Computer Controlled Temperature Programmed Desorption from Noble Metal Surfaces

Nell Lynn Giltinan
Professor Gary Chottiner, Nikola Matic

Department of Physics
Case Western Reserve University
Cleveland, OH 44106

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Abstract

Temperature Programmed Desorption (TPD) is a method of studying molecules as they are desorbed, or released from, the surface of a material while a sample is heated. This process must take place in an ultrahigh vacuum (UHV) environment of at least ~ 2×10^{-9} Torr. At higher pressures the background gases present in the chamber would make measurements difficult and samples would be contaminated. In a TPD experiment a small sample, sometimes a metallic disk or a single crystal about 1 cm in diameter and 1 mm thick, is placed in a UHV environment, cleaned, covered with the molecule(s) of interest and then heated at a constant rate of ~5 K/second. As the sample is heated a mass spectrometer (for this experiment a Dycor Residual Gas Analyzer (RGA)) records what atoms, or masses, are desorbed from the sample and the amount of each as a function of temperature. The temperature at which particles desorb is related to the strength of their bond to the surface. TPD also lets one study how molecules break apart when they absorb on a surface and recombine before they desorb.

Setting initial parameters and running experiments with an RGA is a tedious process due to the many settings that must be manually configured. During this project automation of TPD data collection was created using a separate computer which also able to control and initial experiments. To control the Dycor RGA a control program was written using the C based programming environment of Igor. This program allows a user to communicate with and command the Dycor RGA and create and analyze TPD plots.

Acknowledgements

I would like to thank Professor Chottiner for providing me with his extensive wisdom, support, and resources over the course of this project. Without his help and contributions this project would not have been able to happen. He has also taught me more than I had ever expected to learn, not just about the specific science and methodology of temperature programmed desorption, but also troubleshooting techniques, project organization, and persistence. I would also like to thank Nikola Matic for his assistance with the hardware for this project. He was instrumental in getting the Ni sample set up in the introductory chamber to the UHV chamber. He also gave me tips when I was encountered problems communicating with the NI hardware and I am very grateful that he was able to provide assistance to this project.

Contents

1. Introduction

1.1 Background and Application

The first paper on TPD was written in 1963 by P.A. Redhead, who derived the methods

to calculate the activation energy, order, and the rate constant of the reaction[1]. There were

two different methods of heating the sample used by Redhead, however for the purpose of this

study his simple linear variation of the sample's temperature will be used ($T = T_0 + \beta T$ where

β is the heating rate). The calculation of activation energy proposed by Redhead is based on the

initial Ahrrenius behavior of the desorption

process limited by the finite quantity of the

absorbate[1]. The equation he found to calculate

the desorption from a unit surface area is

written as

$$N(t) = -\frac{d\sigma}{dt} = v_n \sigma^n e^{\frac{-E}{RT}}$$

Where the values are defined as

N(t) = rate of desorption
n = desorption reaction order (1 or 2 in this case)
σ = surface coverage ($\frac{mol}{cm^2}$)
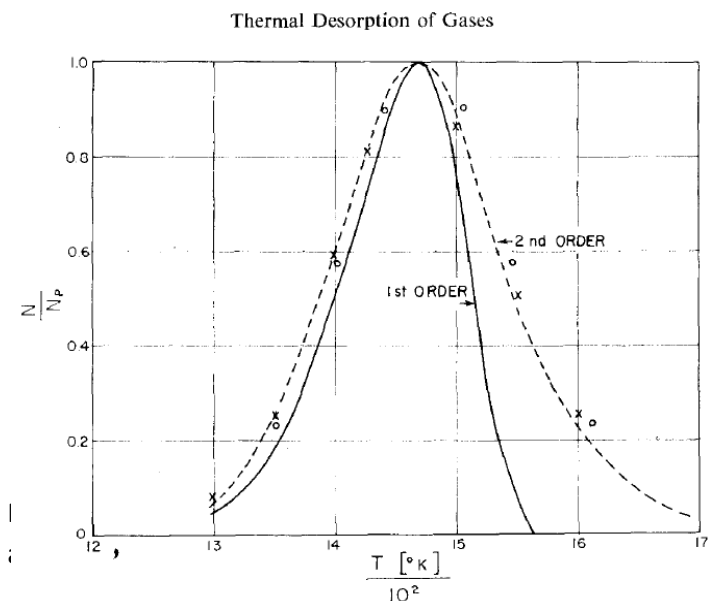v_n = rate constant
E = desorption activation energy ($\frac{cal}{mol}$)
R = molar gas constant
T = temperature in K

A first order reaction occurs when molecules separate, or desorb, from the surface

independently. A second order reaction occurs when two molecules must interact on the

surface of the material before desorbing together as a species. This can give important
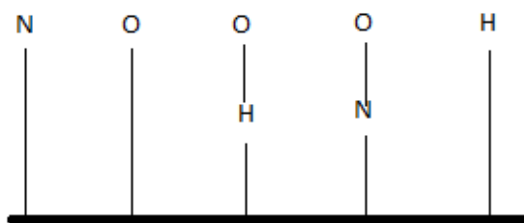
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Fig 4: Surface of Au with broken up pieces of HAM molecule[2]

information about what molecules existed on the surface before they desorbed. For example, in the case of HAM, NH_2OH, when the compound comes in contact with the Au surface, and possibly breaks apart, the individual atoms that make up HAM can bind to the surface in a variety of different ways. The entire HAM molecule could bind to the surface with bonds between the Au atoms and the oxygen or nitrogen, or even both, atoms. If the HAM breaks up then the individual molecules could bind to the surface as either N, O, OH, NO, or H, as shown to the left. If, for instance the N_2 on the far left desorbed from the surface, that would be a first order reaction. An example of a second order reaction would be if a hydrogen and a hydroxide molecule combined and desorbed from the surface as a water molecule, i.e. if H and OH combined to form H_2O. This is a reaction that would be expected from the HAM compound since, as can be seen above, both H and OH could exist on the surface. Indeed, some preliminary inspection of HAM that has occurred already has found that H_2O is present in the UHV chamber after HAM is introduced.

HAM is an intriguing molecule for which this software could be used to study in the future, but for this project the focus will be CO desorbing from a clean Ni surface. This has been shown to occur as a first order reaction in the range of approximately 375 K to 625 K[8], meaning it would be expected that a TPD plot of CO desorbing from Ni would include an asymmetric peak bewtween 375 K and 625 K. Although this behavior is well known, the aim of this project was not simply to observe the behavior of CO desorbing from Ni, but to control the data collection process via computer. Previously, all data for the TPD system used for this project

was collect manually and the system was set up and parameters were also set manually. Some work had been done to automate part of the data collection from the gas anaylzer previously, however that software could no longer be used and new software was necessary. This invovled creating a software to read data from and control both the temperature and pressure components of the data collection.

2. Methods

2.1 Hardware

There were two different vacuum chambers used during the process of this project. Work was originally done in an ultra-high vacuum, UHV, chamber to create the original software design for the mass spectrometer controller and simulated data collection. The process was moved to a high vacuum, HV, chamber where a sample could be more easily introduced and where the temperature software was produced and tested.

Both vacuum chambers used for this project were built from stainless steel plumbing and used conflate flanges, essentially a knife edge on the flange cuts into a copper gasket to ensure a seal of high enough quality to be used on a UHV system. It is important to note the material of the chamber. Due to the stainless steel walls of the chamber, H_2 is able to absorb through the walls of the chamber and is seen in non-negligible amounts.

The first vacuum chamber used, the UHV chamber, was kept at approximately 10^{-10} Torr. This extremely low vacuum environment ensured a clean environment. With fewer other molecules in the chamber and on the surface of the sample, there were fewer masses seen by the mass spectrometer, and thus cleaner data. This very low pressure was also useful due to an

effect described by a unit called a Langmuir[6]. A Langmuir describes the time it takes for a monolayer of molecules to form on the surface of a clean sample based purely on the pressure the sample is experiencing and the amount of time. The Langmuir equation is shown below.

$$1 \; monolayer = \; (10^6) * (pressure \; [Torr]) * (time \; [seconds])$$

This means that in a UHV chamber with a pressure of approximately 10^{-10} the time for a monolayer of molecules to form on the surface would be 10,000 seconds, or approximately 2.8 hours. A standard high quality TPD experiment could be conducted in this time, however slightly lower pressures would be ideal. This project however did not require a sample cleaner than a monolayer, so UHV pressures were not necessary. Instead, a HV chamber was used for final data collection.

The second chamber used, the HV chamber, was kept at approximately 10^{-7} Torr. This chamber was actually the introductory chamber for the main UHV chamber. The introductory chamber was used to bring samples into, or introduce samples, to the UHV chamber. Since it is difficult and time consuming to open a UHV chamber to atmospheric air, a secondary introductory chamber is used to transition a sample from the atmospheric air to the UHV chamber. A T-shaped piece of tubing was attached to this chamber, and the remainder of the project was carried out in the horizontal section of this T. A schematic of the HV chamber setup used for the later part of this project is shown below.
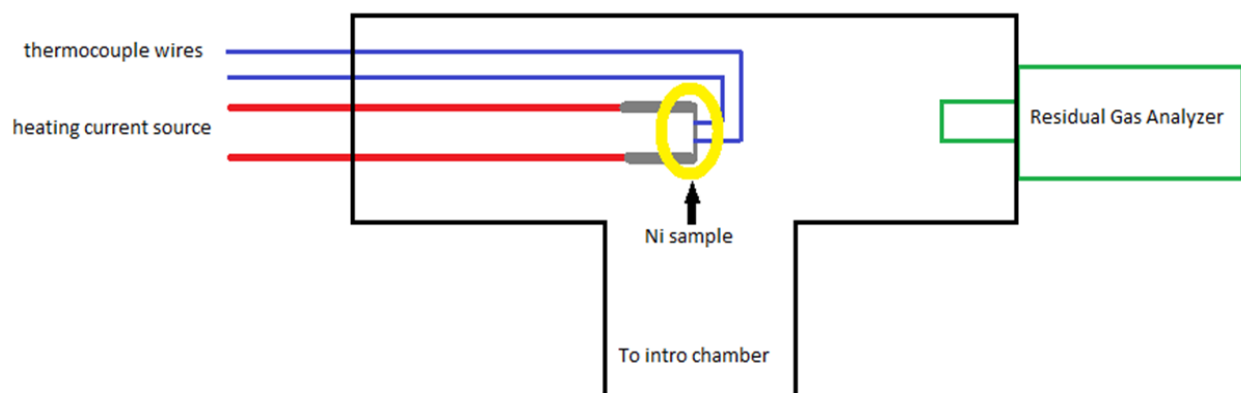
Fig 5: Schematic of chamber used for experiment. Black lines are stainless steel walls of chamber, red are copper rods, grey is the Ni foil sample, blue are thermocouple wires, and green is the Dycor RGA and filament.

The mass spectrometer used for this project was a Dycor quadrupole residual gas analyzer. Dycor is simply the name of the equipment manufacturer and a quadrupole refers to the four parallel metal rods used to measure the mass-to-charge ratio of the ions. Below is a schematic depicting ions interacting with the rods.
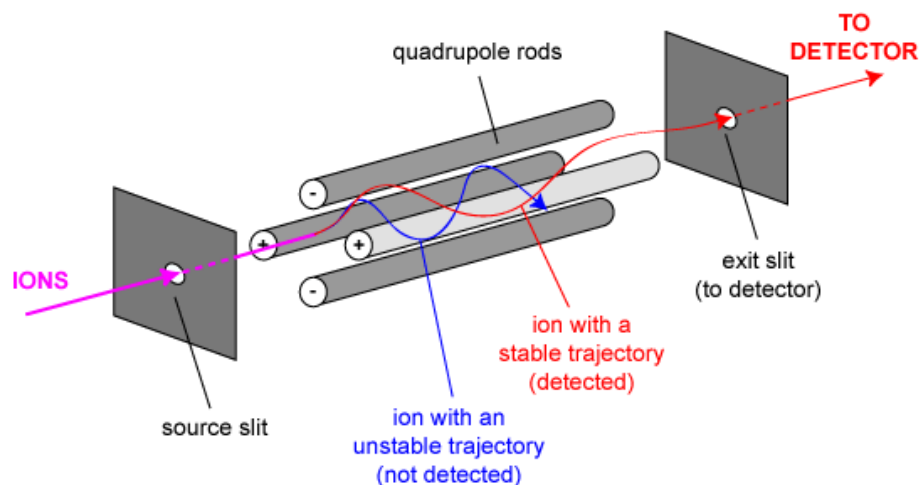

Fig 6: Illustration from the University of Bristol[8] illustrating the process by which an RGA is able to detect a specific charge to mass ratio of an ion.

Essentially what happens is the two opposite rods are electrically connected in such a way that the two opposing pairs of rods have opposite charges. An AC and DC voltage is applied to the rods at specific ratios. As the ions approach on a trajectory parallel to the rods, only ions of a mass specific to the applied voltage ratio are able to maintain a stable trajectory and approach the detector. Ions that do not have the mass specific to the voltage ratio being applied to the pairs of rods, have an unstable trajectory and do no approach the detector.

2.2   Software

The programming environment Igor was used to communicate with the Dycor controller over serial RS-232. Igor uses its own C-based language and has many built in functions to make data analysis much easier. There are also many extension packages available for Igor, two of which were used for this project. One package was VDT2, which includes many built in commands to make communicating with the instruments much easier. VDT2 also is comes with a command window for sending and receiving data to the instrument. This package was used to adjust parameters, query the instrument for data, and receive pressure vs. time data from the Dycor controller.

The other extensively used Igor package used for the project was the NI DAQ package. The thermocouple wires attached to the sample inside of the UH vacuum chamber output a voltage in the mV range. This signal went through an RC low pass filter and into an NI DAQ card. Since NI made the NI DAQ package specifically for Igor, this package made communicating with

the NI card used for temperature data much easier. This package was used to query the NI card for data, filter using data averaging, and store the data for further analysis.

2.3   Experimental Setup and Procedure

For this project, there were four main milestones to hit. First the basic software for setting up and controlling the Dycor controller was established. The next phase was to use this software to collect simulated data of TPD using H_2. After that the temperature collection software was developed. Then the final step was to use both the control software and the temperature collection software to run a full TPD experiment on a Ni sample in an HV chamber.

To develop the initial software for the Dycor controller, first serial communication had to be established between a control computer and the Dycor controller using Igor's VDT2 package. This tedious process involved much reviewing of old, sparse documentation and guess and checking of control computer's settings for stop bits, parity bits, etc. Once established though, much could be done through the VDT2 terminal window to the controller. For instance, simply sending a command of "FIL = ON" could turn on the filament on the mass spectrometer's head in the vacuum chamber. Setup and control commands were tested in the terminal window, and a pressure data collection program was established from there.

To collect the simulated H_2 data, a titanium based sample already inside the chamber was heated using a lab current source. As the sample was heated pure H_2 was desorbed and the amount desorbed with respect to time was monitored and collected by the previously written software.

The next step, writing the temperature data, required first constructing the setup shown in figure 5 with the help of Nikola Matic. Once connected through an RC low pass filter to the NI DAQ card, the setup was ready for temperature monitoring. This was where the NI DAQ package for Igor was required. Again, the initial setup was a bit tedious when it came to establishing initial communication between the computer and the NI card through Igor. Additionally, this package did not have a corresponding terminal window, meaning the process of testing and debugging was a bit more complex. The data coming in from the thermocouple was first filtered through the RC low pass filter, and then in the software using a data averaging algorithm, using a setting of 30, included in the NI DAQ package. The filtered signal was then recorded and plotted with respect to time.

The last step was then to combine the pressure vs. time data and the temperature vs. time data to create pressure vs. temperature data. A K-type thermocouple was used for this project, and this kind of thermocouple has approximately linear voltage change with respect to temperature. Using this assumption, the voltage measurements from the thermocouple could be mapped linearly to temperature with an offset for room temperature (~1 mV). With this mapping, the data collection procedure was complete. The Ni sample in the HV introductory chamber was heated from room temperature up to ~750 C.

3. Results

3.1 Control Program

The main goal of this project was to create a control program to help run TPD experiments. Initializing parameters, setting up the Dycor controller, and collecting both

temperature and pressure data manually are time consuming tasks. Ideally, the final program created during this project would only require input from the user of specific parameters and functions desired. This goal was met. The user can input parameters, and then run the pressure and temperature collections programs. Although the two programs were not formally combined to run as one program, the user simply has to input setup parameters into both and run both simultaneously to get TPD data. This simply requires one more click from the user, this is functionally identical to the desired goal.

3.2   Data

This project consisted of establishing two data collection procedures and then combining them to attain pressure vs. temperature data. Once the original pressure data collection program had been written simulated data was collected of pure H_2, as discussed in section 2.3. Shown below is a plot made in Igor of this simulated pressure vs. time data.
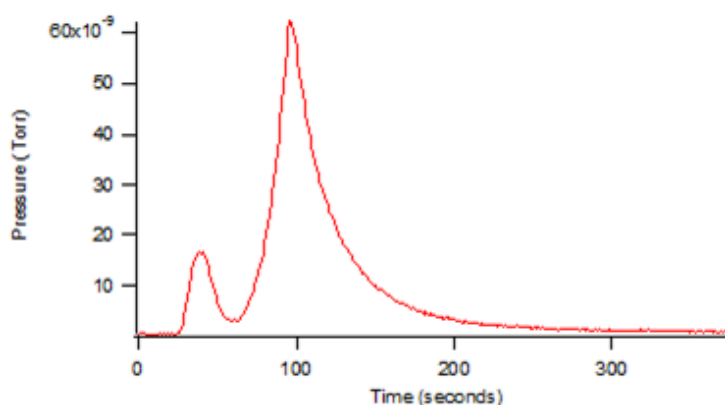

Fig 7: Simulated data of H_2 desorbing showing pressure (or amount) vs. time. The peaks correspond to manual increases of temperature which caused a desorption reaction.

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The heating for the data in figure 7 only occurred briefly and had less linearity than in later data collection events. Temperature was increased roughly linearly from t = 0 until the middle of the first, smaller peak, and then temperature was decreased. Temperature was again increased to cause the rise of the second, larger peak and then reduced at the top of the peak. The two peaks inspected separately give rough approximations of TPD data plots since the heating for positive slopes was roughly linear. This plot is far from ideal though and really was only able to show that the data collection procedure was working as expected. This can be seen by comparing the plots shown below, a photograph of the screen on the Dycor controller showing the collected data next to the collected data.
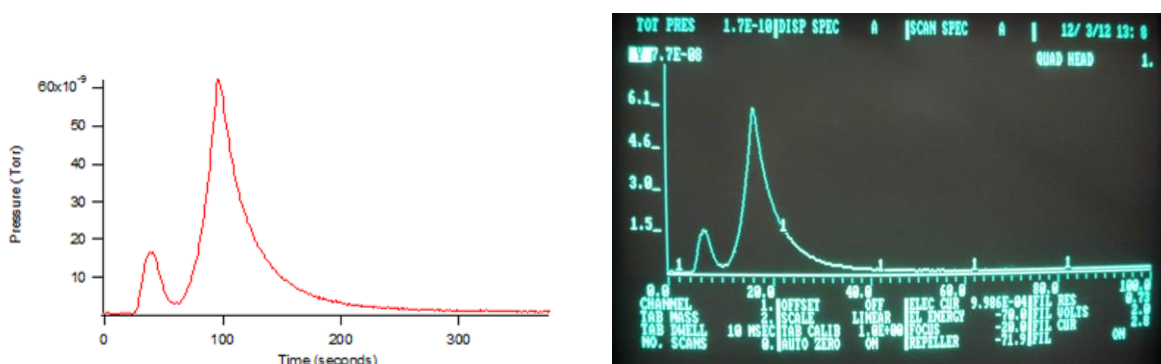

Fig 8: Side by side comparision of original simulated data as shown on Dycor controller and as plotted by pressure data collection program in Igor. X-axis in Igor plot on the left is displaying number of samples instead of time, it is showing 5 samples/second.

With the pressure vs. time program verified, real data of CO desorbing from the surface of Ni could be taken. This data is shown below.
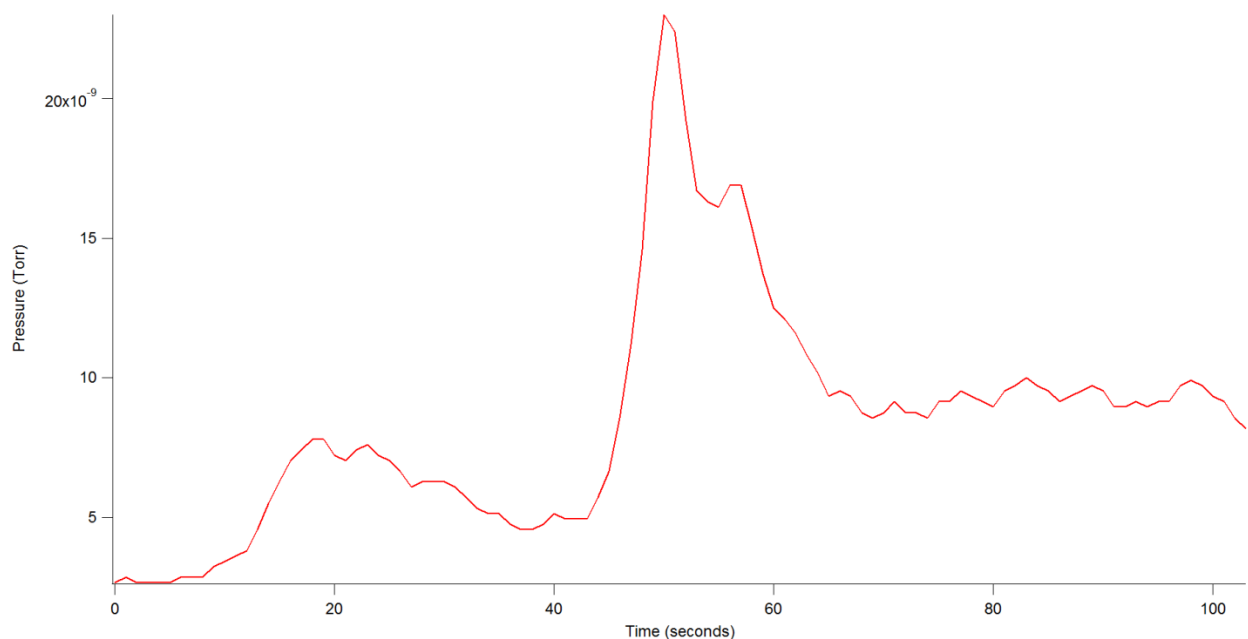
Fig 9: Plot of pressure vs. time of CO desorbing from the surface of Ni up to approximately 750 C.

To make combining the pressure vs. time data and the temperature vs. time data easily, a constant heating rate of the sample was desired. The temperature control of the sample was done manually meaning not a very high degree of linearity could be expected, however the mapping of the thermocouple's voltage reading to temperature had already been approximated, so some error would be acceptable. The behavior shown in the plot shown below is quite close to linear for the purpose of this project.
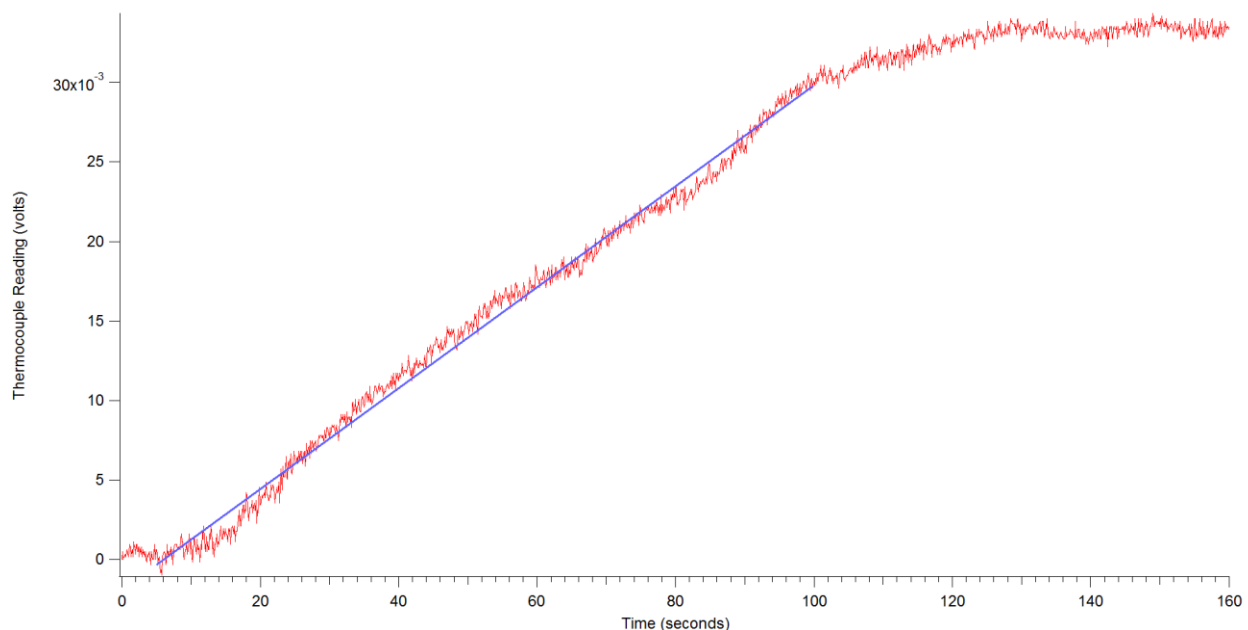
Fig 10: Plot of manual heating of sample vs. time showing approximately linear behavior from 5
seconds to 100 seconds.

Using the approximation shown by the purple line in figure 10, a time to temperature

mapping was calculated. This was then used in combination with the data shown in fig 9 to

attain a true TPD plot, as shown below. Although lower resolution than desired, the plot shows

TPD behavior and has an asymmetric peak as expected. It is expected to see CO desporbtion

behavior between 375 K to 625 K[9], or about 352 C. Looking below at figure 11, it can be seen

that the desorption of CO starts at a little over 350 C, suggesting the data in figure 11 occurred

towards the high end of the expected temperature range. Considering uncertainty was

introduced through the time to temperature mapping, it is expected that the collected data

would not fall perfectly within the suggested range and would have a slight distortion (which

cannot be easily seen due to the low resolution of the plot) and some offset. Data of high

resolution and further analysis of the curve shape would have to the be done to be sure. However, this project ran out of time before these steps could be completed.
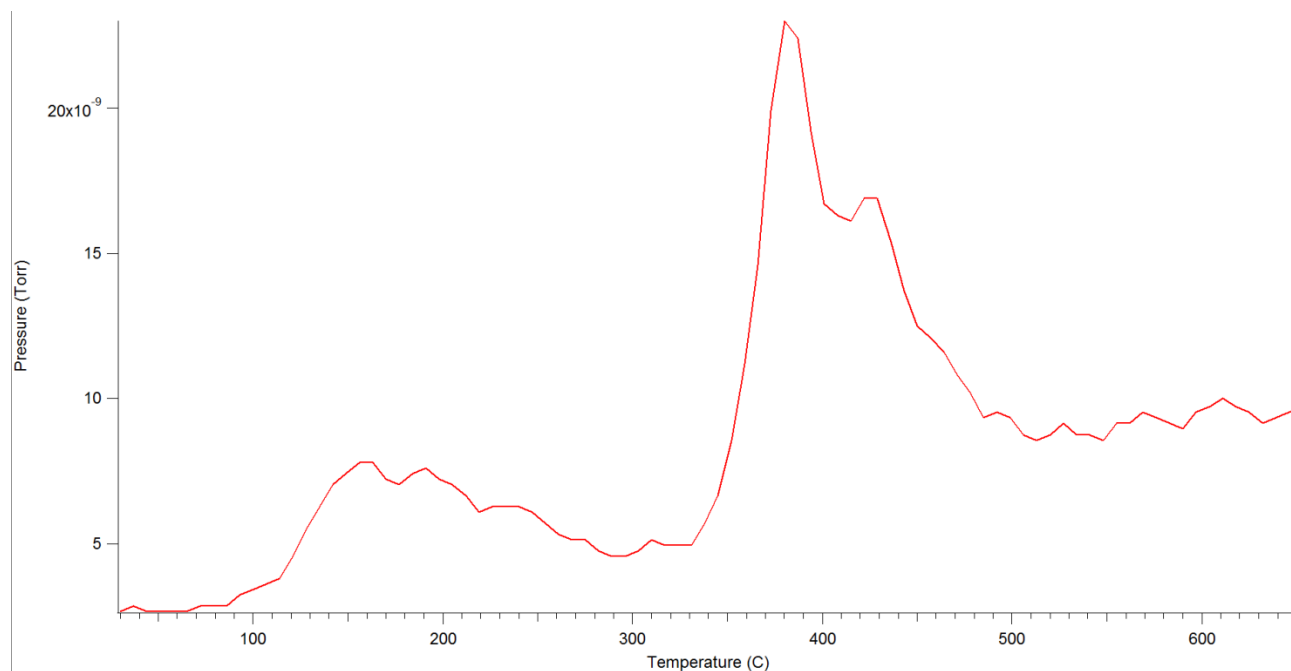

Fig 11: Plot of pressure vs. temperature for CO desorbing from a Ni surface, TPD plot. As expected, an asymeteric peak is seen.

4. Discussion

4.1 Task Completion

The ideal, original desired goals for this project included not just completing a program to control and take data from the Dycor controller and the thermocouple, but also to have control over the heating of the sample via computer automation. This would have involved creating an Igor program for a PID loop to control a lab bench current source to heat the sample. The project ran into unexpected delays when the procedures for establishing communications with the Dycor controller and the NI DAQ card both took far longer than originally planned. This caused delays and the PID control of the current source was not pursued. This was recognized

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from the start as something that could be problematic to implement and the linearity that can be attained by hand is sufficient, so this is not a concern.

4.2 Future and Continuing Work

In the future the work done on this project can be used to collect data for further research into desorption kinetics and activations energies of different molecules desorbing from surfaces. This research has broad applications, including battery efficiency, and stream lining the data collection procedure means more data in less time. To make this procedure even more efficient though, it would be desirable to find a way to combine the pressure and temperature collecting programs in such a way that they can be simply started by one click, instead of needing to start both and then telling the program to combine the data. Although not a significant detour at all, this does take up unnecessary time. It would also be desirable to revisit the PID control of the heater to optimize the linearity of the heating procedure. Manual heating simply cannot compare to the control a properly tuned PID algorithm.

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