Study of the Hydrogen Palladium System

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<u>Abstract</u>

Palladium is a metal which has been found to absorb hydrogen at low temperatures. Releasing the absorbed hydrogen into a closed volume, it is possible to compress the hydrogen and its isotopes to high pressures at modest temperatures. An experimental setup comprising a palladium getter connected to a hydrogen distribution loop was used to measure the hydrogen pressure over palladium hydride as a function of the hydrogen-to-palladium (H/Pd) atom ratio and the palladium-hydride temperature. Equilibrium hydrogen pressures at palladium-hydride temperatures below 293 K are scarce in the open literature. In this study the equilibrium pressures have been measured for H/Pd ratios between 0.0 and 0.8 and temperatures between 123 K and 373 K. This extends the prior minimum temperature of study from 293 K down to 123 K and demonstrates that the H/Pd plateau region extends to 0.8 at the lower temperatures, compared with 0.6 at higher temperatures.

<u>Section 1: Introduction</u>

Prior to this work, published data on hydrogen pressure over palladium-hydride was in the temperature range of 293 K to 1270 K. The hydrogen/metal plateau region in these studies extended for hydrogen-to-palladium (H/Pd) atomic ratios from 0.1-0.6. The plateau region is where the hydrogen pressure does not increase much while the H/Pd ratio is increased, resulting in a relatively flat slope for part of the graph of the pressure vs. H/Pd ratio. Naturally, it is logical to expand the data base of the palladium-hydride system below this temperature range, which would hypothetically correspond to an increase in the range of the hydrogen/metal plateau region. In the known temperature range, a larger percentage of hydrogen atoms bond to palladium at temperatures below 570 K, so it is hypothesized that an even larger percentage of hydrogen atoms will be able to bond to the palladium at temperatures below 293 K.

<u>Section 2: Theory and Motivation</u>

Palladium is one of a special category of metals that can form hydrides. This means that it is able to absorb large quantities of hydrogen gas. Palladium stores hydrogen by breaking the hydrogen molecules into two hydrogen atoms, which then bond to the palladium in three stages. The initial stage is known as the alpha region, shown in figure 1. In this region, hydrogen atoms dissolve in the palladium metal lattice, but are not chemically bonded to the palladium. The second stage is the mixed alpha and beta region, also shown in figure 1. In this region, a fraction of hydrogen atoms is chemically bound to the palladium atoms, while the remainder remain dissolved in the lattice spaces. The third stage is the beta region, where all the possible hydrogen-palladium bonds have been made and any extra hydrogen must dissolve in the metal hydride lattice. The beta region requires much more pressure to insert gas into the structure because the hydrogen is no longer binding to the palladium but just finding space to inhabit within the lattice.
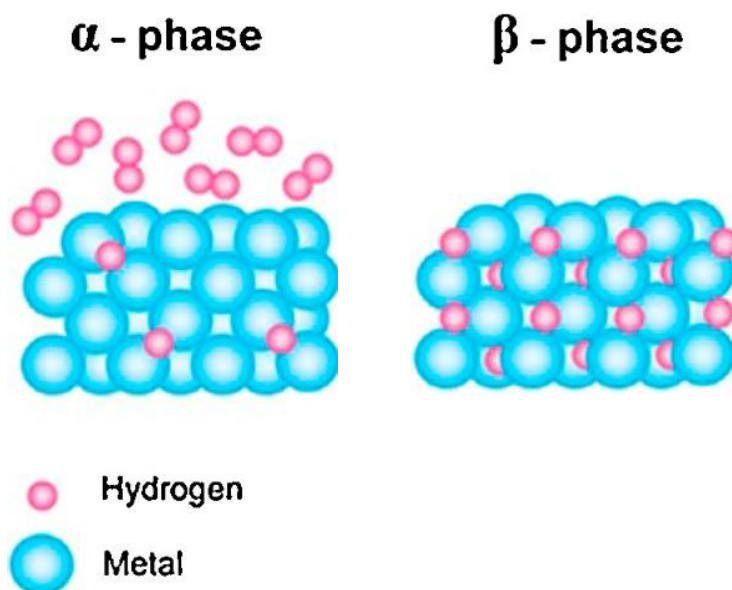
Figure 1: Alpha and beta phases at a molecular level. In the alpha phase, the hydrogen particles are simply occupying the space in between the palladium lattice without bonding to them, resulting in the more disorganized pattern. In the beta phase, the hydrogen atoms are bonded to the palladium atoms which is why the palladium hydride is more structured in the beta phase.

The progression of the three phases is shown graphically in Figure 2.
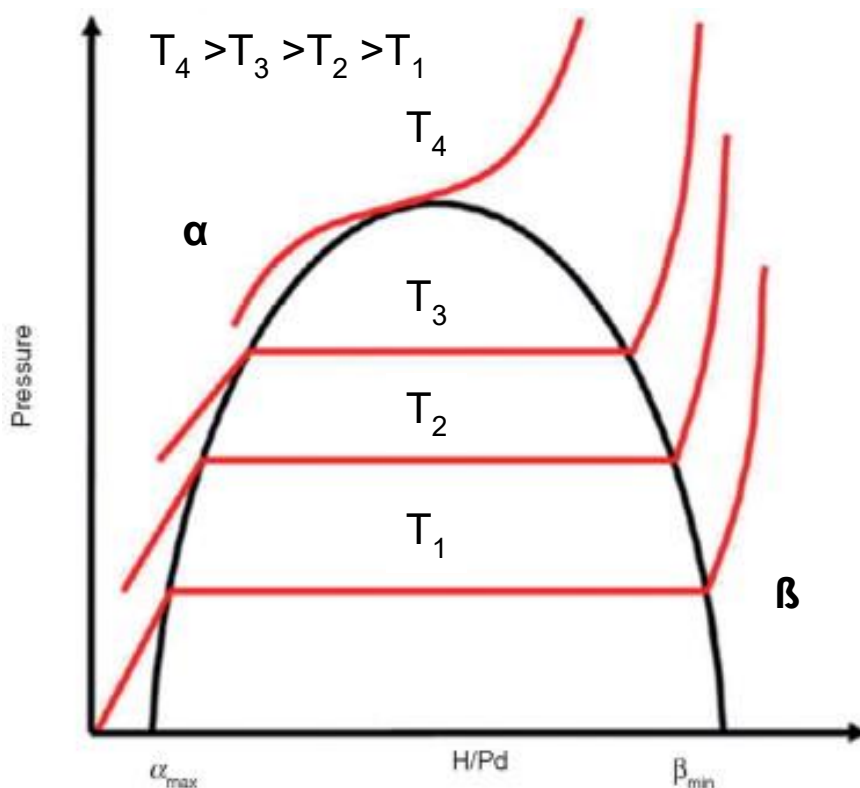
Figure 2: Pressure-temperature-composition curves at increasing temperatures, T_1-T_4. The different regions of palladium hydride are represented by regions around the parabola. To the left of the parabola is the alpha region. In the middle of the parabola is the alpha and beta region. To the right of the parabola is the beta region. α-max shows the end of the alpha region, and β-min shows the beginning of the purely beta phase.

As the temperature increases from T_1 to T_4, the pressure exerted by the hydrogen also increases, which is seen in Figure 1. As the temperature changes, the sizes of the three regions also shift, with the mixed alpha and beta region shrinking as the temperature increases. At the peak of the parabola in Figure 1, the alpha and beta regions coalesce. Extending the trends from the graph to temperatures below T_1, the hypothesis is that the mixed alpha and beta region will extend from lower H/Pd ratios to larger H/Pd ratios, thereby making it possible to store more hydrogen with less pressure.

The van't Hoff equation (1) applies to the palladium hydride region. This equation provides the relationship between the hydrogen pressure and the temperature of the hydride. This relationship depends on the standard enthalpy change, ΔH, and standard entropy, ΔS for the process. The standard form of the van't Hoff equation is

$$\ln P = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad \text{(1)}$$

This equation is often simplified to

$$\ln P = \frac{A}{T} + B \quad \text{(2)}$$

When plotting ln P against 1/T at a given H/Pd ratio, the relationship is linear. The A value is the slope of the graph and the B value, equal to -ΔS/R, is obtained by solving Equation 1 for a given temperature and pressure. An example of a van't Hoff curve is shown below in figure 3.
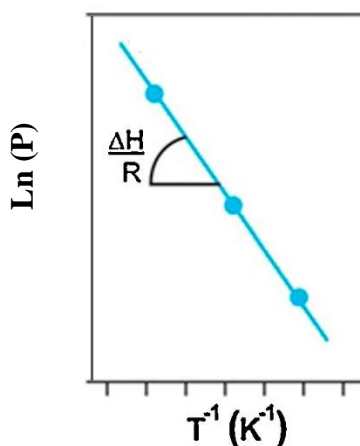

Figure 3: A typical van't Hoff curve, where the y-axis represents the ln of pressure (in torr) and the x-axis represents 1/temperature (in Kelvin). The slope of the graph is ΔH/R (which is also known as the A value).

Palladium is being investigated for use as a storage medium and pump for hydrogen and its isotopes, deuterium and tritium. Current pumps are expensive and mechanically complicated, which increases the potential for the release of radioactive tritium. Palladium offers a simpler and more robust alternative. A palladium sponge would allow inertial confinement fusion targets to be filled by alternating the temperature of the palladium, initially cooling the palladium to absorb tritium from a reservoir and then warming the palladium in a controlled manner to pressurize the targets. For this reason, it is important to collect data on the pressure as a function of hydrogen to palladium ratio at sub-zero temperatures. This data is necessary to test if hydrogen can be stored at higher ratios at lower temperatures to optimize the amount of hydrogen that can be stored in a given volume of palladium. The exact data is also significant so that the relation between temperature, time, and hydrogen absorbed/excreted can be known since the targets require a very precise amount of hydrogen, deuterium, or tritium.

Section 3: Experimental System

      The experimental system used (shown schematically in figure 4) includes a palladium bed, a calibrated volume, a cryogenic cooler (Q-Drive), a hydrogen supply tank, an MKS pressure gauge, a scroll vacuum pump, a turbo vacuum pump and a series of valves labeled as V_H, V_{Pd}, V_{Vac}, V_{Iso}, V_1, V_{Cal}, and V_{2nd}. All components are connected by stainless steel pipes and Swagelok fittings. The integrity of the system was measured using a helium leak detector and demonstrated to be less than $1*10^{-9}$ scc/sec helium.
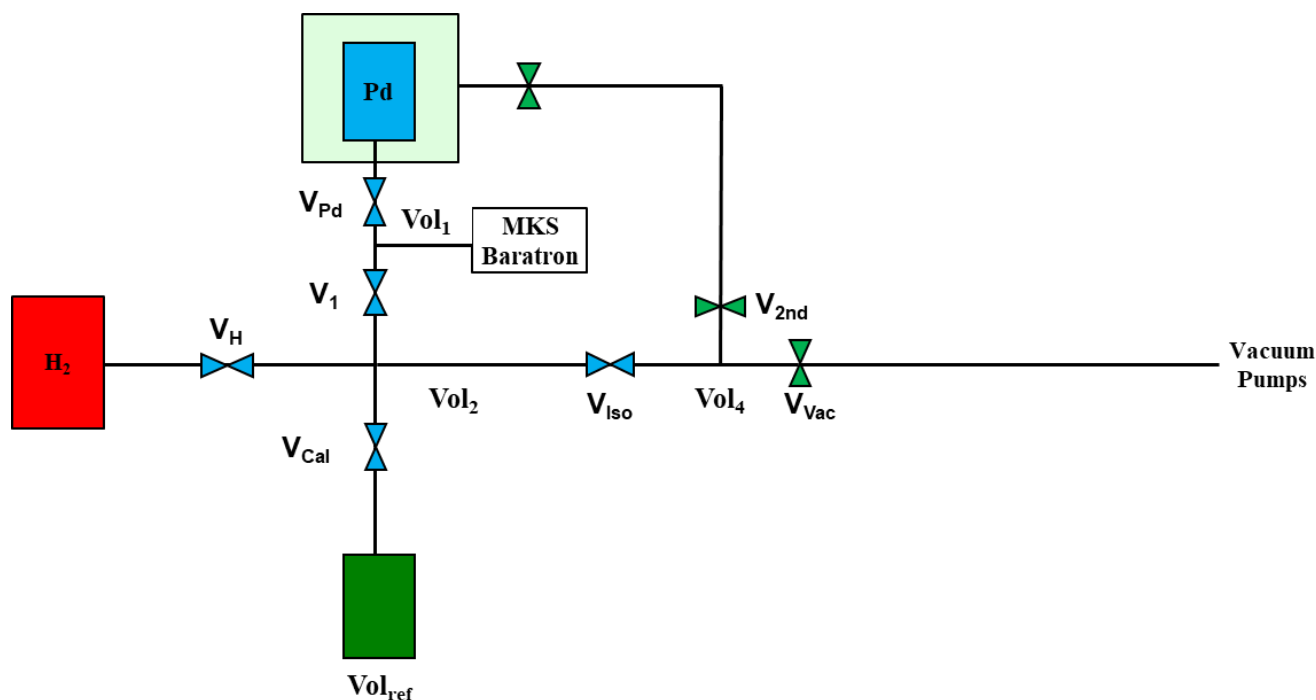

Figure 4: Schematic of the experimental setup used to measure the hydrogen isotherms

      As seen in figure 4, the hydrogen tank is on the left, the palladium bed is on the top, the calibrated volume is on the bottom, and the vacuum pumps are off to the right. The blue color, seen on some valves, represents that they are closed. The position of the valves on the schematic drawing are for when the system is finished unloading and is ready for another run. The volumes labeled are the volumes in the pipes connecting the different parts of the system.

     Data was collected in individual "runs," each of which consisted of a loading and unloading procedure. The loading procedure describes the steps used to administer hydrogen from the hydrogen tank to the palladium bed. The hydrogen is transferred in small amounts, called loads.

Before each load was initiated, V_{Cal}, V_{Pd}, V_H, and V_{Iso} were closed while V_{2nd}, V_1, and V_{Vac} were open. Vol_{Ref} was a calibrated volume only used to find the volume of the other segments, and was not meant to be included as part of the loading process. After all valves were in the correct position, V_H was opened extremely cautiously to begin loading. V_H was closed after reaching the desired pressure for the load. Gas was allowed to reach equilibrium, then V_1 was closed. Pressure measurements were recorded from the gauge and inserted in an Excel spreadsheet. V_{Pd} was then opened to allow the gas to enter the palladium bed. After about 5 minutes, data was taken from LabVIEW and copied into Excel. This data was used to create graphs of pressure vs time, discussed later. Gas was allowed to reach equilibrium, and then pressure measurements were taken from the gauge again. Data was entered into an Excel spreadsheet which tracks pressure vs. the H/Pd ratio. The loading process was repeated until the pressure vs H/Pd graph approached 1000 Torr in the beta region.

Before beginning the unloading process, V_{2nd} was closed and the turbomolecular vacuum pump was turned off so that it does not get damaged when unloading the palladium bed. The Pd bed was heated in increments of 20 °C, with gas being let out of the Pd bed every 20 °C. Gas was released by first closing V_{Vac} and V_{2nd}, then opening V_{Pd} to allow the system to fill with gas. Once it stabilized, V_{Pd} was closed and V_{Vac} was opened. The steps for heating the system and evacuating it in increments were repeated until the system reached 180 °C and all gas was evacuated from the Pd bed. After all the gas was evacuated from the Pd bed, the turbomolecular pump was turned on and the entire system was left at hard vacuum with all valves except for V_H and V_{Cal} open. The system was left with the turbomolecular pump on for multiple hours, often overnight. After the system demonstrated a steady-state hard vacuum, the Pd bed was cooled to the desired temperature by setting the temperature on the controller. Once the temperature cooled to about 20 °C the Q-drive was turned on to accelerate the cooling process. Once the system reached the desired temperature, V_{Iso}, V_{Cal}, and V_{Pd} were closed but V_{vac}, V_{2nd}, and V_1 were left open. The system was then prepared to be loaded.

Section 4: Results and Observations

Pressure-temperature-composition curves were generated in the temperature range 133 K to 373 K. The results are shown in figures 5 and 6 below.
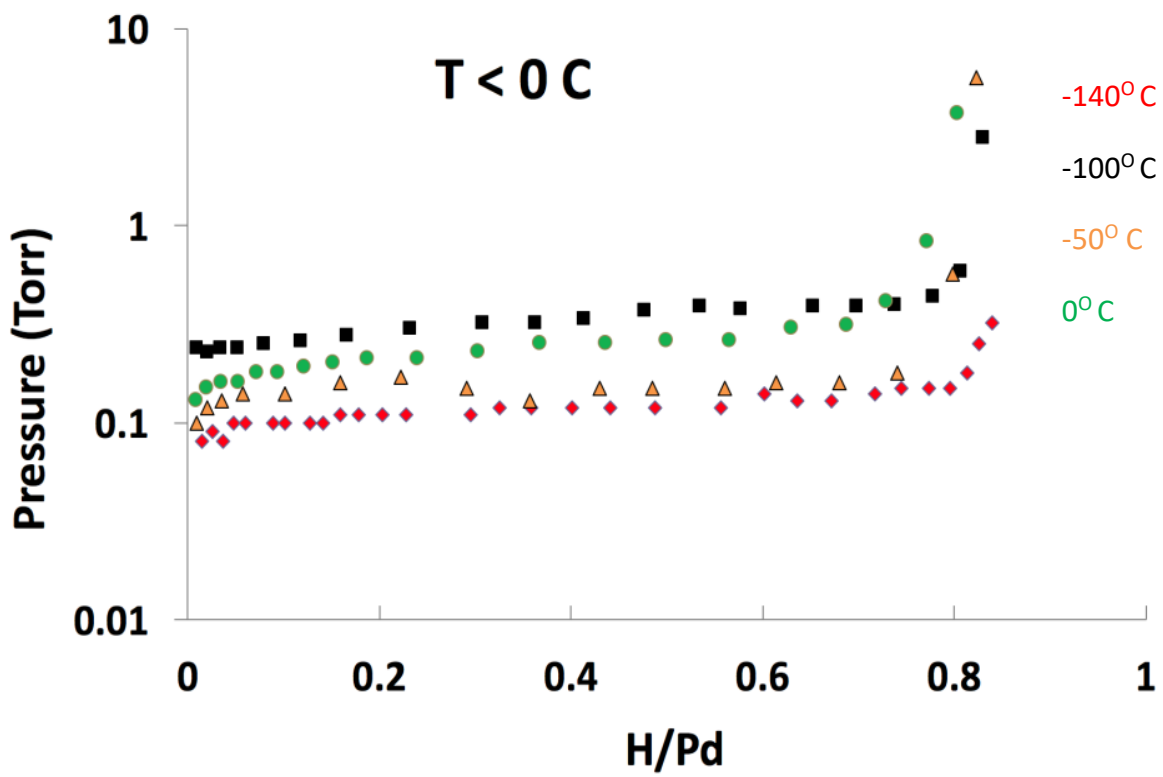
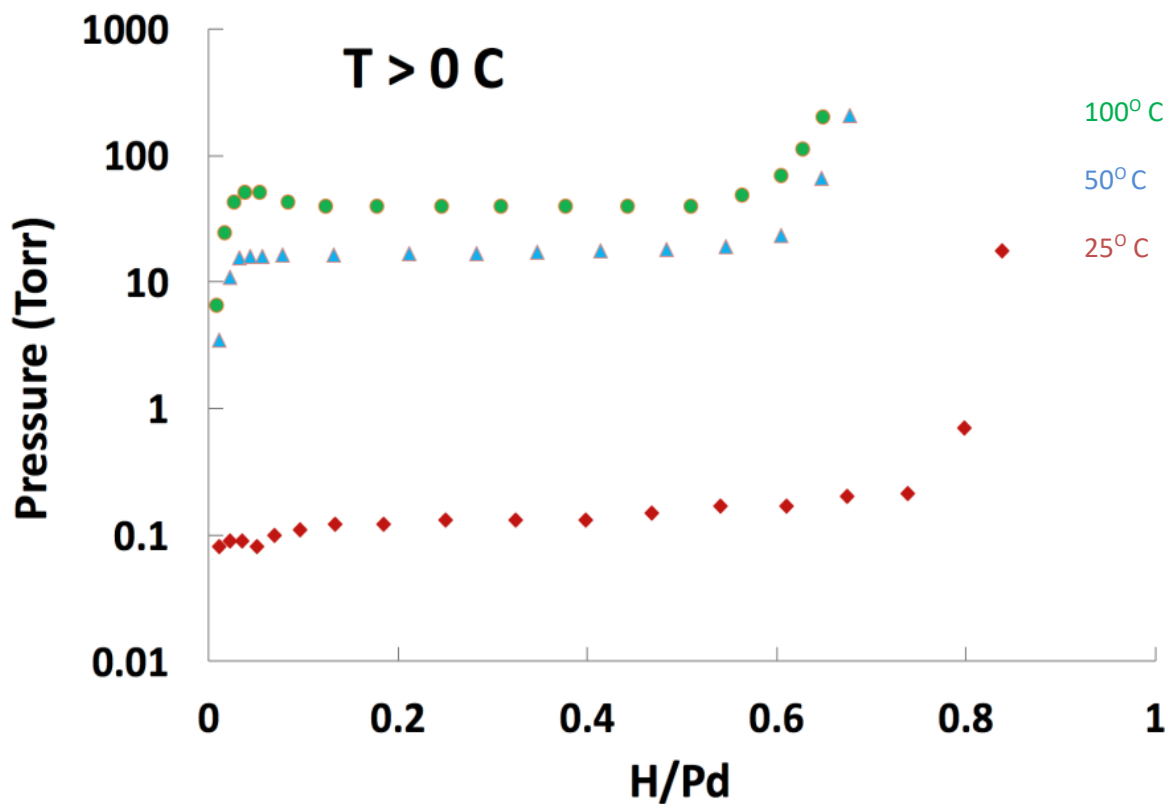Figure 5: Measured isotherms for temperatures 0°C and below

Figure 6: Measured isotherms for temperatures greater than 0°C

For data taken at temperatures above 273 K, increasing temperature corresponded to increasing pressure, but below 273 K decreasing temperature did not correspond with decreasing pressure, as can be seen on figure 5. The data below 273 K went against our hypothesis and the reason for this behavior is presented in the discussion section.

The loading times for different temperatures and hydrogen/metal ratios were obtained by plotting the pressure over the Pd bed as a function of time as shown in figures 7 and 8. The loading time is defined the time required for the pressure to decrease to a steady value.
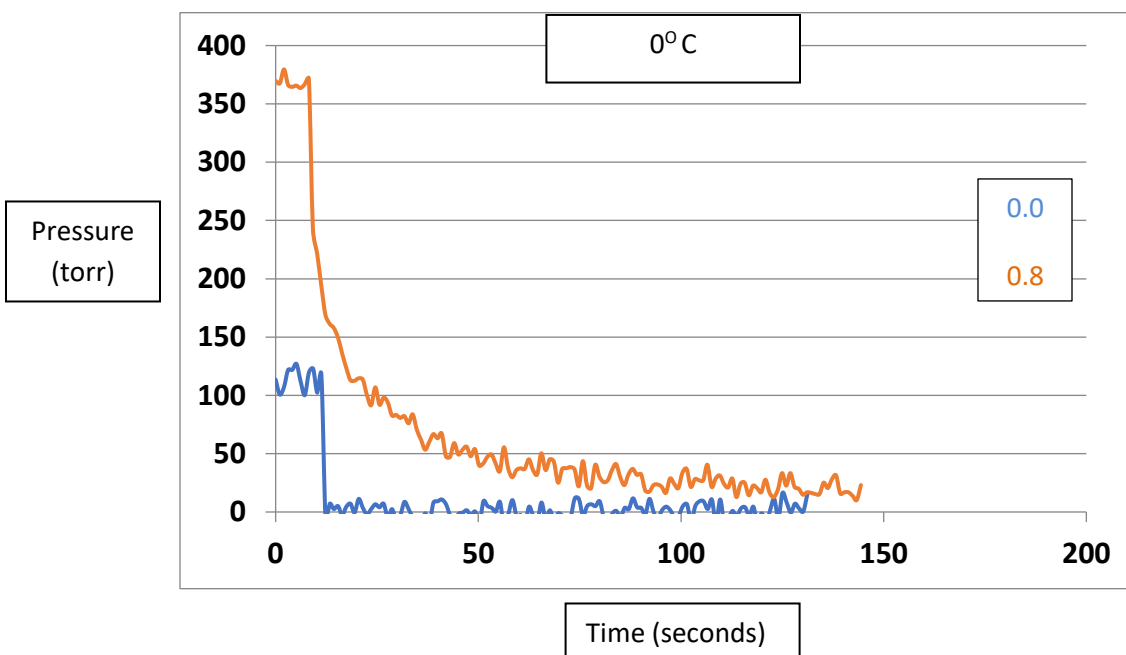
Figure 7: Pressure vs time graph at 0^OC for hydrogen/metal ratios of 0.0 and 0.8.
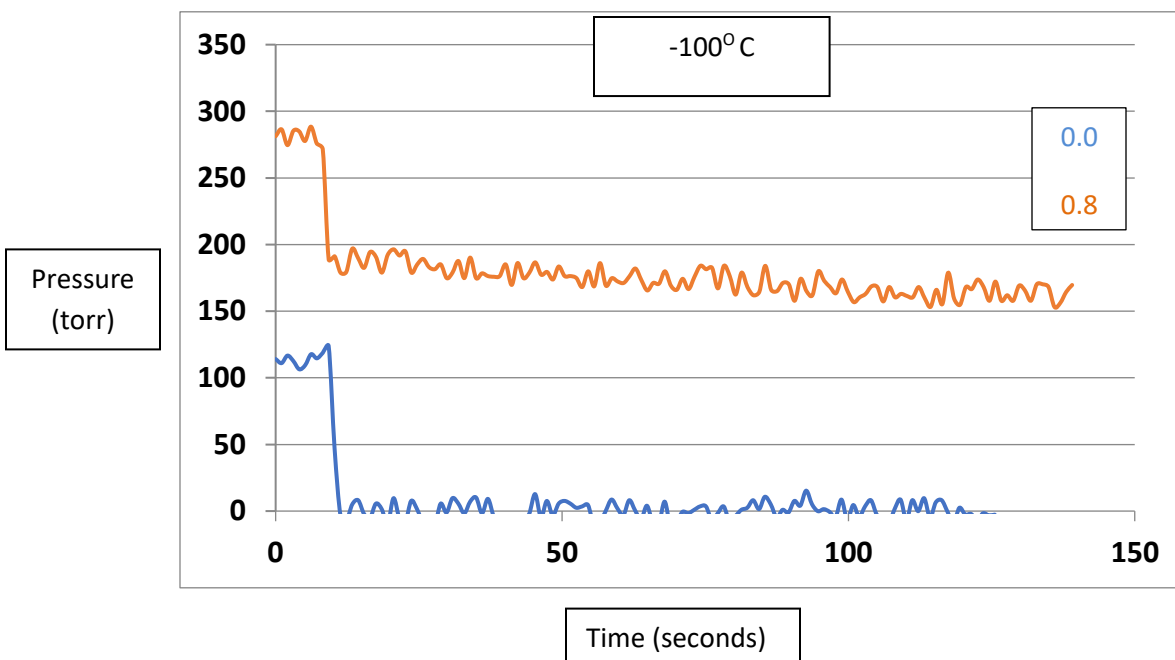

Figure 8: Pressure vs time graph at -100^OC at hydrogen/metal ratios for 0.0 and 0.8.

By comparing Figure 7 and Figure 8, it can be observed that the loading time at a hydrogen/metal ratio of 0.8 is much larger at -100°C than at 0°C. In both figures, the pressure drops rapidly at a hydrogen/metal ratio of 0.0, but at a hydrogen/metal ratio of 0.8 the pressure continues to decrease slowly after the initial drop in pressure. In figure 7, the pressure continues to decrease for 140 seconds until it stabilizes. In figure 8, the pressure continues to decrease slowly for 140 seconds but does not fully stabilize with the measured time. After the initial drop in pressure, the pressure in Figure 8 decreases much more slowly than in Figure 7.

In figure 8 the pressure shown is much greater than the pressure graphed in figure 5 because figure 8 only shows the first 150 seconds of the loading time, while a typical load at -100° C would sit for about 30 minutes before reaching equilibrium.

Section 5: Discussion and Conclusions

The data in Figure 6 above 273 K was consistent with past data in studies such as Gillespie (2,3), but at 273 K and below (Figure 5), the data did not follow the expected trend. While the temperature was above 273 K, the descending temperature corresponded with decreasing pressure as seen in figure 6. The van't Hoff equation applied to the data for temperatures above 273 K and was calculated to be

$$\mathbf{ln(P) = 18.9 - 5497/T}$$

where P is in Torr and T is in Kelvin. The B value, which was calculated to be 18.9, was similar to the value of 16.9 obtained by Gillespie and Hall (3), who conducted research in the temperature range of 273 K to 453 K. In addition, the A value, which was calculated to be -5497, was similar to the value of -4225 obtained by Gillespie and Hall.

However, this van't Hoff equation does not apply to temperatures below 273 K. Below 273 K, the data is not as expected. Lowering the temperature below 273 K resulted in all data being fairly similar, despite spanning a temperature range of 140 K. The disorderly curves shown in figure 3 run counter to expectations. However, while the data were all fairly similar below 273 K, the plateau region did extend to a hydrogen/metal ratio of 0.8, compared to 0.6 at 323 K from Figure 6. This is consistent with the hypothesis that the lower temperatures would allow a larger percentage of hydrogen atoms to bond with the palladium, as seen in Figure 2. This is significant since it proves that palladium is valid as a pump and that it will store the maximum amount of hydrogen at temperatures below 273 K.

The cause of the unexpected plateau pressure behavior below 273 K is attributed to poor temperature control of the palladium powder. While the present design of the Pd bed is adequate for its intended use as a pump and compressor, it does not lend itself to a fine control of the palladium temperature for an investigation of the plateau pressures below room temperature. The cooling power of the Q-drive at the bottom of the palladium column and the heater at the top of

the palladium column establish a strong temperature gradient along the Z axis. While one portion of the bed is pumping the other portion is releasing hydrogen. The temperature gradient is not constant and is affected by the hydrogen gas pressure in the Pd bed, thereby changing the ratio of which part is releasing and which part is pumping. The investigation of the Pd/hydrogen isotherms at temperatures below room temperature requires a redesign of the test Pd bed with emphasis on maintaining the palladium at a uniform temperature.

Section 6: Acknowledgements

Section 7: References

1: Metal Hydrides; Mueller, Blackledge, Libowitz Academic Press, 1968 Chapter 6

2: L. J. Gillespie and W. R. Downs. The Palladium-Deuterium Equilibrium. Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology. Jul 10, 1939

3: L. J. Gillespie and F.P. Hall, The Palladium-Hydrogen Equilibrium and Palladium Hydride, American Chemical Society (1964)