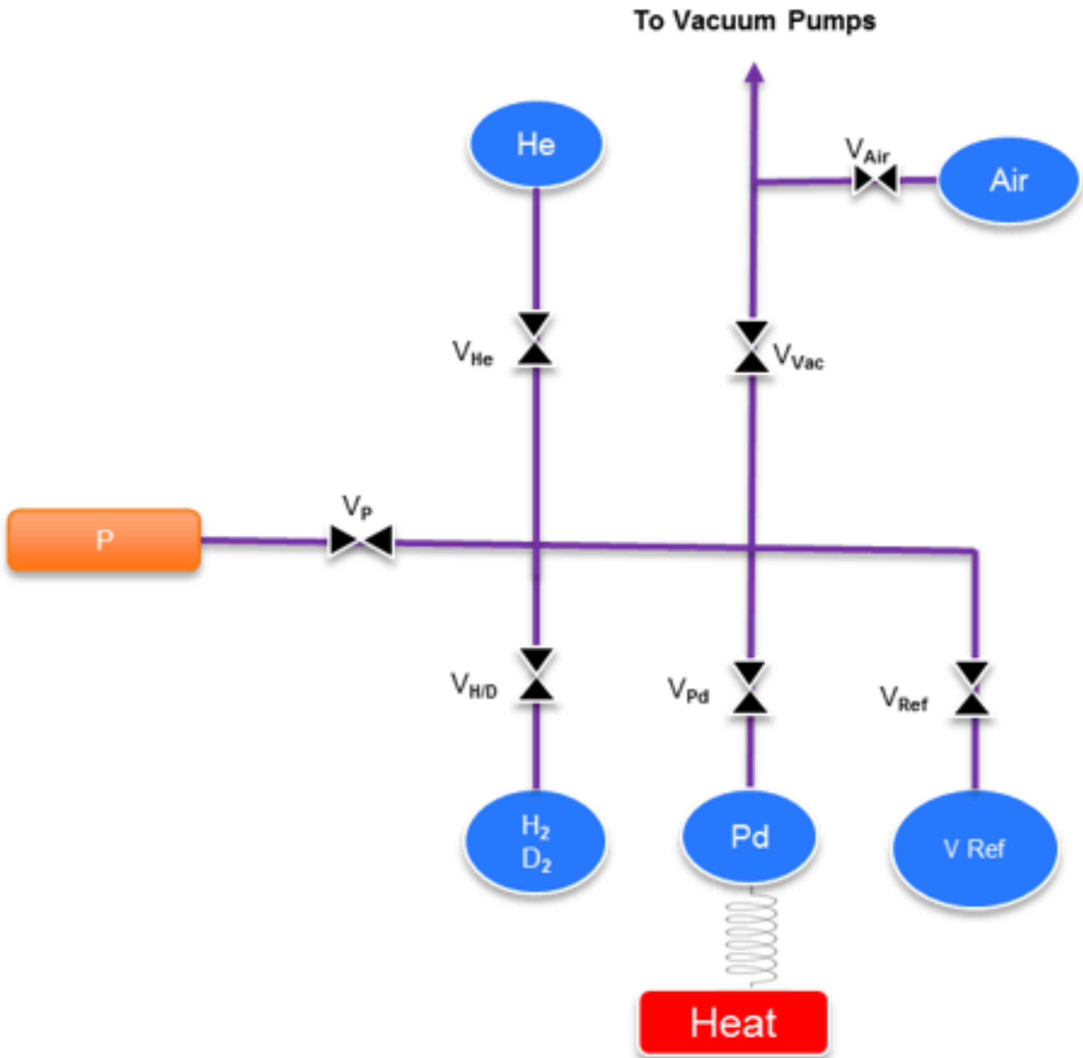

Figure 3: Schematic drawing of the experimental setup.

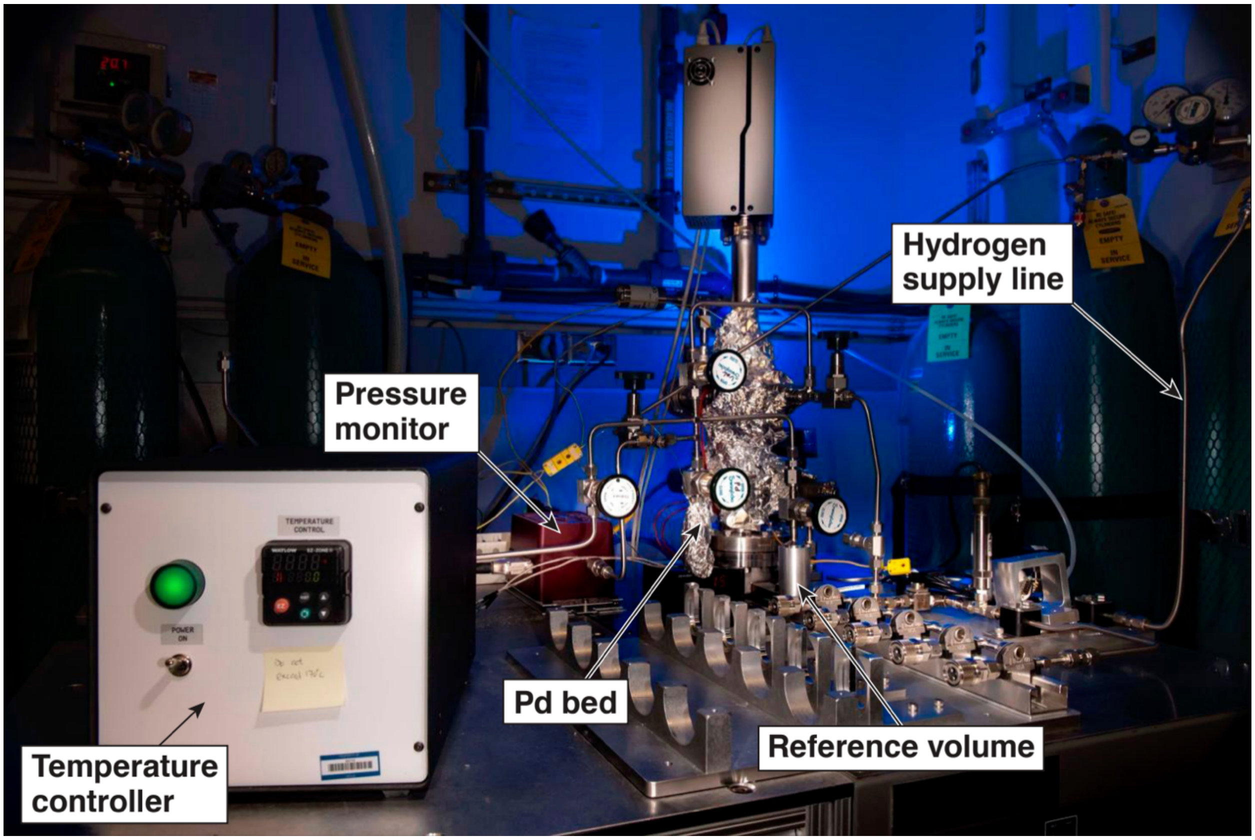

Figure 4: Photograph of the experimental setup.

The palladium bed consists of 2.4 grams (0.0226 moles) palladium sponge, which is held in a stainless-steel container with a head volume of 2.98 cubic centimeters. The palladium bed has foil wrapped around it as a means of insulation. The bed is connected to a turbomolecular vacuum pump that maintains a vacuum of less than 10^{-7} Torr.

The ion gauge is a low-pressure measuring device that measures the quality of the vacuum. The ion gauge uses a heated filament to emit electrons into an electric field. The electric field accelerates the electrons to 80 eV to ionize gas molecules. The ions are collected on a cathode. The ion current is proportional to the gas density in the vacuum.

Helium gas was introduced into the system in order to measure the manifold volume, the palladium bed head volume, and the reference volume. Helium forms a monolayer on the palladium. This layer interferes with the palladium reacting with hydrogen. Therefore, the system must be baked for several days to remove all helium from the system after volume calibrations are complete.

Air was used to purge the space between the turbomolecular pump and the scroll pump. Hydrogen molecules are so small that the scroll pump cannot completely remove all hydrogen gas on its own. Hydrogen molecules back diffuse from the downstream side of the pump into the space between the two pumps, which becomes evident when hard vacuum cannot be achieved within minutes while the vacuum pumps are running. By purging the interspace with air, the larger molecules help flush the smaller hydrogen molecules from the downstream line.

The system was connected to a computer that used LabVIEW to show real-time measurements of temperature and pressure. LabVIEW is a systems engineering software for applications that involve tests, measurements, and control. A program was created to show the hardware of the system, collect data at various time intervals (standard data collection is in 5 second intervals), and provide data insights.

4. Experimental Procedure:

The collection of data for each isotherm consisted of loading and unloading procedures. The following loading procedure describes the steps for introducing hydrogen to the palladium bed. The hydrogen is administered sequentially in small aliquots, which are all part of a single “run” for a given isotherm. The loading procedure is detailed below:

1. Close all valves.
2. Start data acquisition in LabVIEW and collect background pressure.
3. Slowly open the hydrogen valve to pressurize the charge volume to the desired amount. Monitor the pressure gauges and close the hydrogen valve when finished.
4. Record pressure measurement in the charge volume ($P_{\mathbf{Charge}}$).
5. Open $V_{\mathbf{Pd}}$.
6. Allow gas to reach equilibrium (constant pressure).
7. Record pressure measurement over the palladium ($P_{\mathbf{eq}}$).
8. Close $V_{\mathbf{Pd}}$.
9. Repeat steps 3-8 until the isotherm is complete.
10. Close all valves.

The desired amount of hydrogen injected into the system depends on the region of the isotherm for which data is being collected. In the alpha region and the beta region, the system is pressurized by increments of about 150 Torr. In the mixed region, the system is pressurized by increments of about 900 Torr. In the transition regions between the alpha and mixed region or the mixed and beta region, the system is pressurized by increments of approximately 75 Torr. Smaller aliquots (those that introduce small amounts of hydrogen and therefore smaller pressure increments) produce data points that are closer together. Larger aliquots produce larger differences in the H:Pd ratio, leading to data points that are farther apart in a plot of the equilibrium pressure vs. the H:Pd ratio. For this reason, it is crucial to introduce small loads during transitions between regions, in order to accurately measure the transition regions. However, it is acceptable to introduce large loads to the system during the mixed region because the equilibrium pressure remains relatively constant.

An isotherm is complete when several data points have been taken in the beta region, or when the pressure has reached 1000 Torr. The pressure gauge that was used had a maximum rating of 1000 Torr.

After each run, the hydrogen or deuterium must be removed from the system. The unloading procedure is detailed below:

1. Open $V_{\mathbf{Pd}}$.
2. Slowly open $V_{\mathbf{Vac}}$ until the Hastings pressure gauge is greater than 1000 µmHg (1 Torr).
    a. If the pressure does not decrease within five minutes, close $V_{\mathbf{Vac}}$ and open $V_{\mathbf{Air}}$ briefly.
    b. When the pressure decreases to less than 50 µmHg on the Hastings pressure gauge, re-open $V_{\mathbf{Vac}}$.
    c. Repeat steps 2a – 2b (air purge) as necessary.

3. Once the pressure on the MKS pressure gauge is at background pressure, open V_{Vac} fully and turn on the turbo pump.
4. After the turbo fully spins up, wait 30 seconds and turn on the ion gauge.
5. Evacuate for several hours.
6. Heat the Pd bed to 160°C.
    a. Turn the temperature up in increments of 10°C.
    b. Do not allow the system to exceed 170°C.
7. Evacuate while heating for at least 8 hours.
    a. The ion gauge should read less than 10^{-7} Torr.
8. Turn the heat down to the desired setting for the next isotherm.
9. Close V_{Vac} and V_{Pd}.
10. Turn off the turbo and wait 15 minutes for it to spin down before starting the next run.

5. Results and Discussion:

Measurements of pressure, temperature, and composition were used to create isotherms in the temperature range 293 K to 393 K, plotted in Figure 5. These isotherms illustrate the hydrogen absorption into palladium that is occurring in the alpha, mixed, and beta regions. The experimental data are represented by stars. Data in this temperature range followed the general trend published by Gillespie[2,3] and Lasser,[4] but differ from the data published by Cross,[1] which show some inconsistencies.

During each hydrogen loading onto the palladium bed, the pressure and temperature were recorded. This data was used to plot the isotherms of hydrogen pressure versus the hydrogen to palladium atom ratio. Loadings were made from 293 K to 393 K. It is apparent that hydrogen vapor pressure increases as temperature increases.

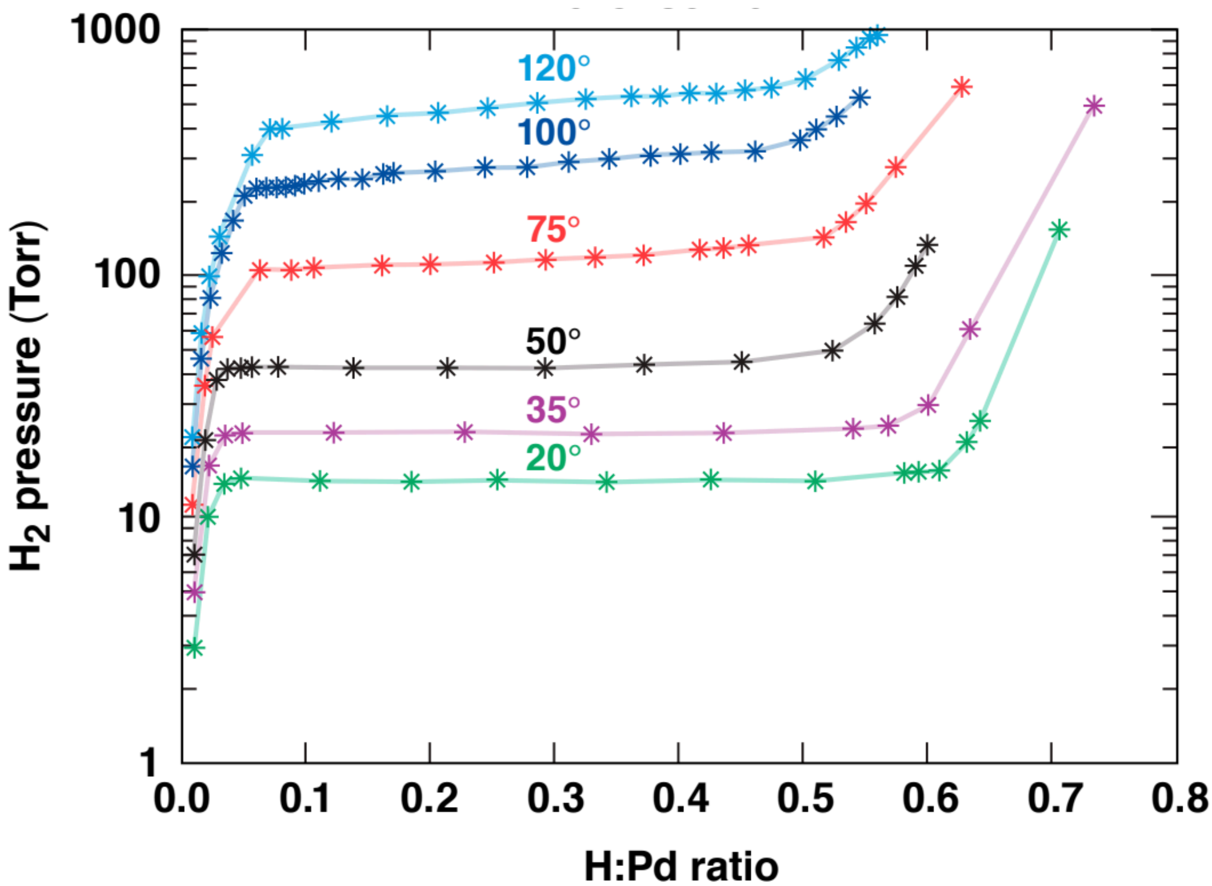

Figure 5: Hydrogen isotherms at various temperatures.

Each loading was duplicated to show consistency in the current study. Figure 6 shows two sets of data taken at the temperature 75°C. The data sets are highly consistent with each other, showing that the mixed region spans the H:Pd range of 0.08 to 0.54, and has an equilibrium pressure increasing from 105 to 110 Torr.

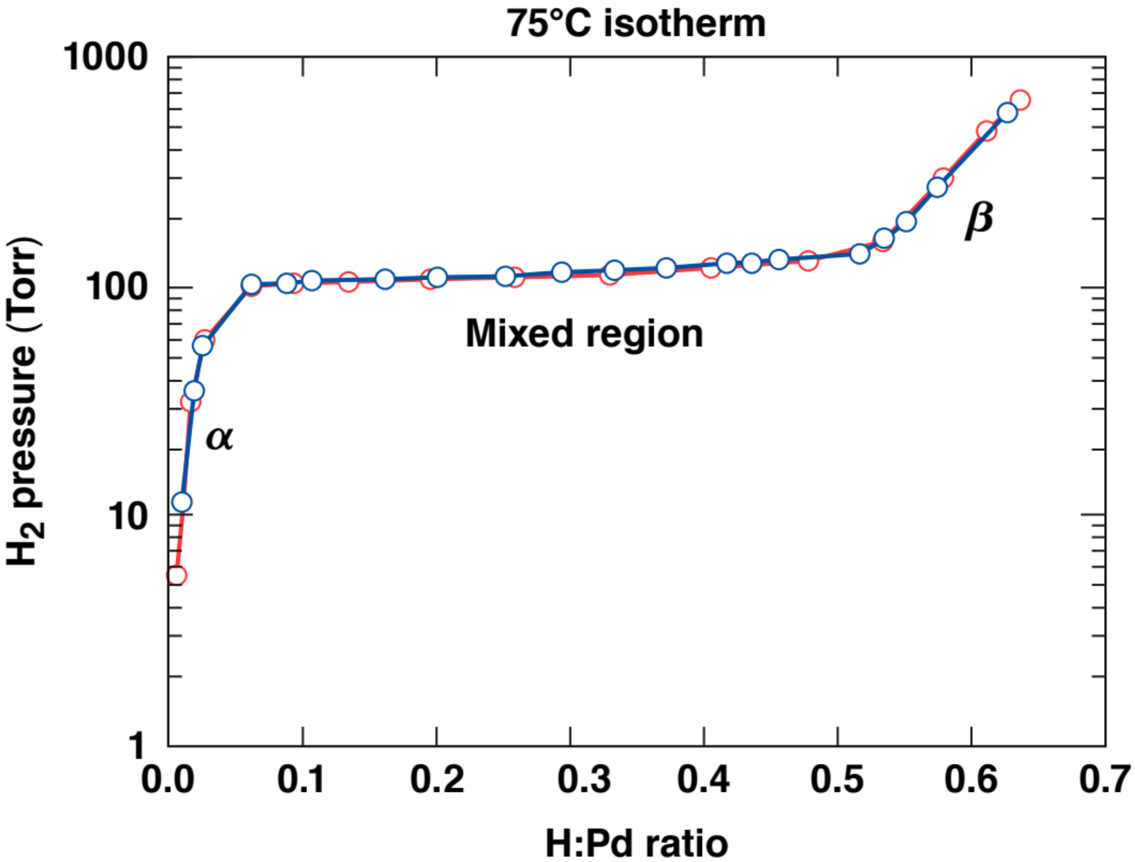

Figure 6: Two isotherms generated at 75° C to demonstrate reproducibility.

Figure 7 shows a plot of $\ln(P_{eq})$ vs. 1/RT for the 0.4 H:Pd ratio.

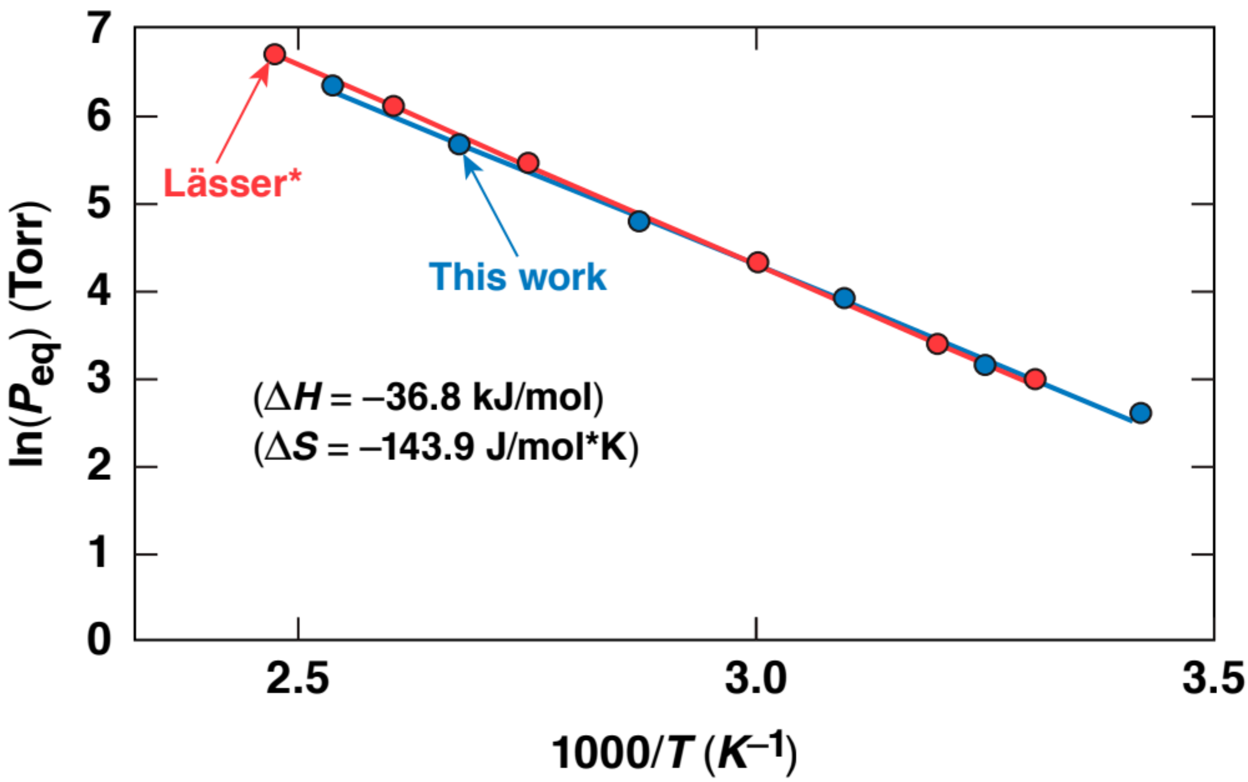

Figure 7: The van't Hoff plot at the 0.4 H:Pd ratio for Lasser (red) and this study (blue). The two van't Hoff plots match, indicating that the current work has reproduced literature data within experimental error.

The van't Hoff equation obtained from the current data set is

$$\ln(P_{eq}) = -36801/RT + 17.688.$$

Using this equation, the enthalpy of formation was determined to be:

$$\Delta H = -36.8 \text{ +/- } 0.9 \text{ kJ/mol}$$

and the entropy of formation was determined to be:

$$\Delta S = -143.9 \text{ +/- } 2.7 \text{ J/mol/K}.$$

6. Conclusion:

Palladium is a viable storage medium and pump for hydrogen, deuterium, and tritium. Palladium absorbs and reacts with hydrogen and deuterium to form palladium hydride and palladium deuteride, respectively. Palladium absorbs a significant amount of hydrogen within its crystal lattice. An experimental setup was used to measure the formation of palladium hydride at modest temperatures. The enthalpy and entropy of reaction can be used to predict the required pressure at a fixed H:Pd ratio and at a given temperature. A higher H:Pd mole ratio can be achieved at lower temperatures. This experiment validates prior data on the hydrogen-palladium system.

Now that the experimental setup has been validated, it can be used for several investigations. Future work is already underway for isotherms of the deuterium—palladium system. After that, work will be done on the hydrogen—deuterium—palladium system. This will address mixed isotopes and serve as a model for the deuterium—tritium—palladium system. Future work will also include isotherms at cryogenic temperatures, which is highly relevant to the new target-filling concept.

7. Acknowledgments:

This research would not have been possible without the guidance or Dr. Walter T. Shmayda and Dr. Matthew Sharpe. Also, thank you to Dr. Stephen Craxton and Jean Steve for organizing the University of Rochester Laboratory for Laser Energetics High School Research Program and making this research project possible.

8. Works Cited

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