# Hydrogen and Helium Isotope Separation by Permeation Through a Palladium Foil

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## Abstract

The Princeton Field-Reversed Configuration research experiment is a type of magnetic confinement device that utilizes odd-parity rotating magnetic fields to induce closed field lines, drive current, and heat the plasma. The fuel, D-$^3$He, that would be used in this type of device is aneutronic. However, deuterium (D) atoms in the plasma can fuse with each other to produce tritium (T). The T must be extracted to stop D-T reactions from occurring, which produce high energy (14 MeV) neutrons. Removing T from the plasma will allow for a cleaner and lower radioactivity plasma. One way to separate Hydrogen (H) and Helium (He) isotopes is to utilize a high Z material – permeation barrier – high Z material (ZBZ) configuration. Palladium (Pd) has a high H/He sorption rate and high selective permeability through conversion to a metallic hydride when heated to high temperatures, which increases H/He diffusion. This experiment focuses on how H permeability through a Pd foil is affected by temperature and pressure. In the conducted experiments, H and D were found to permeate through the Pd, while other atoms did not permeate which confirmed Pd selective permeability. The permeation was found to be temperature dependent, which was expected prior to the experiments. An increase in temperature was found to increase the permeation rate through the foil. Atomic H created in an unaccelerated ECR plasma source was found to be important in the overall permeation. Experimental values of the frequency factor and activation energy were close to those found in literature. With confirmation of selective H/D permeation, further experiments will be conducted.

## 1. Introduction

The Princeton Field-Reversed Configuration (PFRC) research experiment is a type of FRC that is being researched at Princeton Plasma Physics Laboratory (PPPL) that is headed by Professor Samuel Cohen. The PFRC confines plasma by using odd parity rotating magnetic fields to create closed field lines, drive current within the plasma, and heat the plasma. The PFRC is a type of magnetic confinement device that is different than a tokamak and stellarator, the two main magnetic confinement fusion devices that are researched today. The PFRC has the ability to be much smaller in size and is a modular device, however, would not produce as much power as a

larger tokamak. For this reason, two types of applications that are being examined is for a device like the PFRC is to be used in space travel applications and environmental disasters. The project that was conducted this summer worked towards the application of the PRFC for space travel. The PRFC is essentially a modified magnetic mirror, confinement device that has the ability to keep the plasma confined in the center. However, there are still magnetic field lines that trace the outer layer of the plasma and leave towards the back of the device, and this is where thrust can be produced by allowing the back end to be open.

Tokamaks and stellarators use deuterium (D) and tritium (T) as their fuel, D-T reactions, which produce a high energy 14 MeV neutron. The PFRC would utilize D-$^3$He fuel instead of D-T. Since a device like the PFRC can be used for space applications, the radiation shielding needs to be limited to save weight. That is one of the reasons why D-$^3$He fuel is chosen. However, D-D reactions can take place, which then would create a T atom. This means that a D-T reaction can still occur within the D-$^3$He fuel. Therefore, the T must be extracted in order to mitigate the D-T reactions from occurring and to also make the plasma less radioactive. Using a permeable membrane in the exhaust stream of the reactor is one of the ways that is currently being examined to extract the T out of the plasma. The scope of the permeation project was to examine using palladium (Pd) for hydrogen (H) and helium (He) isotope separation.

## 2. Palladium, Permeation, and ZBZ Configuration

Permeation is the penetration of a gas atom on a material's surface and its transport through the solid by diffusion. A material's permeability is determined by the solubility and diffusion of the respective gas through the material. This means that different gases will have different permeabilities for different materials. The permeability is the product of the solubility coefficient and diffusion coefficient.

$$P = S \times D \tag{1}$$

Where S is the solubility coefficient and D is the diffusion coefficient. Diffusion is seen to be the dominant factor when it comes to permeability. Diffusion is the process by which the gas atom is transported from one part of the system to another as a result of random molecular motions. Diffusion can be solved by Fick's first and second law.

$$J = -D\frac{dC}{dx} \tag{2}$$

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{3}$$

Where D is the diffusion coefficient, C is the permeate concentration, and x is the material thickness. Since diffusion is the result of random molecular motions within the material, it would be assumed that temperature would have some sort of effect on it. This is true, and it is seen that as temperature of the material is increased, then the gas atom diffusion is seen to be increased and solubility is seen to decrease. Multilayer configurations that still obey Fick's first and second law can be added by treating each material as a parallel resistor setup.

The mechanism of H₂ permeation through a piece of Pd metal follows this path: the H₂ dissociates into monatomic H and adsorbs onto the surface, then a hydride effect occurs creating PdH which allows the H to diffuse through the surface, and at the back of the surface after diffusing through, the H associates back into H₂ and desorbs off the surface.
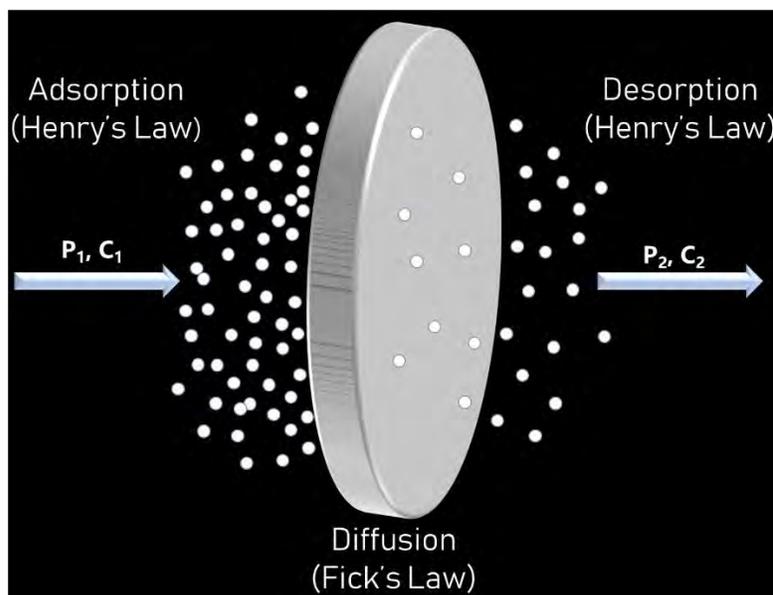


Figure 1: Permeation of gas through a surface.

Palladium is a precious metal with the atomic number 46, 60 neutrons, and an atomic mass of 106.42 amu. Pd is a dense material, having a slightly higher density than that of lead. Pd has been shown to have selective permeability to H and He isotopes, which means it is the perfect candidate for experimenting with isotope separation by permeation. Selective permeability means that isotopes within a gas will only permeate through if it has the ability to diffuse through the surface. This is crucial because extraction of unwanted gas molecules wants to be limited as possible. Since T is an H isotope, this means that if H and D permeation is tested, then it should be able to be translated to T. Pd was also chosen as a candidate because it has low sputtering yields, which is important because impurities do not want to be added into the plasma. Impurities within the plasma will lead to more instabilities, so this wants to be mitigated. It is a high Z-material, which will play a role in future work and experimentation of the hypothesized high Z-material - permeation barrier – high Z-material (ZBZ) configuration for isotope separation. The way that H isotopes permeate through the Pd is due to its high sorption rate and high permeability of H and He at high temperatures, which the high temperatures allow the Pd to convert to a metallic hydride which increases H diffusion through the surface. In this project, a Pd foil with a thickness of 1 mm was used.

The ZBZ configuration would be the final configuration which would be implemented into the exhaust stream of a fusion reactor, in which Pd is a candidate for the first high-Z material layer. The first high-Z material must have a low sputtering yield and high H and He permeability, which as mentioned Pd contains those traits. The permeation barrier would be used to prevent high energy

ions from diffusing back into the plasma. One current candidate for the permeation barrier is $Al_2O_3$. The last high-Z material would just need to have high H and He permeability, since this layer is at the back there is no need to worry about sputtering since it is not in direct contact with the plasma. In the D-$^3$He fuel, the D atoms would have low energy, while the H, T, $^3$He, and $^4$He atoms would have high energy. This means that any D atoms that are implanted on the surface would diffuse back into the plasma, allowing for less consumption of fuel. The higher energy atoms would penetrate the permeation barrier layer, which would also slow down the atoms, and then become implanted in the back high-Z material layer. The permeation barrier would stop those isotopes from diffusing back into the plasma. Due to the possibility of He entrapment within the back high-Z material layer, the layer is being considered to be a more porous material to mitigate He bubble damage from occurring.
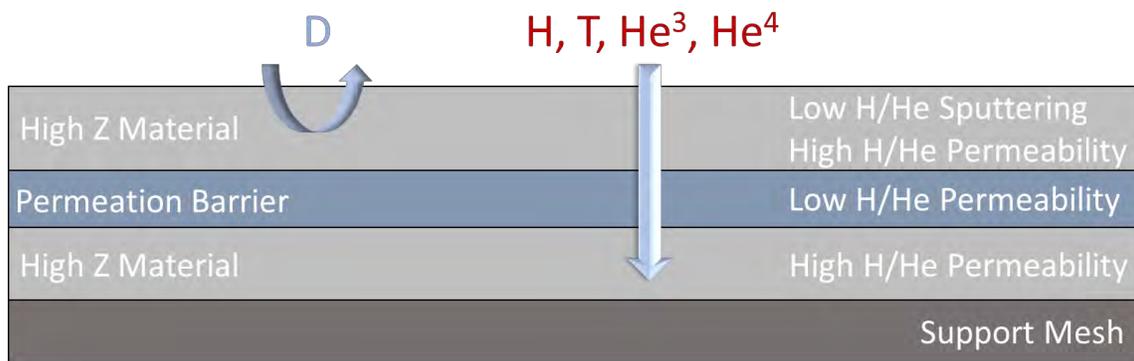


Figure 2: Example ZBZ configuration, not drawn to scale.

## 3. Preliminary Work

To conduct the permeation experiments in the project, preliminary work was needed to be done. The preliminary work comprised of testing residual gas analyzers (RGAs), having a Pd foil holder fabricated, final chamber design, final chamber assembly, chamber leak checking, and heater testing.

The final chamber design has two chamber sides, chamber side one which is the plasma source side and chamber side two which is the permeation reading side. To see how much gas is permeating through the Pd, a mass spectrometer was used. The RGA uses a quadrupole arrangement to detect the weight-to-charge of each ion passing through it. The filament in the probe head is directly exposed to the gas. A spectrum is created using computer software that plots the peak intensity versus mass to charge ratio. The way that the quadrupole arrangement works can be modelled by the Mathieu Function.

$$\frac{d^2y}{dx^2} + [a - 2h^2\cos(2x)]y = 0 \tag{4}$$

The ions are filtered based on their mass to charge ratio by biasing the four rods at different voltages. This means that ions are separated and able to be read based on their stability in the trajectory within the oscillating electric fields. Therefore, ions that are not in the voltage range will

become unstable and not reach the detector, which is modeled by the Mathieu Function. Sweeping the rods across a wide voltage range will allow a spectrum to be created showing atoms of different weights. The RGA that was used in this project was made by a company called UTI and was mainly used in the 1980s.
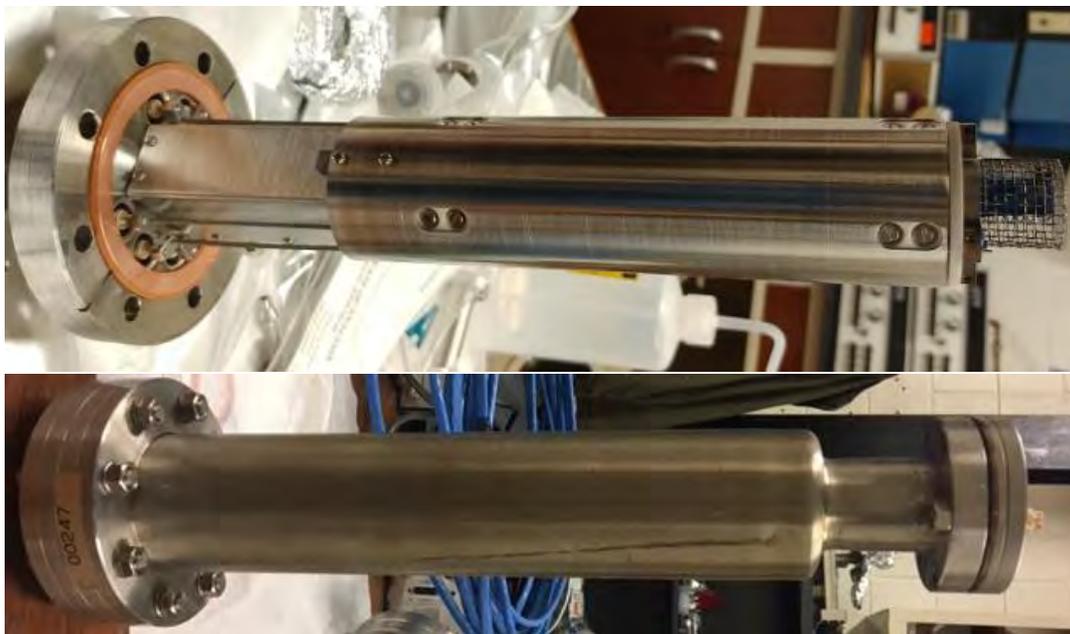


Figure 3: The RGA probe head (top) and RGA with vacuum shield around it (bottom).

There were 5 probe heads and 7 controllers that were available to use. However, since these RGAs sat dormant with no use for many years, it was unsure which ones worked and which ones did not. A testing vacuum chamber was created in order to test each probe to find the RGA that gave us the highest resolution spectra.



Figure 4: RGA testing vacuum chamber setup.

After the probe and controllers were tested, then the Pd foil holder apparatus needed to be fabricated. The final holder apparatus consisted of 5 nichrome wires wrapped around a 0.75" OD

tube, with a stainless-steel shield wrapped around to ensure as much heat retention as possible to allow for quicker and better heating of the Pd foil. A mini conflat flange was machined down to allow for the knife edges on the flange to be able to bite into the Pd foil. The normal gasket that is used is a copper gasket, and Pd has a similar malleability and therefore knew it would create a vacuum seal at the edges. A copper gasket was still used in order to assure that the Pd foil was creating a vacuum seal at the flange knife edge.
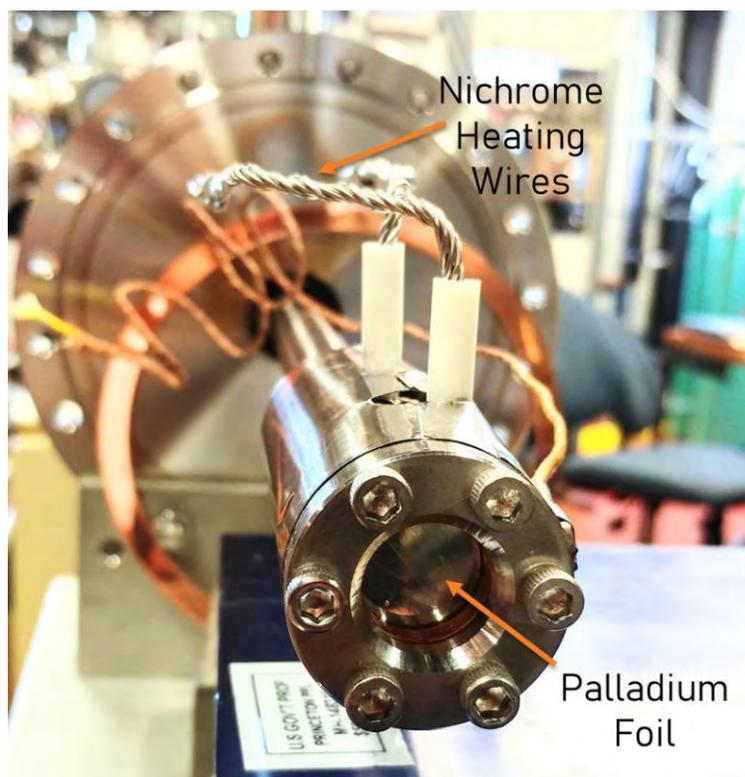


Figure 5: Pd foil holder apparatus.

The final chamber was then assembled. As mentioned, there were two chamber sides to the final setup. Chamber side one was the gas inlet side. Chamber side two was the side that if any gas permeated through the Pd foil, it would permeate into this side. This is where the RGA was mounted, which allowed us to get a spectra of only chamber side two due to the both chamber sides being isolated from each other due to the vacuum seal at the Pd foil. Both sides had a pumping system to allow them to get into the high vacuum regime, as well as ion gauges to measure the respective pressures in each side. There was a small pipe connecting both sides by a needle valve. This was implemented as a fail-safe way of ensuring if too high of a pressure gradient was on the Pd foil, we could open the valve to equalize both chamber side pressures to stop any damage on the foil from occurring. The system was leak checked and baked out due to the pressure in chamber side one not getting as low as we wanted. The Pd foil was aligned to be 10 cm from the plasma source.
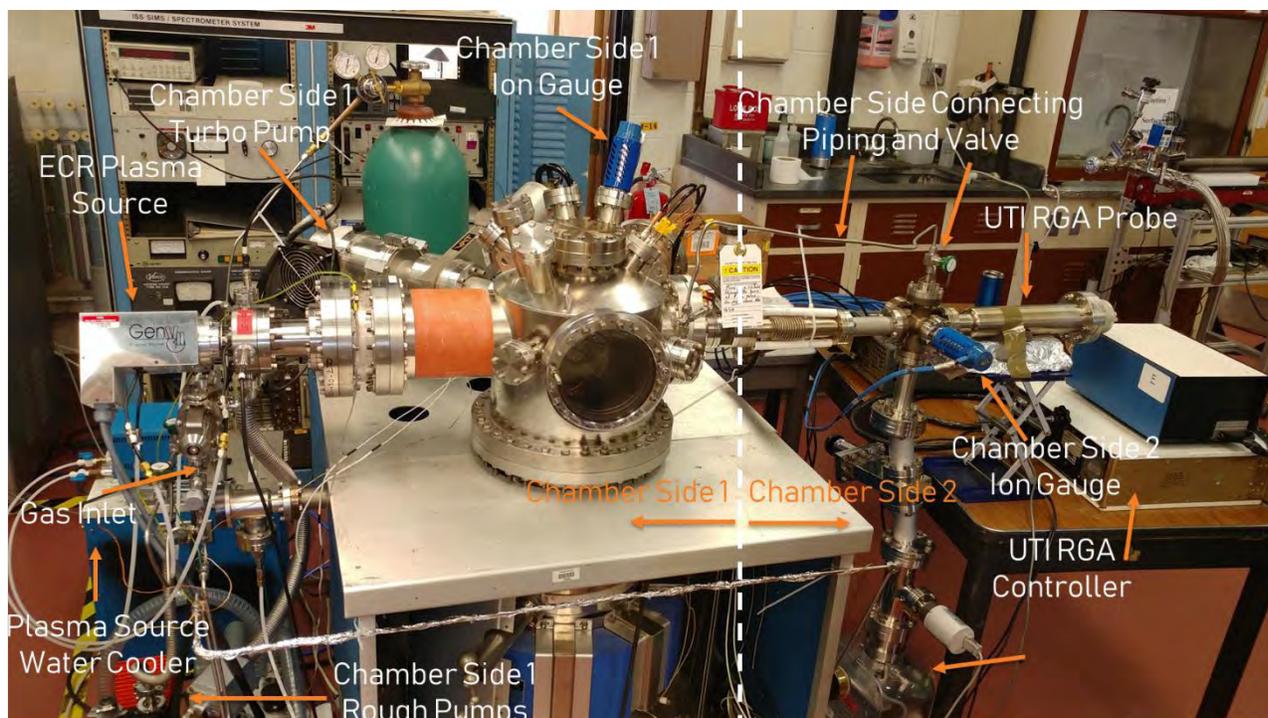
Figure 6: Final experimental chamber, showing both chamber sides and their components.

The nichrome wires on the Pd holder apparatus were connected to the heater source by thick gauge copper wires. A thermocouple was attached to the stainless-steel shielding right above the Pd foil to allow us to read what temperature the Pd foil was at.
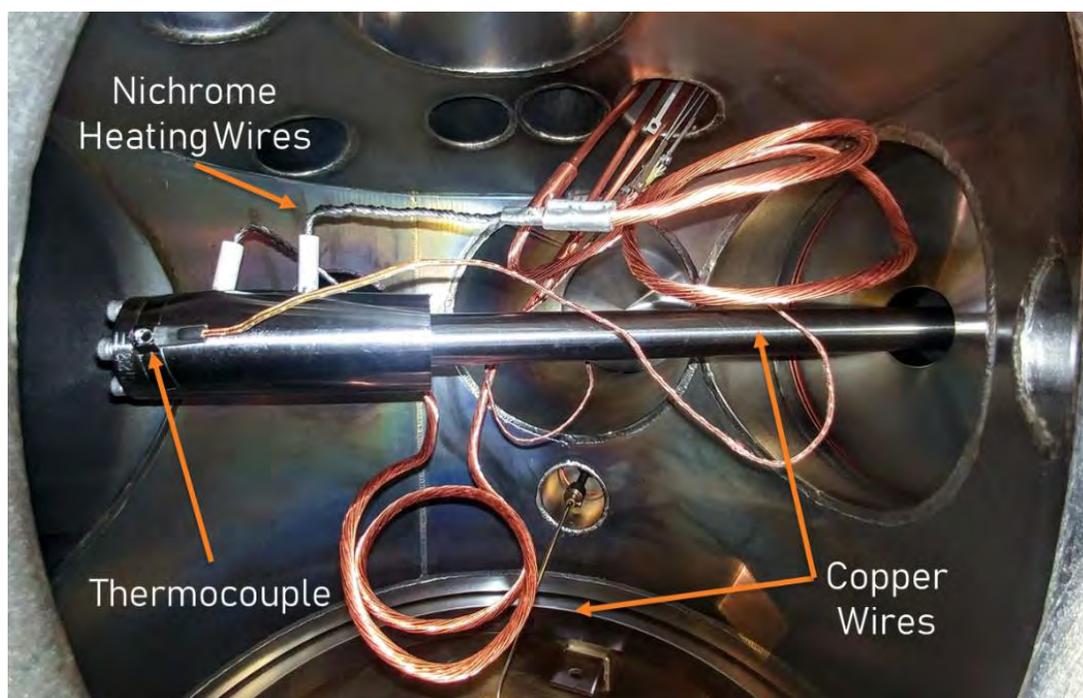


Figure 7: Pd foil holder apparatus in chamber side one.

Figure 8: Pd foil holder apparatus showing relative location to the plasma source.

The heating system was tested before any permeation experiments were conducted. The preliminary test was to see the relation between current from the heater and the foil temperature, the pressure changes due to foil being heated, and the time it took for the foil to reach certain temperatures. For the preliminary test, the foil was heated from room temperature to 200 ºC.
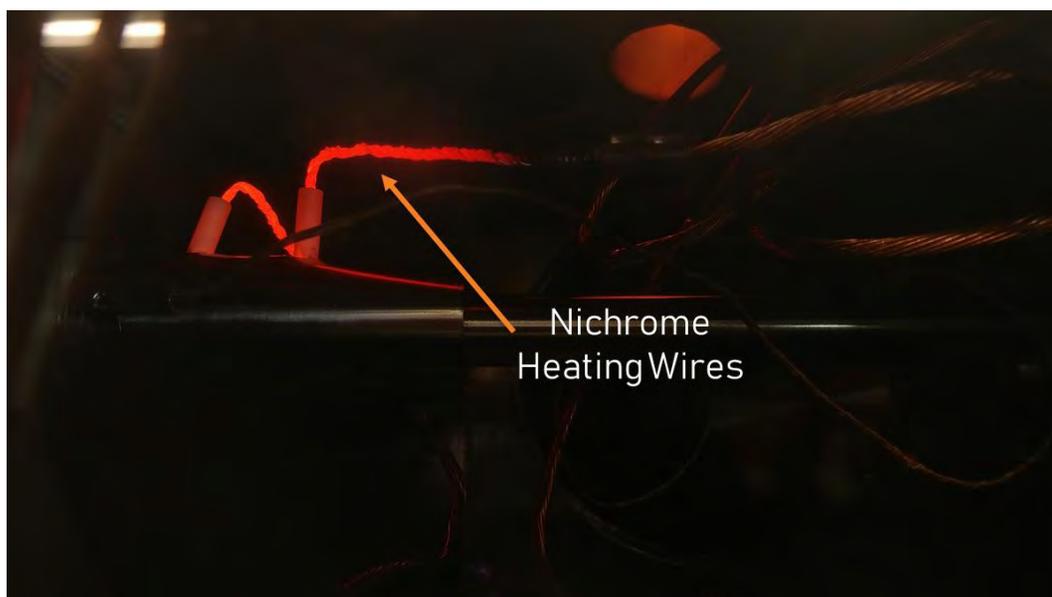


Figure 9: The apparatus while the Pd foil was being heated.
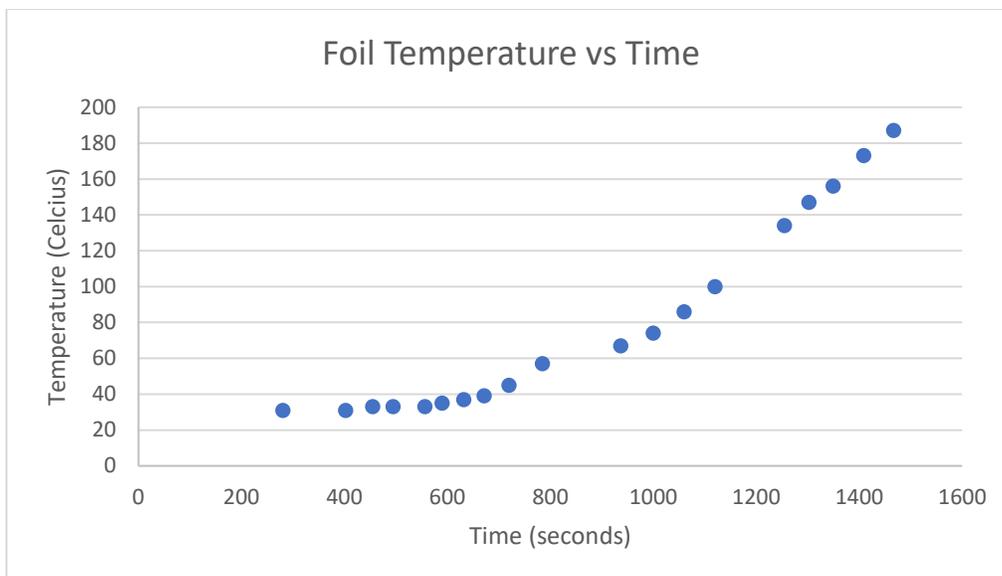
Figure 10: Preliminary heater test showing Pd foil temperature versus time.
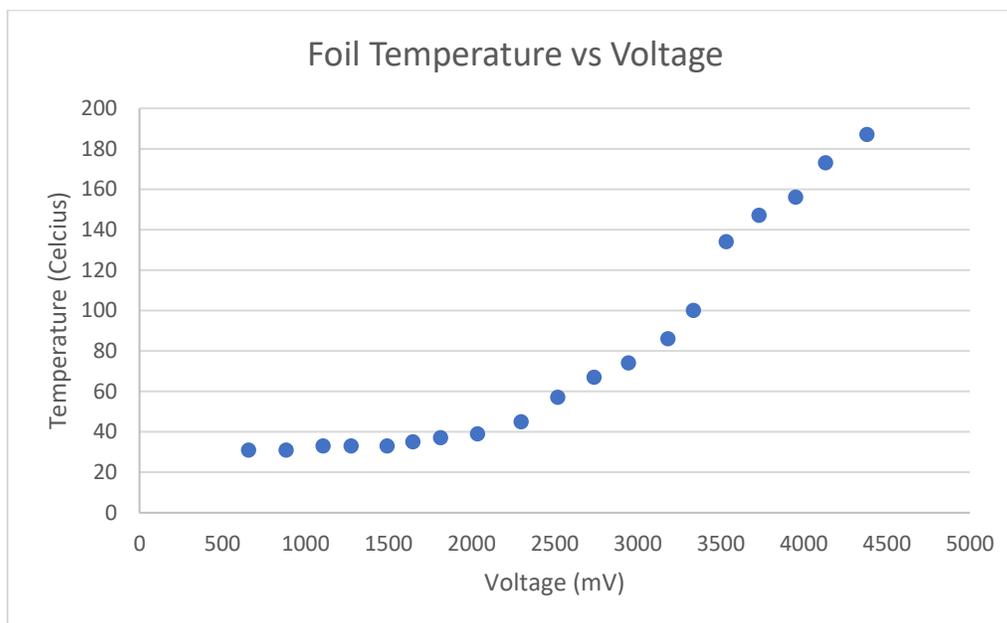


Figure 11: Preliminary heater test showing Pd foil temperature versus heater voltage.
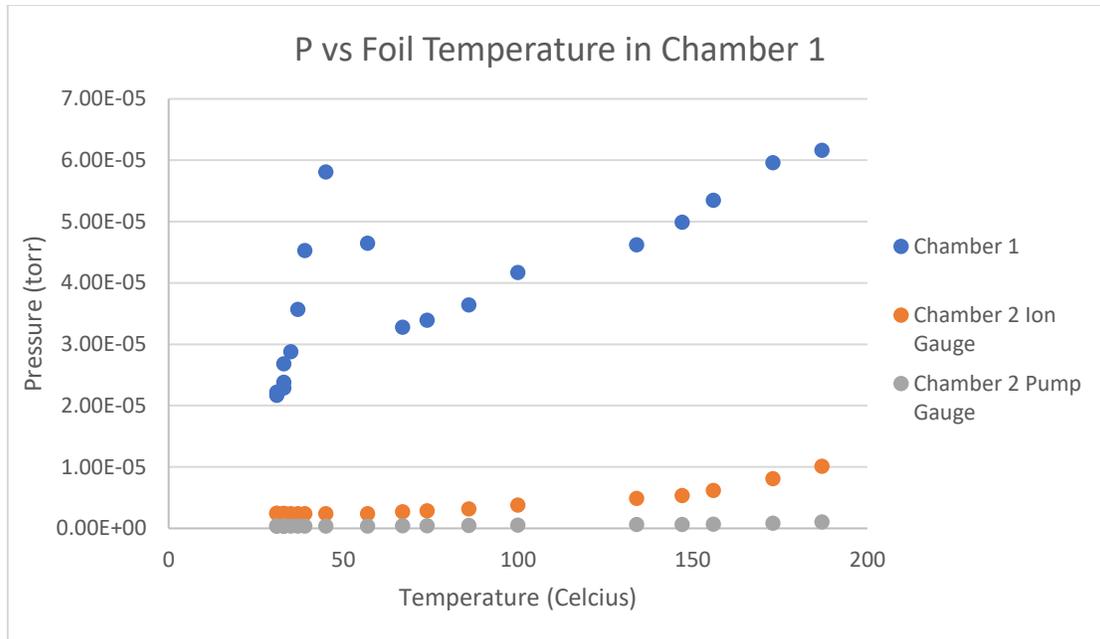
Figure 12: Preliminary heater test showing Pd foil temperature versus system pressures.

From the preliminary heater test, it was shown that the heating configuration worked properly. We could get into our temperature range of 300-500 ºC with ease at relatively low current being applied by the heater. A pressure change was also seen which was expected, as the chamber heats up the pressure will rise, and also due to the high temperatures there could have been outgassing occurring from the walls which would also increase the pressure. After the preliminary tests were conducted, the permeation experiments were conducted.

## 4. Permeation Experiments

The permeation experiments that were conducted in this project used D gas that was injected into an electron cyclotron resonance (ECR) plasma. Diffusion within the system is a function of the activation energy and the temperature of the material.

$$D = D_o \exp\left(-\frac{Q}{T}\right) \tag{5}$$

Where $D_o$ is the frequency factor, Q is the activation energy, and T is the Pd foil temperature. The experiments that were conducted included: looking at the D peak amplitudes with the Pd foil at various temperatures and finding experimental Q value, looking at the D peak with the plasma on and then shut off, rapid temperature rise to try and calculate the experimental $D_o$ value, ions at different energies, and rapid temperature rise to a constant temperature and then rapid temperature rise again to examine the solubility effect.

The first experiment was to examine the peak amplitude at 4 amu at a temperature range of 300-500 ºC. This was done to see if there was any D permeation occurring through the Pd foil. Every 25 ºC interval, the temperature was held constant for 15 minutes to see what happened to the D peak.
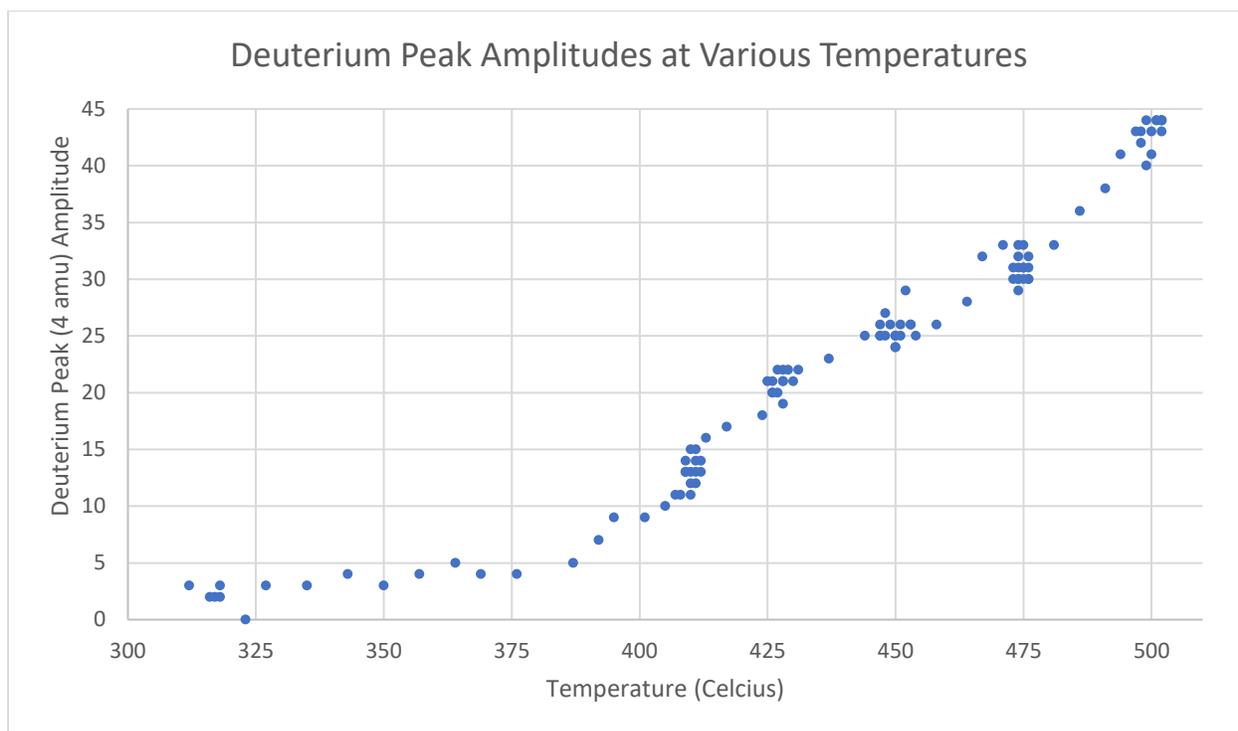
Figure 13: D peak at various temperatures from interval of 300-500 ºC.

From the data collected, we observed that there was in fact D permeation through the Pd foil due to the 4 amu peak being observed. It was confirmed that permeation is in fact temperature dependent, and that increasing the foil temperature increased the D permeation through the foil. The spectra that was collected during the experiment showed a noticeable 4 amu peak. The spectra also showed that the water, nitrogen, oxygen, argon, and carbon dioxide peak remained about the same. This confirms that Pd has selective permeability to H isotopes, as well as that there was no vacuum leak at the foil.
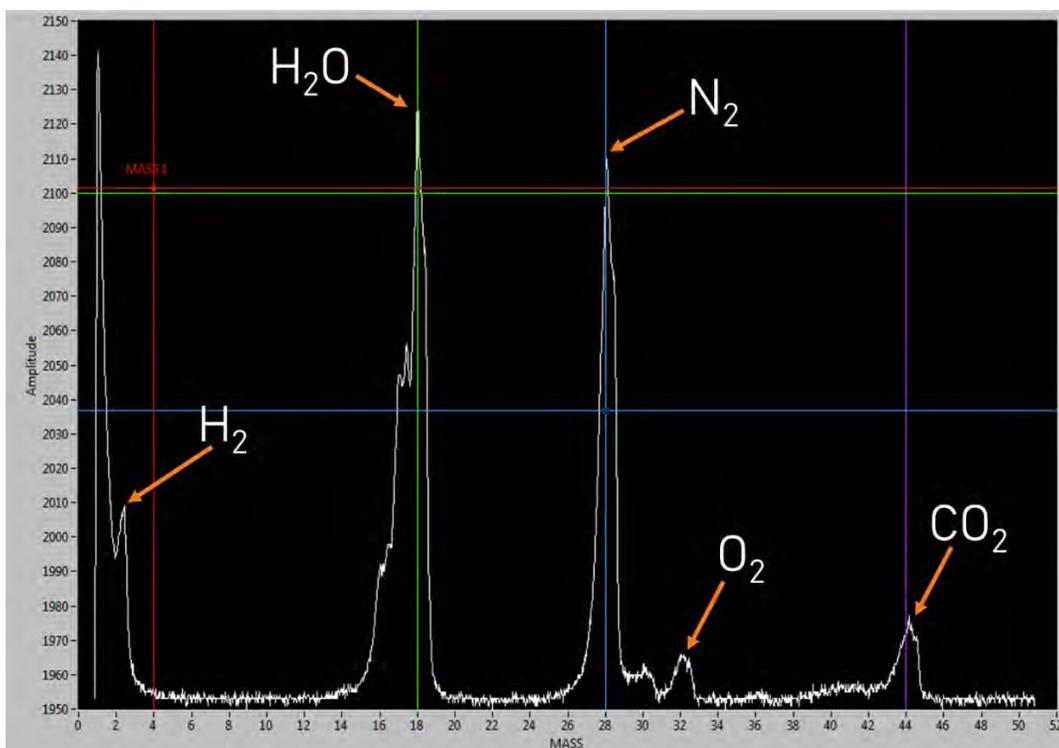
Figure 14: Chamber side two spectrum prior to D gas at 200 °C.
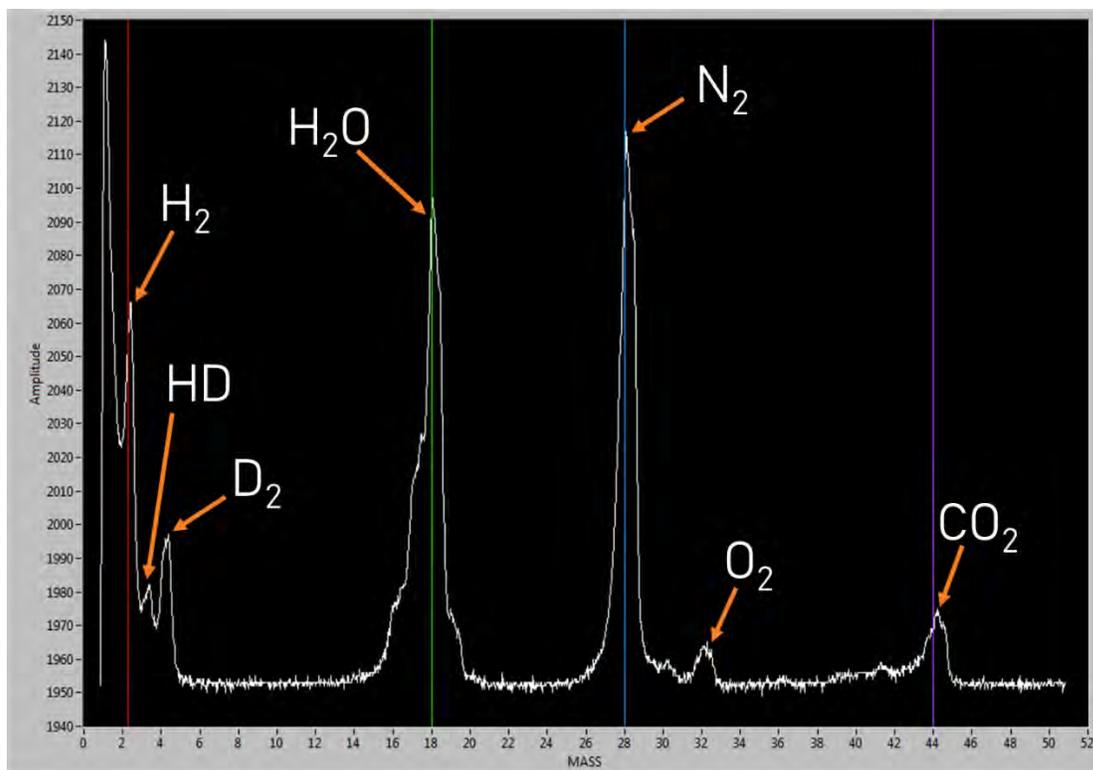


Figure 15: Chamber side two spectrum with D permeation at 500 °C.

Making an Arrhenius plot of the data that was collected allowed for the experimental calculation of activation energy. Our experimental Q value was 0.30 eV, compared to that in literature of 0.25 eV.
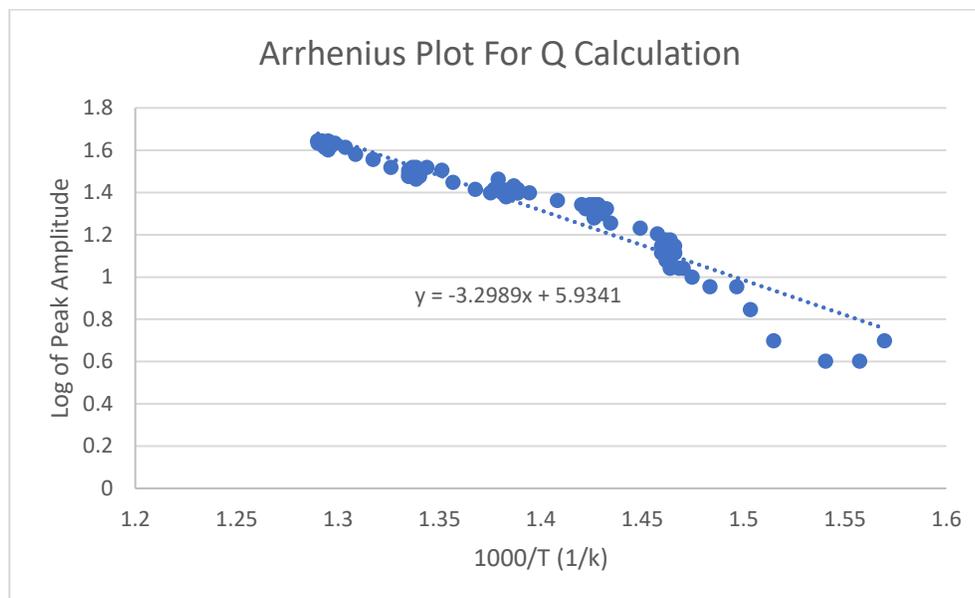


Figure 16: Arrhenius plot of D permeation experiment to calculate Q.

The next experiment examined keeping the foil at a constant temperature of 450 ºC and shutting off the plasma. This allowed us to test the importance of monatomic H isotopes in respect to permeation. The plasma was kept on for 5 minutes and the peak was measured on the spectra, and then the plasma was shut off for 15 minutes and the peak was measured.
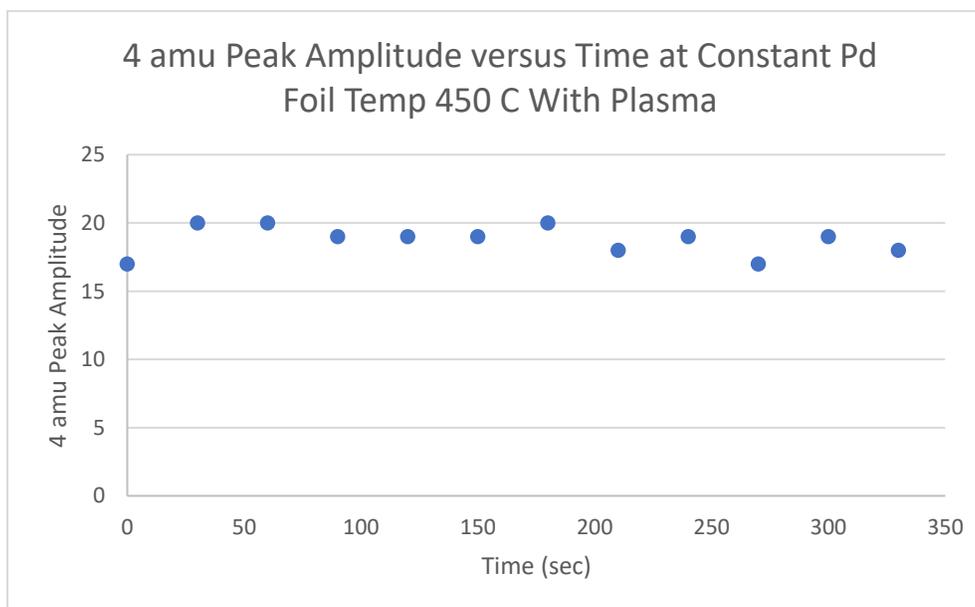


Figure 17: D peak amplitudes versus time at a constant Pd foil temperature of 450 ºC with plasma on.
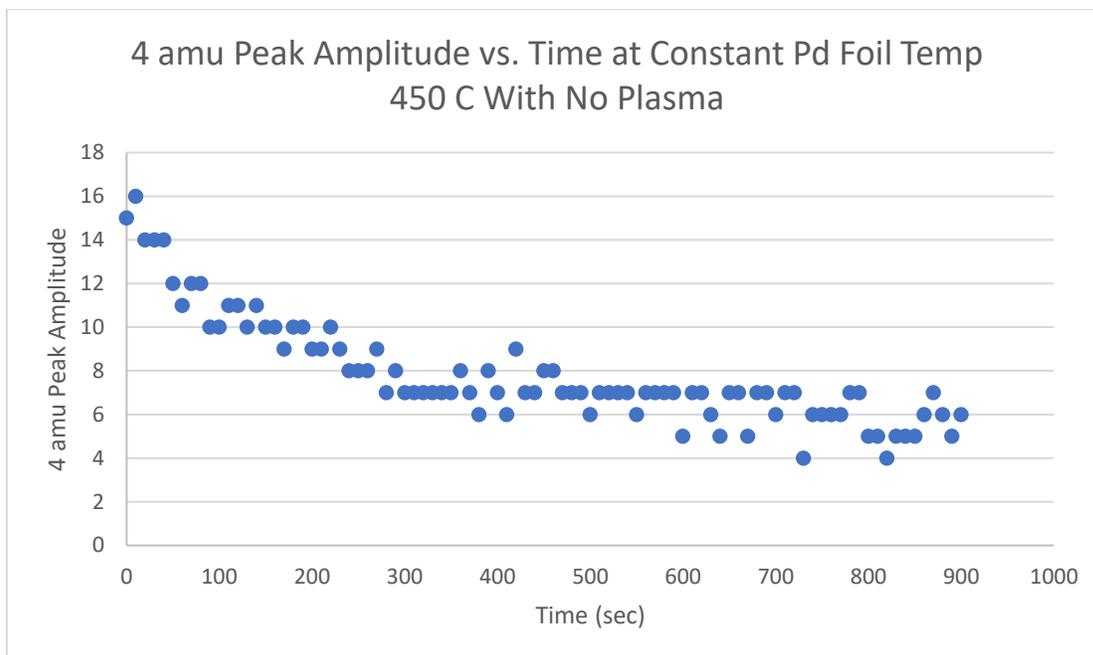
Figure 18: D peak amplitudes versus time at a constant Pd foil temperature of 450 °C with no plasma.
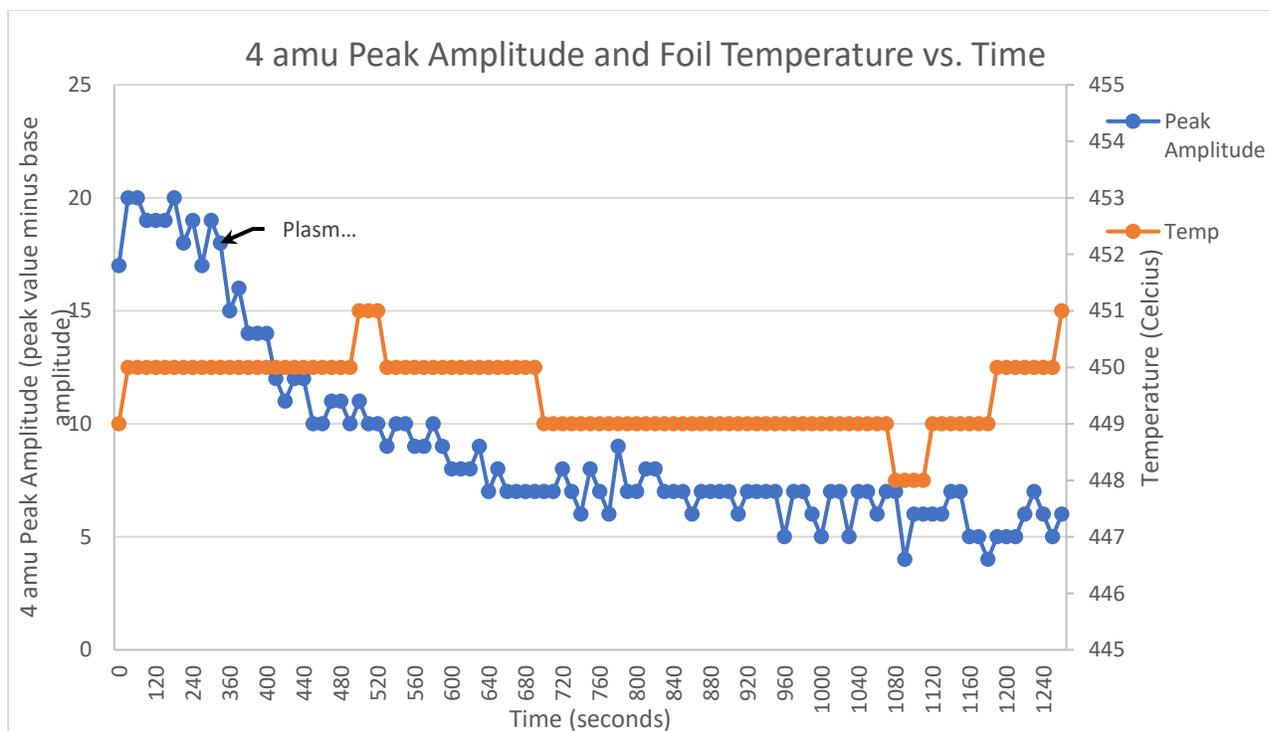


Figure 19: D peak amplitudes versus time at a constant Pd foil temperature of 450 °C with plasma on and off.

From this experiment, once the plasma was shut off there was a large decrease in the D peak amplitude. This means we were able to see that the presence of monatomic D is important to the permeation through the Pd foil.

The next experiment looked at rapidly increasing the temperature of the Pd foil to get a view of the diffusion and pressure rise lag.
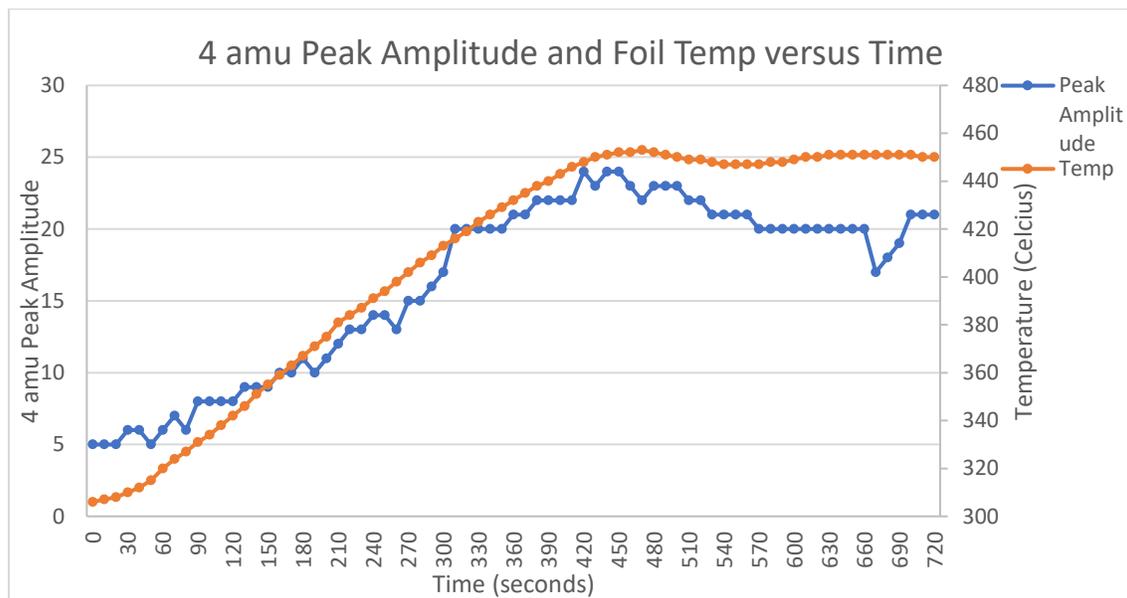


Figure 20: Rapid temperature increase from 300-450 ºC examining D peak amplitude versus Pd foil temp and time.
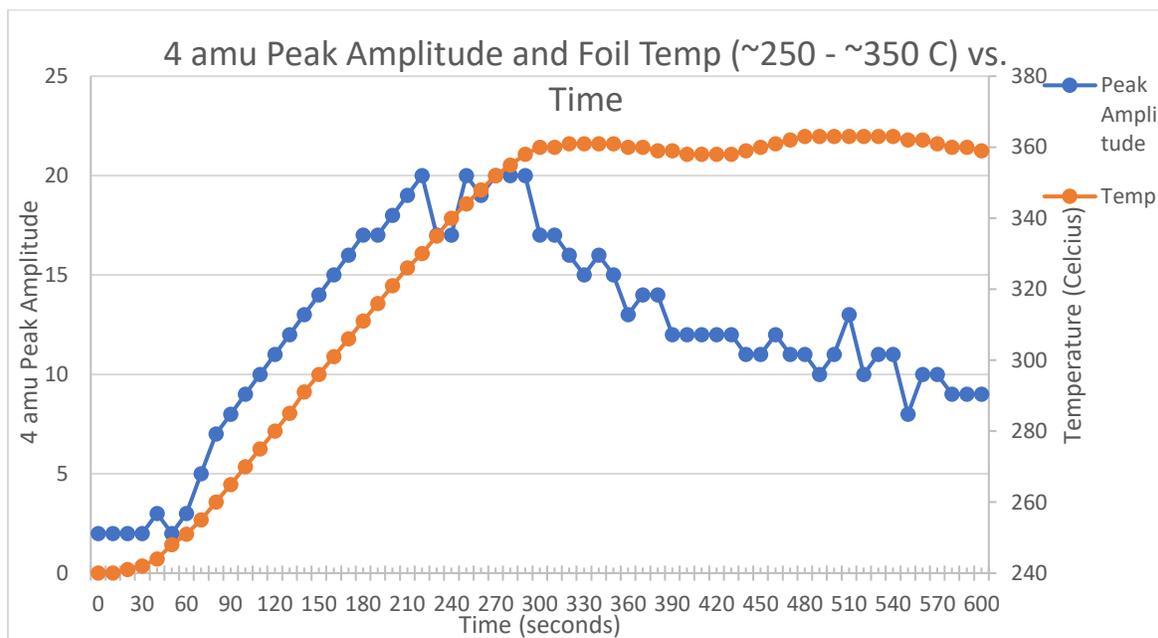


Figure 21: Rapid temperature increase from 250-350 ºC examining D peak amplitude versus Pd foil temp and time.

Analyzing the lag time allows for the ability to calculate an experimental $D_o$ value. The experimental $D_o$ value that was calculated was 2.4E-6 $m^2$/s, which is close to the literature value of 2.4E-7 $m^2$/s.

The next experiment examined the effects of ions accelerated to different energies. The ECR plasma source that was used allowed for ion energies of 0-2 keV. The ion energies of 0-1 keV was examined at 400 $^oC$ and 500 $^oC$.
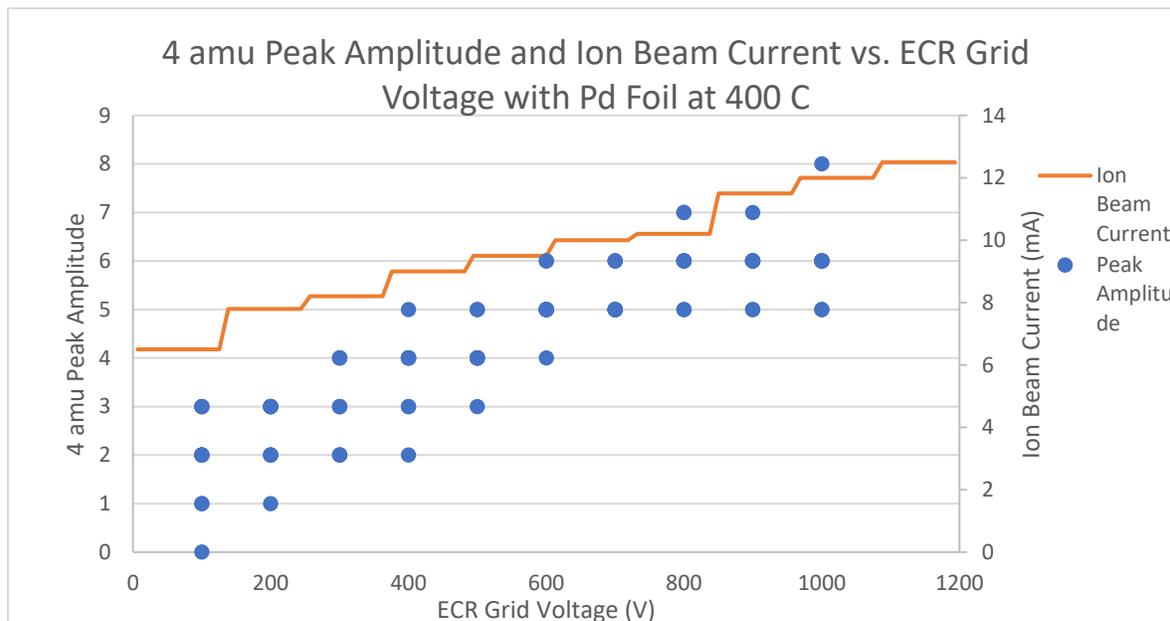


Figure 22: D peak and ion beam current versus ECR grid voltage with Pd foil at 400 $^oC$.
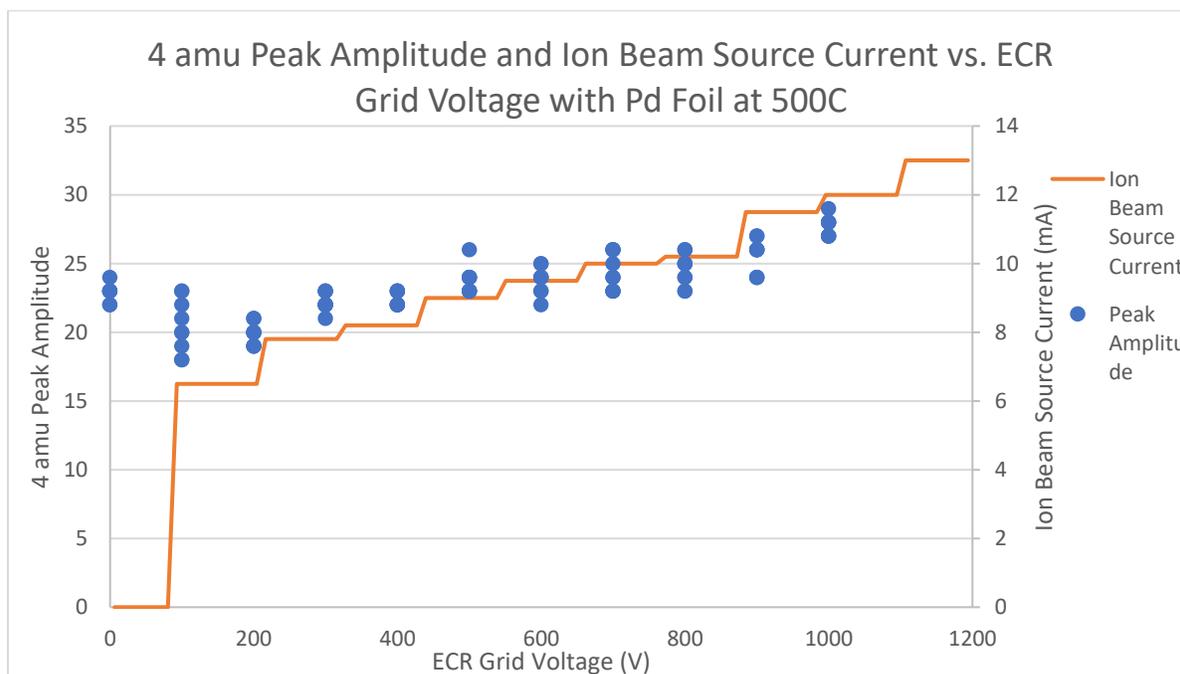


Figure 23: D peak and ion beam current versus ECR grid voltage with Pd foil at 500 $^oC$.

The data that was collected for this experiment was inconclusive, which means conducting this experiment again is for future work.

The next experiment looked at testing solubility, if at lower temperatures there was more D within the Pd foil that when it was heated up initially its peaks were higher.
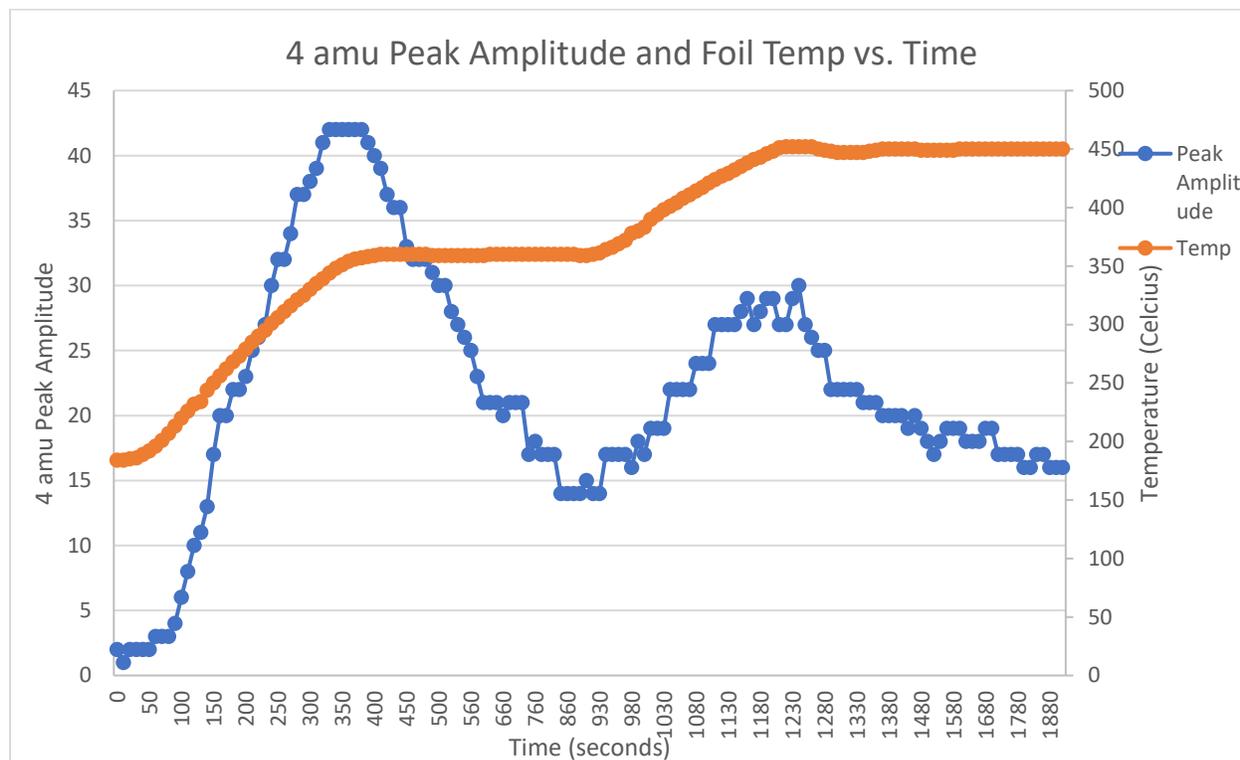


Figure 24: D peak and Pd foil temperature versus time with rapid temperature increase and held constant.

From the experiment, it is seen that as temperature was increased from 200-350 ºC, the D peak amplitude was seen to rise rapidly, but when kept constant at 350 ºC the D peak amplitude dropped rapidly. When the Pd foil temperature was raised again from 350-450 ºC, the peak amplitude increased again but not as quickly as the first temperature rise. Once 450 ºC was reached and kept constant, the peak amplitude dropped once again but not as quickly as the first constant temperature of 350 ºC. This could mean that at lower temperatures the solubility plays a role in how quickly the D peak amplitude rises because of the higher amount of D within the foil. At higher temperatures most of the D within the foil would have already diffused through and that is why the slope is not as steep. This would explain why the peak drops when the foil is kept at a constant temperature. This hypothesis needs to be tested further, which is the plan for future work on this project.

## 5. Future Work

Future work of this permeation project includes continuing analyzation of the data that was collected so far using D gas. The further examination of how ions at different energies affect permeation through the Pd foil needs to continue due to this project not showing any results. Since

He permeation was not able to be conducted in the summer project due to time constraints, it is indicative to examine how He permeation occurs within Pd. After examining H and He permeation further, then the effect of partial pressures would be conducted. This permeation would then be examined on the PFRC-2 device to test it in a real situation. If results are promising, then the Pd foil would be adapted into a ZBZ configuration and experiments would be conducted.

## 6. Conclusion

The PFRC research experiment in the future would use D-$^3$He fuel. In the fuel, D-T reactions must be mitigated to reduce any structural damage that can occur from the high energy neutron being produced, thus reducing the amount of shielding that is needed on the device. A device like the PFRC is being applied to space travel for a planetary orbiter, and to get in to space, weight needs to be saved. Reducing the amount of shielding will save weight, which is at a premium when trying to get to outer space. One way that is being considered to extract the T out of the plasma and the device is to utilize a permeable membrane. This summer project at PPPL looked at testing H isotope separation through a Pd foil. The work included testing RGAs, building vacuum chambers, and conducting multiple permeation experiments. From the experiments, there was indeed D permeation through the Pd foil. It was found that permeation is temperature dependent, and an increase in temperature increased the permeation through the foil. Pd was found to have selective permeability to H isotopes. It was found that monatomic H isotopes play an important role in the effectiveness of permeation. The frequency factor and activation energy were close to that of the ones found in literature. Ion acceleration in the ECR source was found to not play a role, however, this is hypothesized to not be correct, so further experiments must be conducted. The solubility effect must also be tested further to see if the theory of solubility playing an important role at lower temperatures and during initial heating is correct. This type of system shows to be promising for T extraction if incorporated into an exhaust stream of a nuclear reactor. This portion of the project at PPPL showed interesting data, while it also made the team ask more questions. Therefore, as in scientific work, there is much more to examine and more experiments to conduct.

## 7. Acknowledgments

## References

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