Investigations of the Hydrogen-Palladium and Deuterium-Palladium Systems

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Abstract:

Palladium is a metal that is used to store hydrogen and its isotopes. It can interact with hydrogen by either physically storing it in the spaces between palladium atoms, or by reacting with it chemically to form palladium hydride, which can be separated later to release the stored hydrogen. This work examines the change in vapor pressure over palladium as hydrogen is added to change the ratio of hydrogen atoms to palladium atoms, with the temperature held constant. This data is represented as an isotherm. Little data exists for the formation of palladium hydride at temperatures below 0°C. This work serves to expand the data available at low temperatures. Data has now been collected at temperatures ranging from 140 K to 393 K (-133°C to 120°C). The formation of palladium hydride at low temperatures has been observed to deviate from high temperature data, following a separate trend on the van ‘t Hoff plot. This created a total of two lines on the van ‘t Hoff plot, one for the high temperature data and a separate one for the low temperature data. This is likely due to the physical adsorption of hydrogen onto the surface of the bed. A relationship between temperature and the surface coverage of the palladium bed by hydrogen via physical adsorption was calculated using this new data.

1. Introduction:

Studying the formation of palladium hydride is important because of its use as a method to store, transport and release hydrogen and its isotopes, deuterium and tritium. This is especially significant to the Laboratory for Laser Energetics (LLE) because LLE carries out inertial confinement fusion experiments using cryogenic targets filled with deuterium and tritium, isotopes of hydrogen. Using palladium hydride to release these isotopes is being investigated as a method of filling the targets with fuel.

The interaction between palladium and hydrogen is well-studied at temperatures above 0°C, [1], [2], [3], [4] but the data for sub-zero temperatures is very limited.[5] Isotherms, which relate the vapor pressure of the system to the H/Pd atom ratio of the bed, need to be measured for palladium hydride at low temperatures in order to fill in the data gap that exists for sub-zero temperatures, and can be used to predict how the composition of mixed isotopes (deuterium and tritium) in the hydrogen changes as a bed of palladium hydride is unloaded at low temperatures. From this experiment, it was found that the formation of palladium hydride did not behave the same at low temperatures as it did at high temperatures.

2. Theory:

Palladium interacts with hydrogen to form palladium hydride according to the following reaction:

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

The letter "x" represents the number of moles of hydrogen as palladium hydride, "s" indicates the solid state and "g" indicates the gaseous state. The formation of palladium hydride passes through three different stages: the first being the alpha stage, the second stage being the alpha-beta stage (or plateau stage) and the third being the beta stage. In each of these stages the palladium and hydrogen interact in different ways as shown in figure 1.

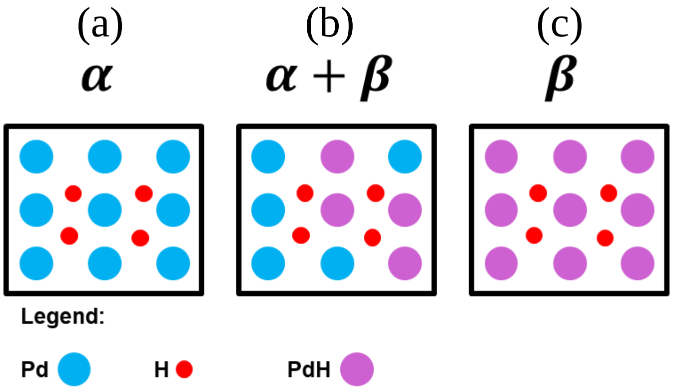

Figure 1: Diagram of the stages of palladium hydride formation

As hydrogen is added, the system progresses through the alpha, alpha+beta, and beta stages. Figure 1(a) shows the alpha stage of palladium hydride formation. Figure 1(b) shows the alpha+beta stage, or plateau stage. Figure 1(c) shows the beta stage.

As hydrogen is introduced to the palladium metal in the alpha stage, hydrogen atoms do not begin to chemically bond with the palladium. Instead they enter the interstitial spaces between palladium atoms to physically store themselves in the palladium atomic lattice as shown in figure 1(a). Next, hydrogen atoms begin interacting chemically with the palladium atoms to form palladium hydride. This is the beginning of the plateau stage. During this stage there are both free palladium atoms and palladium hydride molecules as well as hydrogen in the palladium atomic lattice as shown in figure 1(b). The beta stage begins when all the palladium has been chemically bonded with hydrogen to form palladium hydride. In this stage, there are no additional free palladium atoms and the palladium lattice is now a palladium hydride lattice. Additional hydrogen is physically stored in the spaces in this new lattice of palladium hydride molecules, as shown in figure 1(c).

The vapor pressure of the system follows different trends during each stage. The relationship between H/Pd ratio and pressure at a given temperature is exemplified in figure 2. As the H/Pd atom ratio increases during the alpha stage, the pressure increases also, but less rapidly as the plateau stage is approached. The plateau region sees no increase in pressure as more hydrogen is added to the system, and the H/Pd ratio continues to increase during this phase. During the beta stage, any additional hydrogen added to the system increases the pressure of the system once again.

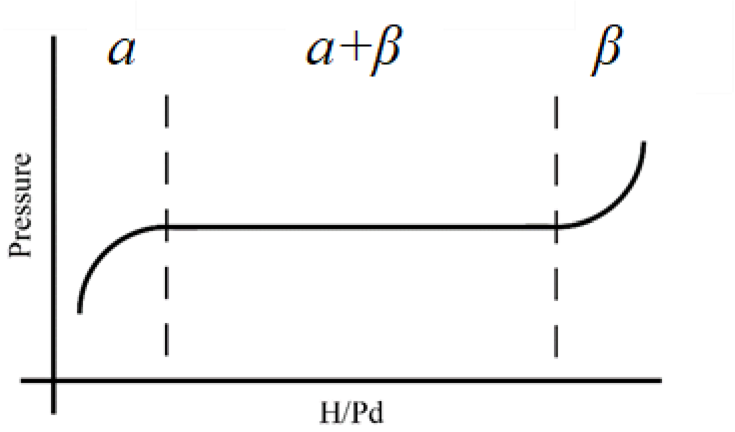

Figure 2: Diagram of the relationship between pressure and H/Pd ratio

The three stages of palladium hydride formation are represented by the three separate parts of the figure. The alpha region is the leftmost separation, labeled "a," the plateau region is in the middle, labeled "a+b," and the beta region is on the left, labeled "b."

This relationship between pressure and the H/Pd ratio at a given temperature creates a distinct s-shaped curve as shown in figure 2. This curve is known as an isotherm curve, which means "same temperature," because the various data points that are collected to form this curve are found while the system is held at constant temperature. The formation of palladium hydride always follows the same general s-shaped curve, but at higher temperatures the pressure for the entirety of the formation curve is higher and at lower temperatures the pressure is lower. This is shown in figure 3.

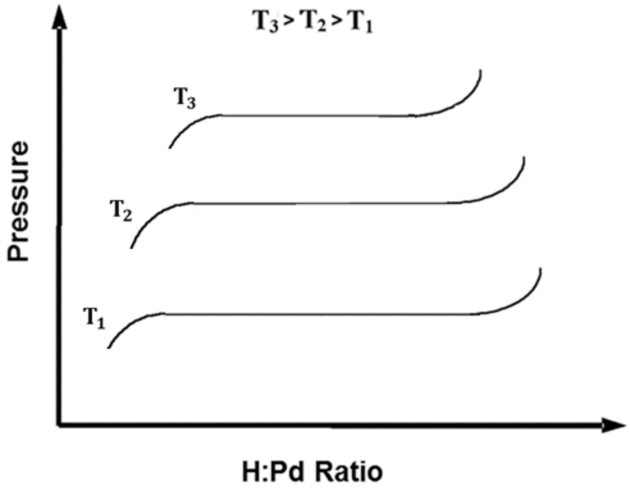

Figure 3: Diagram of the effect of temperature on isotherm position

The lowest temperature, T_1, features the lowest pressures of all three isotherms shown. As the temperature increases to T_2 and then to T_3, the overall pressure increases. It can be thought of as translating the isotherm up and down on the figure depending on the temperature.

The effect of temperature on the pressure of the system shown in figure 3 can be modeled using the van 't Hoff equation which relates the change in pressure to the change in temperature as shown in the following equation:

$$ln(P_{eq}) = \frac{2\Delta H}{xR} * \frac{1}{T_K} - \frac{2\Delta S}{xR} \qquad (2)$$

The variable "P_{eq}" epresents the equilibrium pressure of the system, "ΔH" represents the enthalpy of formation of the system, "ΔS" represents the entropy of formation of the system, "x" represents the number of moles of hydrogen in the system, "R" is the universal gas constant and "T_K" represents temperature in Kelvin. This equation relates temperature to pressure for the formation of palladium hydride, showing the effect that temperature has in “translating” the isotherm curve up or down on the graph as described in figure 3.

The van ‘t Hoff equation follows a linear relationship when plotted on a semilog scale, which is easy to see when comparing it to the equation of a straight line:

$$y = m * x + b \tag{3}$$

where “y” is the natural log of pressure, “m” represents the slope of the line, “x” is the inverse of temperature, and “b” represents the y-intercept of the line. In comparing equation 2 to equation 3, it becomes clear that the y-intercept is related to the entropy of formation of the system and the slope is related to the enthalpy of formation of the system.

Each point on a van ‘t Hoff plot represents the same H/Pd ratio, but different pressures depending on the isotherm, and therefore different temperatures. These points are then plotted on a graph of ln(pressure) vs. (1/temperature), according to the van ‘t Hoff equation and the result is a straight line as shown in figure 4(b), which shows the van ‘t Hoff plot created from the example isotherms in figure 4(a).

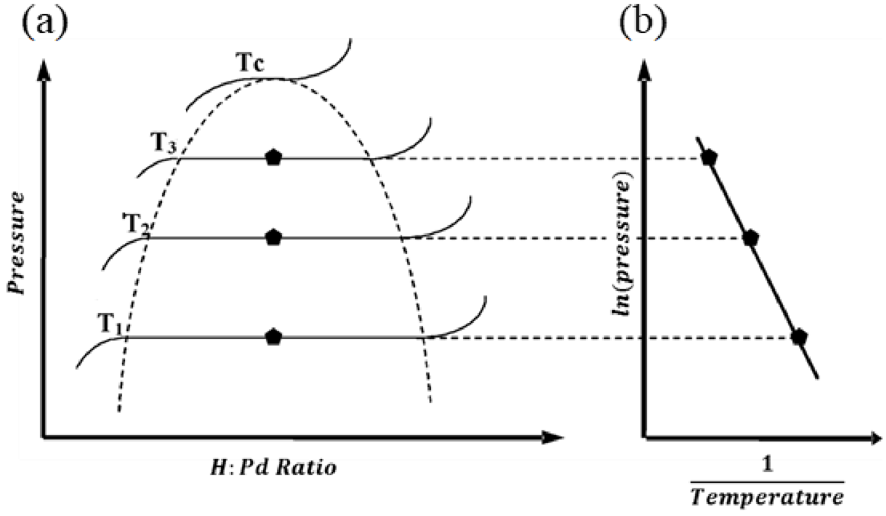

Figure 4: Diagram of the derivation of the van ‘t Hoff plot from isotherm curves

Figure 4(a) shows various example isotherms with a single point at a fixed H:Pd ratio highlighted on each curve. Figure 4(b) shows the corresponding van ‘t Hoff plot.

3. Experimental Setup:

A diagram showing the setup of the equipment to measure the pressure-composition isotherm for a range of temperatures is shown in figure 5.

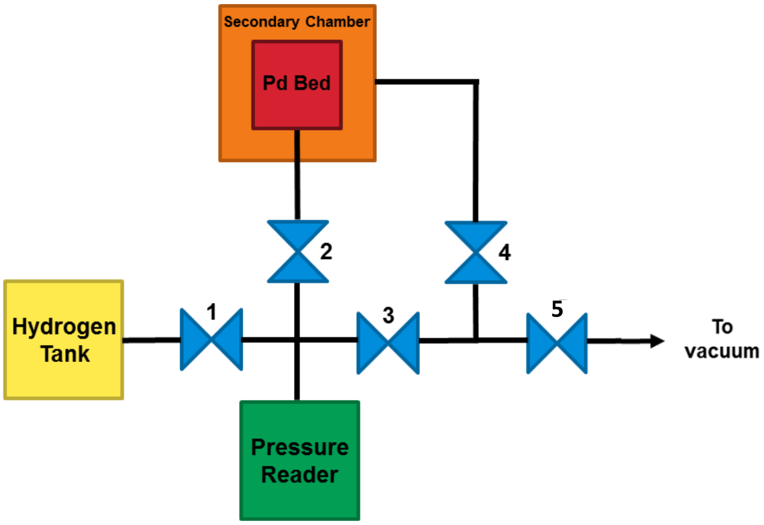

Figure 5: Diagram of lab setup

Black lines represent the tubing between each component, and blue hourglasses represent valves. The arrow that reads "to vacuum" represents the tubing that leads to a turbomolecular pump and a scroll pump. A Q-Drive cryocooler and Sorenson heaters (not pictured) control the temperatures of the Secondary Chamber and Pd Bed.

The palladium bed is made up of 2.5 g of palladium sponge. It is surrounded by a secondary chamber that is vacuum sealed to minimize heat loss or heat gain from the environment. A turbomolecular pump backed by a scroll pump was used to maintain a high vacuum in this chamber. Different valves were used to direct the flow of hydrogen gas to the system and to maintain a vacuum in the secondary chamber as well as to pump the hydrogen out of the system at the end of each run. The volume between valves 1, 2, and 3, including the pressure transducer, known as the charge volume, is 20.1 ± 0.1 cm^3. The volume between valve 2 and the Pd bed is 4.76 ± 0.05 cm^3.

The quality of the vacuum was measured with an ion gauge, which uses a heated filament to emit electrons that ionize gas molecules that pass through it. The ions are collected on a cathode, and the current measured from this cathode can be used to determine the gas density in the vacuum. The system was cooled to subzero temperatures by a Q-Drive, a Stirling pulse-tube cryocooler which uses the compression and expansion of helium to pull thermal energy from a cold head that in turn cools the palladium bed. A Sorenson power supply delivered a DC current to a heater embedded in the body of the palladium bed.

The system's properties such as its temperature and pressure were recorded using a computer running a LabVIEW program to collect real-time measurements. The LabVIEW data was updated every 5-second interval and analyzed using MATLAB.

4. Procedure:

A procedure was developed that outlines the step-by-step process used to add hydrogen to the system to form palladium hydride. Once the system is under vacuum and the desired temperature has been reached and is maintained, the steps to collect data are shown below using the valve diagram shown in figure 5. The load procedure is as follows.

Load Procedure:

1) Close valves V_1, V_2, and V_3, open valves V_4 and V_5
2) Record pressure of system as background pressure
3) Slowly open V_1 to allow hydrogen to enter the charge volume
4) Close V_1 when the desired pressure of hydrogen is reached, and record this pressure as charge pressure

5) Open V_2 to allow hydrogen to enter the palladium bed and interact with the palladium
6) Wait for the pressure to stop changing and reach equilibrium, record the pressure of the system as the equilibrium pressure
7) Repeat steps 4-6 until the isotherm is complete
8) After the isotherm is complete, run unload procedure

This process increases the H/Pd ratio of the system little by little with each iteration of the load procedure to slowly form an isotherm. The H/Pd ratio of the system is found using the following equation:

$$H/Pd = \frac{2*(P_{load}*V_{charge}+P'_{eq}*V_{bed}-P_{eq}*(V_{bed}+V_{charge}))}{R*T_{room}*n_{Pd}} \tag{4}$$

This equation relates the total amount of hydrogen that has entered the system to the total amount of palladium, “n_{Pd},” where “P_{load}” represents the charge pressure of the hydrogen before it’s put onto the bed (see load procedure), “V_{charge}” represents the volume the charged hydrogen is put into, “P'_{eq}” represents the equilibrium pressure after the previous loading, or the background pressure of the system if this is the first charge of a new isotherm (see load procedure), “V_{bed}” is the volume between valve 2 and the Pd bed, “T_{room}” is the room temperature, and “R” is the universal gas constant.

After each isotherm is completed, the hydrogen that was loaded onto the bed must be removed. The removal of this hydrogen is known as “unloading.” The process for unloading at the end of a run is outlined as follows:

Unload Procedure:

1) Close V_4 and V_5 to prevent the vacuum in the secondary chamber from being degraded
2) Open V_2 and V_3 to allow the hydrogen in the Pd bed to escape into the charge volume and surrounding tubing
3) Turn off the turbomolecular pump, Q-Drive, and ion gauge
4) Open V_5 to remove the gas stored in the tubing and Pd bed by evacuating the loop out with the scroll pump
5) Turn on the Sorenson heater to bake off any residual hydrogen in the palladium bed
6) Turn on the turbomolecular pump to improve the vacuum
7) Evacuate for several hours
8) Turn off the Sorenson heater, turn off the turbomolecular pump
9) Close V_3, open V_4 to start maintaining the vacuum of the secondary chamber
10) Turn on the turbomolecular pump, turn on the ion gauge, turn on the Q-Drive
11) Run load procedure

5. Results:

Figure 6 shows isothermal data collected during the current study quantifying the relationship between the H/Pd ratio and pressure for subzero temperatures ranging from -120°C to -36°C. These isotherms are also shown in figure 7 together with high temperature isotherms[4], [6] and additional low-temperature isotherms[6] obtained independently by other LLE researchers.

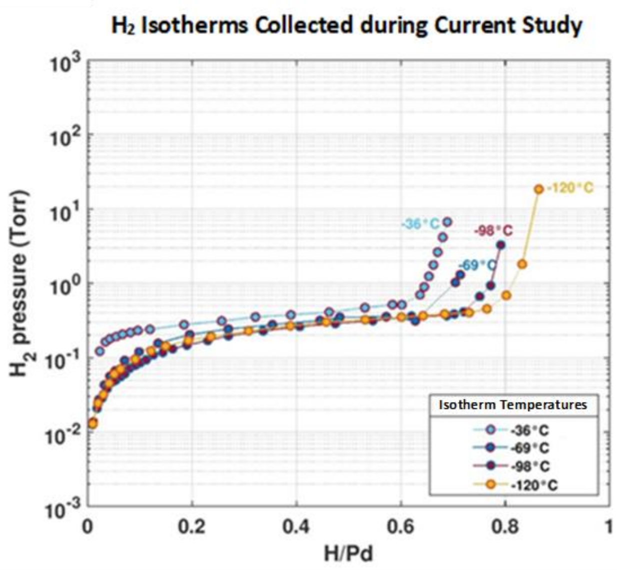

Figure 6: Palladium hydride isotherms collected during the current study

Isotherms were obtained for temperatures ranging from -120°C to -36°C.

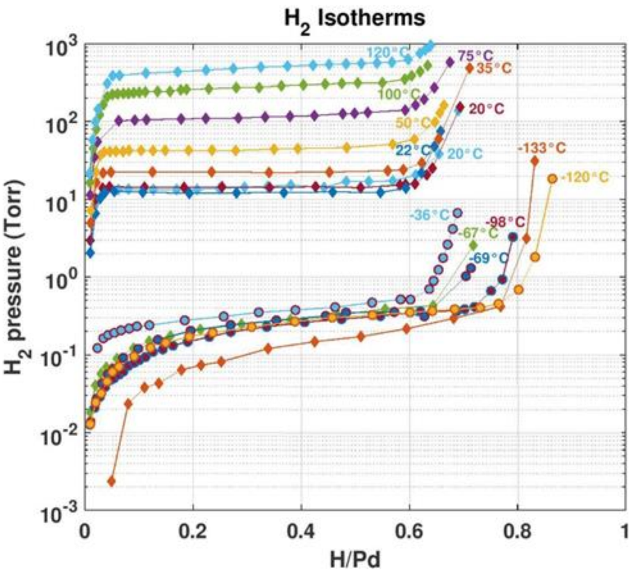

Figure 7: Complete set of palladium hydride isotherms

Figure 7 shows the palladium hydride isotherms of figure 6 together with isotherms collected by other LLE researchers using the same experimental setup[4], [6].

Figure 7 features two groups of isotherms: a low temperature group clustered in the 100 mTorr range with temperature ranging from -133°C to -36°C, and a high temperature group spanning pressures from 10 Torr to 600 Torr with temperatures from 20°C to 120°C. The H/Pd ranges for the lower temperature isotherms are broader than for the higher temperature isotherms suggesting that more hydrogen can be stored at lower temperatures for a given amount of palladium before the pressure starts increasing dramatically. The slope of the plateau regions of the low temperature isotherms is more of an upwards slope rather than the traditional flat plateau shown in the high temperature data.

It should be noted that the yellow isotherm collected at -120°C in figure 7 seems to have been collected with substantial error. The other isotherms in this figure all follow the trend outlined in figure 4, where a decrease in isotherm temperature shows a decrease in overall isotherm pressure, causing the isotherms to vertically shift downwards as the temperature decreases. The isotherm at -120°C, however, is shown to be in line with or above collected isotherms of higher temperatures, such as the -98°C isotherm. Because of this error, the yellow -120°C isotherm was not included in data sets used to calculate van ‘t Hoff lines.

The isotherms of figure 7 were used to create a van ‘t Hoff plot for the formation of palladium hydride with a selected H/Pd ratio of 0.4, shown in figure 8. It is seen that

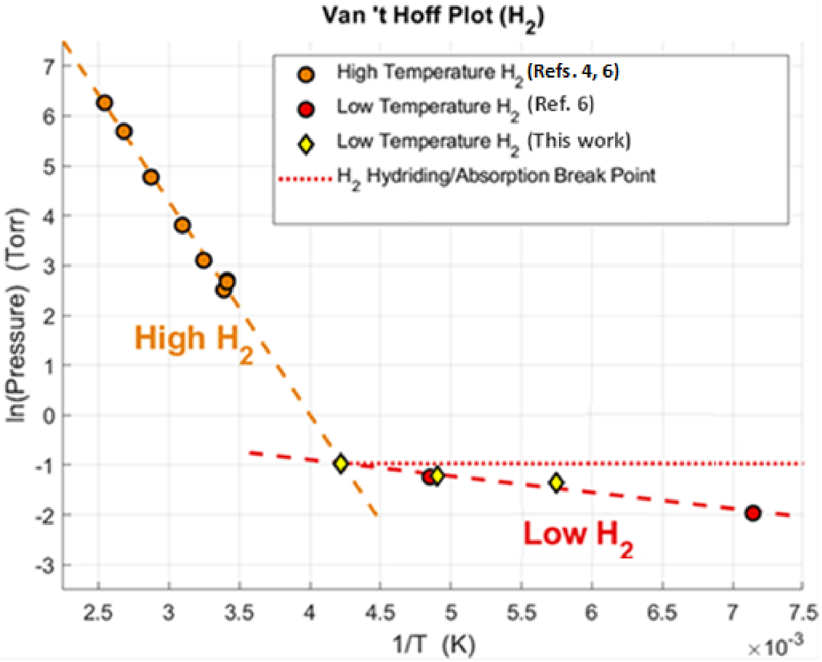

Figure 8: Van ‘t Hoff plot of collected palladium hydride isotherms

The higher temperature isotherms follow a different van’ t Hoff line than the lower temperature isotherms. This suggests a different interaction is occurring at lower temperatures.

the low temperature points deviate from the high temperature points. The points that are shown in orange represent the high temperature isotherms from figure 7. The van ‘t Hoff line for these high temperature isotherms is shown as the dashed orange line. The points shown in red represent the low temperature isotherms from reference 6 shown in figure 7. The van ‘t Hoff line for low temperature isotherms is shown as the dashed red line. The points represented as yellow diamonds are from the current study and are part of the low temperature data set.

The different trends of the low and high temperature van ‘t Hoff lines suggest that the interaction between hydrogen and palladium changes below a critical temperature. In other words, at low temperatures the interaction between hydrogen and palladium is no longer solely the formation of palladium hydride. According to figure 8, this shift occurs at the intersection of the two van ‘t Hoff lines, at -36°C ($1/T \approx 4.22\times10^{-3}\ K^{-1}$). The dotted pink line is a horizontal reference line passing through this intersection. An isotherm that was collected at this temperature is shown in figure 8 as the yellow diamond in the intersection.

6. Discussion

This new interaction was theorized to be physical adsorption of hydrogen onto the surface of the palladium bed. This process begins with the hydrogen that enters the system pooling onto the surface of the palladium sponge rather than entering the palladium atomic lattice or bonding with palladium atoms to form palladium hydride. Next, some of the hydrogen particles bond with the palladium on the surface of the sponge and form palladium hydride, which heats up the palladium slightly because of the exothermic nature of the hydride formation reaction. This slight increase in temperature allows some of the hydrogen to diffuse deeper into the palladium sponge, but only allows it to permeate the first few layers of particles, while the rest of the hydrogen continues to adsorb onto the surface. Because only the first few layers of palladium are permeated, there is a fixed quantity of hydrogen that can absorb into the palladium. This theory was investigated using Brunauer-Emmett-Teller (BET) theory[7] to find the percent surface area of palladium covered by hydrogen at different temperatures. The equation used is as follows:

$$PSAC = 100 \times \frac{\Delta p * V_f * \left(3.53 * 10^{16}\, \frac{particles}{cc-torr}\right) * \left(\frac{273K}{T_K}\right) (2r_H)^2}{\left(\frac{SA}{g}\right) * (m_{Pd})} \qquad (5)$$

where “PSAC” stands for Percent Surface Area Covered, and “Δp” is the change in pressure calculated by finding the difference in pressure between a selected low-temperature isotherm point (the yellow diamond points in figure 8) and the pressure value of the pink horizonal reference line from figure 8 that shows where the high and low temperature van ‘t Hoff lines intersect. This difference in pressure is a result of hydrogen adsorbing onto the surface instead of forming a hydride. Hydrogen that enters the system will form a hydride until the system reaches the critical point ($1/T \sim 4.25 \times 10^{-3}$ in figure 8), at which point new hydrogen added to the system will begin to adsorb onto the surface or form a hydride within the first few layers, which results in this pressure difference. “V_f” represents the free volume of the system, estimated to be 22.1 cc. “($3.53 * 10^{16}$ particles/(cc-torr))” is the number of particles per cc-torr at 273K, a constant found using equation 6 below. “T_K” is the temperature in Kelvin. In the numerator, “r_H” is the Van der Waals radius of the hydrogen atom. Thus, “$(2r_H)^2$” represents the area associated with a hydrogen atom. “(SA/g)” represents the surface area per gram rating of the palladium sponge used, and “(m_{Pd})” represents the total amount of palladium used, in grams.

The value “(3.53*10^{16} particles/(torr-cc))” was found using the following equation:

$$\frac{(6.02*10^{23}\frac{particles}{mol})}{(22.414\frac{L}{mol})(1000\frac{cc-atm}{L})(760\frac{cc-torr}{cc-atm})} = 3.53*10^{16}\ \frac{particles}{cc-torr} \tag{6}$$

This equation takes the number of particles per mol, “(6.02*10^{23} particles/mol),” and converts it to particles per liter using the conversion rate of “22.414 L/mol.” Next, the liters are converted to cc-atm using the conversion rate of “1000 cc-atm/L.” Then, this value of particles per cc-atm is converted to particles per cc-torr using the conversion rate of “760 cc-torr/cc-atm,” which is used in this case because our pressures are measured in torr, not atmospheres. This leaves us with the number of particles per cc-torr, which we can use in equation (5) to find the percent surface area covered.

The entire numerator of equation (5) computes the amount of surface area covered by hydrogen at that temperature, while the entire denominator computes the surface area available. Dividing the amount of surface area covered by the total surface area available and multiplying by 100 gives the percent surface area covered.

The expected percent surface area covered at the four low temperature isotherm points shown in figure 8 is shown on figure 9. The surface coverage was found to be much less than 1%, varying from 0.01% to 0.1% in the range of temperatures studied.

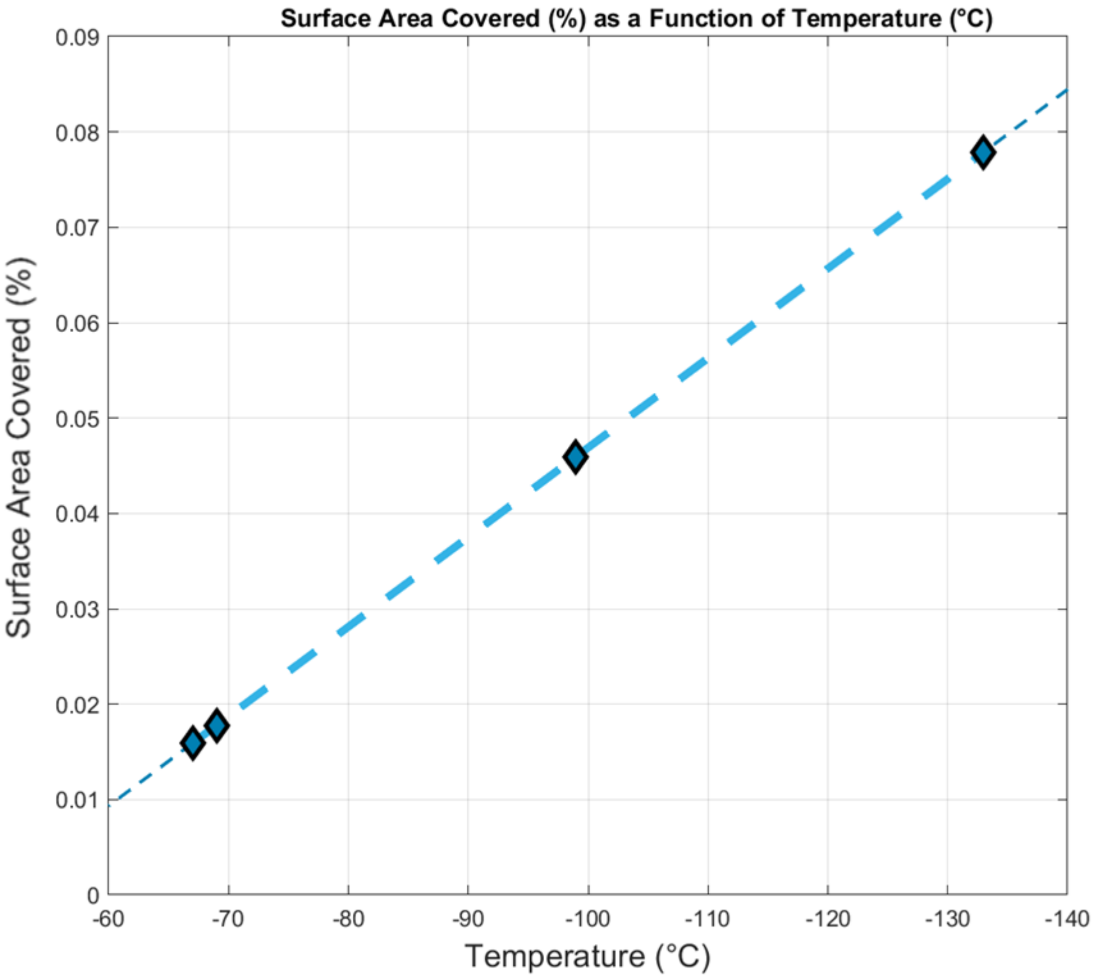

Figure 9: Percent surface area covered as a function of temperature

The four points represented by blue diamonds correspond to the temperatures of the four low temperature isotherm points in figure 8. The light blue dashed line represents the line of best fit for these data points. The thinner dark blue dashed line represents this line of best fit extrapolated outside of the domain of data.

This data set does not include the low temperature isotherm point that lies at the intersection of the high and low temperature van ‘t Hoff lines shown on figure 8, as this is the point at which it is theorized that the process of adsorption begins, and therefore there would be no adsorbing species. All of the hydrogen will absorb and form a hydride at this temperature. It also omits the -120°C isotherm from figure 7 that was collected with substantial error. The calculated low surface coverages indicate that the surface has more than enough space to accommodate the measured quantities of hydrogen taken up by the bed.

In the future, isotherms of mixed isotopic composition (hydrogen and deuterium) will be collected at varying hydrogen to deuterium ratios. Data for deuterium isotherms was collected [2] and a van ‘t Hoff line created for the deuterium palladium system. The deuterium and hydrogen van ‘t Hoff lines are shown together in figure 10.

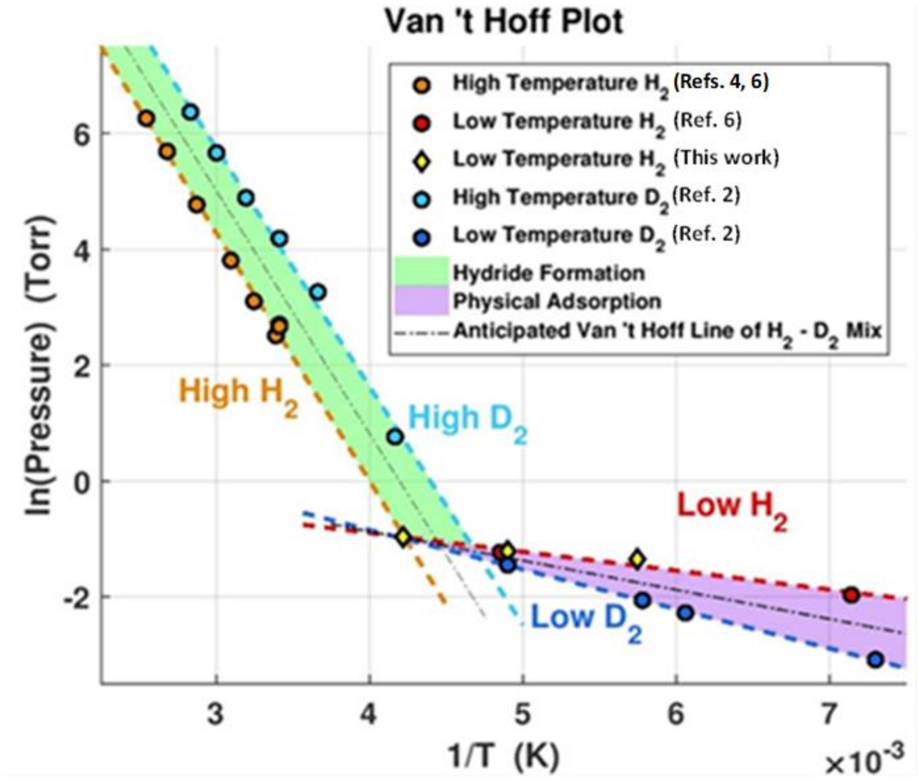

Figure 10: Hydrogen and deuterium van ‘t Hoff plot

The red, orange and yellow data points and van ‘t Hoff lines are the same as those in figure 8 and represent the isotherms and van ‘t Hoff lines collected for hydrogen. The light blue points represent high temperature deuterium isotherms, and the light blue line is the van ‘t Hoff line for these points. The dark blue points represent low temperature deuterium isotherms, and the dark blue line is the van ‘t Hoff line for these points. The shaded regions represent the regions between the hydrogen and deuterium van ‘t Hoff lines, with green representing the high temperature region and purple the low temperature region.

The low temperature deuterium isotherms follow a different trend than the high temperature deuterium isotherms, similar to the shift in trends between high and low temperature hydrogen. This again suggests a shift in interaction between deuterium and palladium at low temperatures.

The shaded regions between the deuterium and hydrogen lines represent the expected locations of the mixed isotopic composition van ‘t Hoff lines. A perfect 50/50 ratio of hydrogen to deuterium is expected to fall on the dashed black line shown in the shaded regions.

7. Conclusions:

The formation of palladium hydride has been well studied at temperatures above 0°C. This work has obtained new data for low temperatures from -120°C to -36°C that have not been studied previously. The new data show a trend that deviates from the higher temperatures. Two separate van ‘t Hoff lines can be created from the high and low temperature data, with an intersection at about -36°C. This deviation suggests a shift in the interactions between hydrogen and palladium at lower temperatures. This different interaction was theorized to be physical adsorption onto the surface of the palladium. This is consistent with the low percent surface area coverage, obtained using BET theory.

A higher amount of hydrogen can be stored at lower temperatures. By forming palladium hydride at a low temperature and then subsequently heating it to a set temperature, large hydrogen pressures can be generated. This could be highly beneficial to LLE for loading precise amounts of fuel into cryogenic targets.

In the future, isotherms of mixed isotopic composition using hydrogen and deuterium will be collected. These are expected to behave similarly to the hydrogen and deuterium isotherms. A mixed isotope van ‘t Hoff line is expected to fall between the hydrogen and deuterium van ‘t Hoff lines.

8. Acknowledgements:

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