

Nitrogen Gas Adsorption in Zeolites 13X and 5A

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Abstract. Since the discovery of zeolites there has been a consistent interest in the potential applications of these microporous structures. Of current particular interest is the possible use of zeolites as storage devices for fuel cells in the hydrogen economy. The adsorption kinetics of zeolites are not fully understood, and therefore the potential of such materials has not been optimized. In this study, the nitrogen adsorption isotherms for zeolite 13X in its commercial, pellet form and then as a crushed sample were obtained at 95K and 77K. This study compares the two isotherms obtained from zeolite 13X in its pellet form with those obtained after the zeolite was crushed. Once obtained, the isotherms showed that it is beneficial for adsorption volume to crush the zeolite. The experiment also revealed that more adsorbate (in this case nitrogen gas) is adsorbed at lower temperatures. The same procedures were performed on a crushed sample of zeolite 5A. This report includes the adsorption isotherms for Zeolite 5A at 95K and at 77K. It was found that zeolite 5A reaches its saturation point more rapidly at higher temperatures. Also included is a section focused on informing the reader of some possible sources of error in this study, and of some techniques that were found to be useful in zeolite experimentation.

Keywords: nitrogen, adsorption, zeolites, 13X, 5A, isotherms

Introduction

In 1756, a mineralogist named A.F. Cronstedt discovered the first of a group of minerals that, when heated, appeared to boil. Cronstedt soon realized that the boiling effect was due to very fast water loss. The observation that the mineral had been able to hold so much water within it suggested that it was very porous, and as Cronstedt and other scientists further explored the molecular structures of such minerals they were determined to have very open molecular frameworks. Cronstedt named this group of micro-porous minerals **zeolites** (from the Greek “zein” and “lithos”, meaning “stones that boil”) [1]. More specifically, a zeolite is a hydrated alumina-silicate mineral that has a very micro-porous structure. The corners of the structures are composed of $[\text{AlO}_4]$ - and $[\text{SiO}_4]$ - tetrahedra. In order for a mineral to be considered microporous, the channels or pore openings must be less than 20 Å. Most zeolites have pore openings much smaller than this. In general, zeolites (also called “molecular sieves”) are defined to be three dimensional frameworks of tetrahedrally coordinated atoms (T-atoms) with cavities or channels for which the smallest opening is *larger* than six T-atoms [1].

Since their discovery a little over 250 years ago, much interest has been devoted to the study of zeolites, and they have benefited myriad industries with their numerous uses. Some of these applications include purification of gases and liquids by adsorption of impurities, conversion of organic molecules in liquid and gaseous phase for catalysis in petrochemical industries, removal of fission products in nuclear waste, and soil fertilization (infusing them with potassium, ammonium, and phosphate to be slowly released into the soil) [1].

Natural zeolites are mined using conventional mining techniques, although synthesized zeolites have some advantages over their natural counterparts; the synthetic zeolites can be designed to have structures that do not occur in nature, structures that optimize their intended purpose. They can also be produced in a phase-pure, uniform state. Since the raw materials that zeolites are composed of (alumina and silica) are very abundant on Earth, their supply is virtually limitless [2].

The two types of zeolite used in this study were first synthesized in 1950, and are now readily

available as commercial molecular sieves: 13X and 5A. The first specimen, zeolite 13X, has the chemical formula $\text{Na}_{86}[(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot \text{H}_2\text{O}$. The second, zeolite 5A, is represented by the formula $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$ [3].

The growing need for a hydrogen economy invokes much interest in molecular sieves because of their potential as hydrogen storage devices. If hydrogen is able to be stored and extracted efficiently within a zeolite, it can then be used in a fuel cell. Fuel cells (electrochemical devices) are desirable because they combine hydrogen and oxygen to produce water, heat, and electricity [4]. Current hydrogen storage systems, which are used for stationary applications such as residential heating and air-conditioning, occupy large areas and are able to operate at high pressure and temperature. The slow kinetics of the processes can be compensated for with added capacity. However, these storage methods do not sufficiently meet the requirements for a transportation application, which are understandably more stringent [4]. The overall efficiency of the cells must be high enough to be competitive with modern engines in order for their use in transportation to be widespread.

Nanoporous solids such as zeolites display unique properties that cannot necessarily be predicted in the bulk. Of particular interest are the significant improvements in the efficiency of various materials' catalytic activity, which depends on the materials' nanoscale shape and size. Catalysts are an integral component in energy conversion as well as in materials synthesis and processes for the hydrogen economy [4]. A limiting factor in the advancement of hydrogen technology is catalytic performance, and the growing need for better catalysts is motivating much research aimed at grasping the chemical and physical processes involved in catalysis. Catalytic properties affect the efficiency, storage kinetics, and production capacity of fuel cells, all of which need to be understood in order for the transition to a hydrogen economy to occur [4].

Storage in metal hydrides, in chemical storage materials, and in nanostructured materials is referred to as solid-state storage. Solid-state storage is preferable to conventional storage techniques (i.e. pressurized tanks and cryogenic containers) because it allows hydrogen to be stored reversibly and irreversibly [4]. In a reversible process, the uptake and release of hydrogen gas is controlled mainly by

pressure and temperature, allowing the reaction to be manipulated. In an irreversible process, hydrogen is stored and then released by a chemical reaction, producing heat energy that can then be utilized. Many scientists consider storage to be the most challenging and necessary component of the hydrogen economy. Thus, fundamental research into the hydrogen/solid-state materials interaction is crucial [4].

My ultimate intention for studying zeolites is to understand the kinetics of adsorption processes (uptake *and* release), and to compare the efficiency of various commercial zeolites. Some of the properties that we look for in different materials are 1) favorable thermodynamics, 2) high storage capacity, 3) large volumetric and gravimetric densities (lightweight and space-conservative), 4) structural durability, 5) fast kinetics, 6) chemical stability (for safety reasons), and 7) effective heat transfer [4].

The specific goal of this research was to obtain the isotherm graphs for nitrogen adsorption in two commercial zeolites, and thus gain insight into the kinetics of the processes. I performed experiments on both zeolites in two forms; leaving them intact in pellet form first, and then crushing them. Nitrogen was used instead of hydrogen because of the danger involved in using the latter. However, much information can still be gathered by using nitrogen. The experiment was performed 95K and 77K so as to reduce the “noise” caused by increased thermal energy and allowed me to observe some of the more elementary processes of the interactions.

Experimental Apparatus

My experimental apparatus consisted of a cryogenic refrigerator, a tank of nitrogen gas, and a vacuum pumping system connected to the zeolite chamber. The panel displaying the connections between the zeolite chamber, the vacuum pump, the gas intake nozzle, and the open air is displayed in Fig. 1. The most relevant aspects are labeled. Fig. 2 shows the zeolite chamber apparatus.

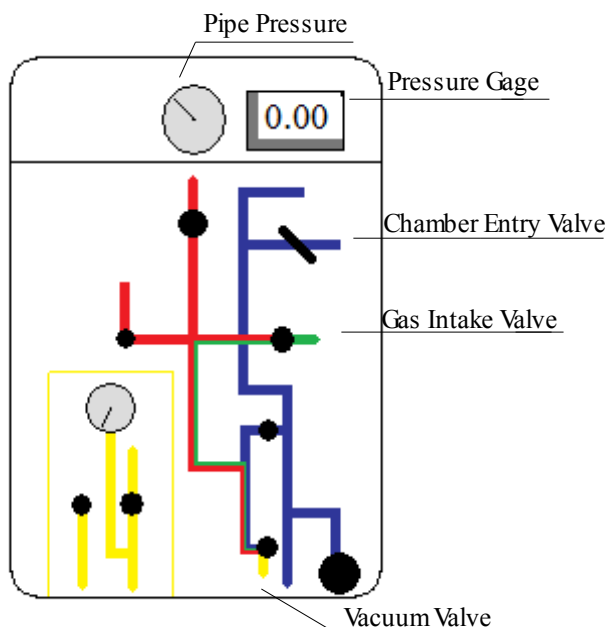


Figure 1. Control panel diagram

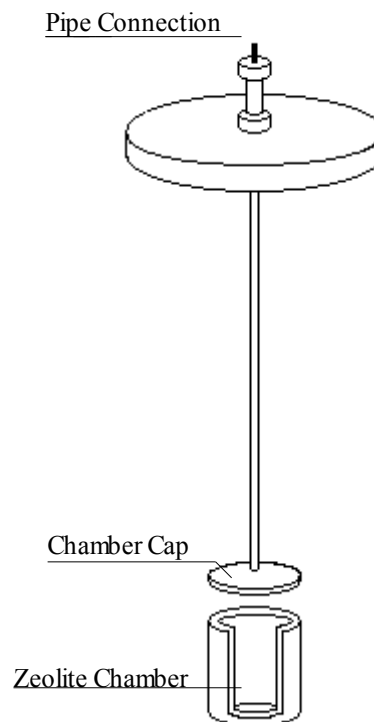


Figure 2. Chamber apparatus

As the experiment progressed, I sequentially put all zeolite samples inside the chamber shown in Fig. 2 and covered each one with a thin layer of glass fiber so as to prevent zeolite particles from migrating up the pipe into the vacuum system. Once the chamber was prepared, Dr. Sullivan and I soldered it to the chamber cap. We tested the system for leaks, sealed them when found, and vacuumed the chamber out completely (requiring some time due to out-gassing).

Experimental Procedure

The first zeolite adsorbent I experimented with was 13X, and the adsorbate was nitrogen gas (molecule length $\sim 3\text{\AA}$ [7]). Some of the relevant properties of 13X are listed in Table 1 [3, 5-7]. Figure 3

shows the structure of 13X [8].

Table I. Properties of Zeolite 13X

Chemical Name	$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot \text{H}_2\text{O}$
Pore Diameter	$\sim 8\text{\AA}$
Mesopore Volume	$0.165\text{ cm}^3/\text{g}$
Micropore Volume	$0.17\text{ cm}^3/\text{g}$
Langmuir Surface Area	$571\text{ m}^2/\text{g}$
Mass of Pellet Sample	2.37 g
Mass of Crushed Sample	2.49 g

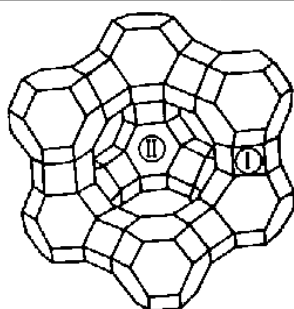


Figure 3. Zeolite 13X molecular structure

We used the cryogenic refrigerator to reach 95K (the lower limit of its cooling capabilities), and later on in the experiment used liquid nitrogen to reach 77K. Dr. Sullivan was curious about the difference in speed and volume of adsorption that would arise out of crushing the zeolite (thus increasing the surface area), so this was planned into the procedure. In the first part of the experiment, I left the pellets intact. Nitrogen gas was released into the zeolite chamber (now cooled to 95K) in 0.02 atm increments, and I measured the pressure in the pipe system every 15 seconds. Upon turning the cryogenic refrigerator off, letting the zeolite sample warm to room temperature, and then re-cooling the sample to 95K, I found that the equilibrium pressure of nitrogen in the zeolite had increased. We hypothesized that the drastic temperature change had caused some of the zeolite's molecular cages to break, increasing the area accessible to nitrogen molecules and thus allowing more of them to be adsorbed. This hinted at what the results of crushing the zeolite would be and affirmed our interest in doing so.

The recorded data consisted of only the pressure remaining in the tubing system shown by the

panel in Figure 1, and the time it took for equilibrium to be reached. The measured pressure (P_f) was read by the pressure gage and indicated the pressure in the tubes. The amount of adsorbed nitrogen could be deduced from this measurement by a simple calculation, noting that the pressure in the zeolite was the input pressure minus that gage's equilibrium pressure: $P_{in} - P_f = P_{fc}$. Once the isotherm for 13X pellets was obtained at 95K, I prepared a crushed sample and plotted an isotherm for 13X crushed at 95K and at 77K.

The same procedure was then performed with Zeolite 5A. Table 2 lists some of the properties of 5A [3, 5-7]. Figure 4 displays its molecular structure [8].

Table 2. Properties of Zeolite 5A

Chemical Name	$\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$
Pore Diameter	5 Å
Mesopore Volume	0.062 cm^3/g
Micropore Volume	0.176 cm^3/g
Surface Area	571 m^2/g
Mass of Crushed Sample	2.046 g

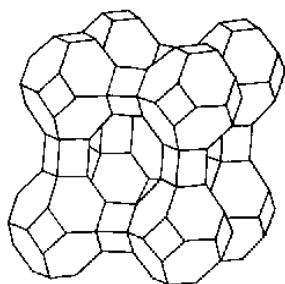


Figure 4. Zeolite 5A molecular structure

Results for Zeolite 13X

When 13X was tested in pellet form, I put nitrogen gas into the system in 0.02 atm increments throughout the experiment. The data in Table 3 lists the input pressures and equilibrium (saturation) pressures. The isotherm for 13X pellets at 95K is shown in Fig. 5 as a function of the equilibrium pressure

in the system outside of the zeolite itself (P_f) vs. the equilibrium pressure of adsorbed nitrogen (P_{fc}).

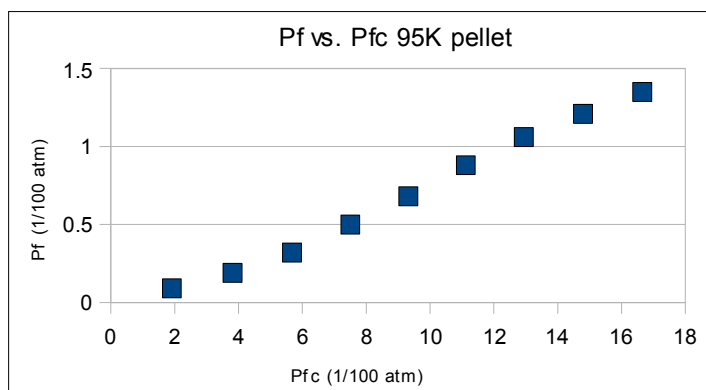


Figure 5. Adsorption of nitrogen in zeolite 13X pellet at 95K

When I crushed 13X and tested it, I put nitrogen into the system in 0.1 atm increments. With each addition of N_2 gas, the saturation point was approached. When the zeolite adsorbed about 90% of the initial input pressure, I would raise the input amount. For example, after putting in x number of 0.1 atm units, the sample became somewhat saturated. I then raised the input portion by 0.2 atm, until that pressure was again approached, at which point I added 0.3 atm, and so on. From this I obtained the isotherm for 13X crushed at 95K, as well as the isotherm for 77K. Fig. 6 shows the equilibrium pressure (P_f) in the tubes as a function of the adsorbed equilibrium pressure (P_{fc}) for 13X crushed at 95K. The isotherm for 13X crushed at 77K is shown in Fig. 7 in the form of P_f vs. P_{fc} . Fig. 8 shows the comparison of 95K and 77K isotherms for 13X crushed. On the plots in Figures 6-8 we are able to see the saturation points, indicated by the isotherms shape-change from logarithmic to linear after approximately the fifth data point. The location of this saturation point is significant to know for any research that might follow.

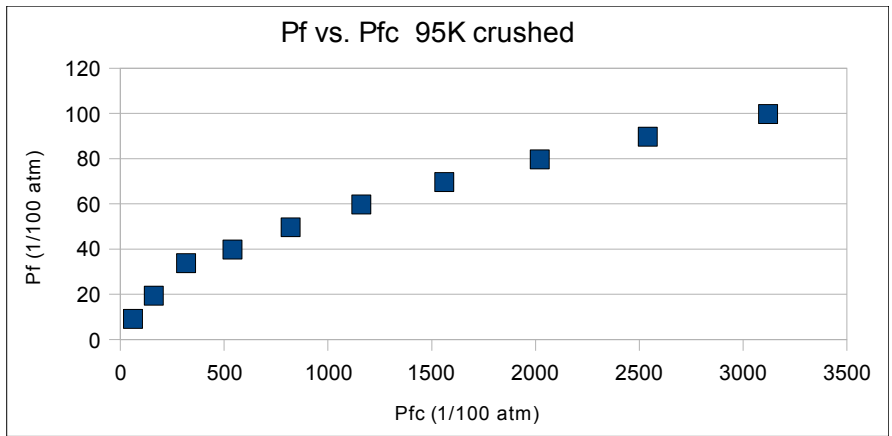


Figure 6. Adsorption of nitrogen in zeolite 13X at 95K

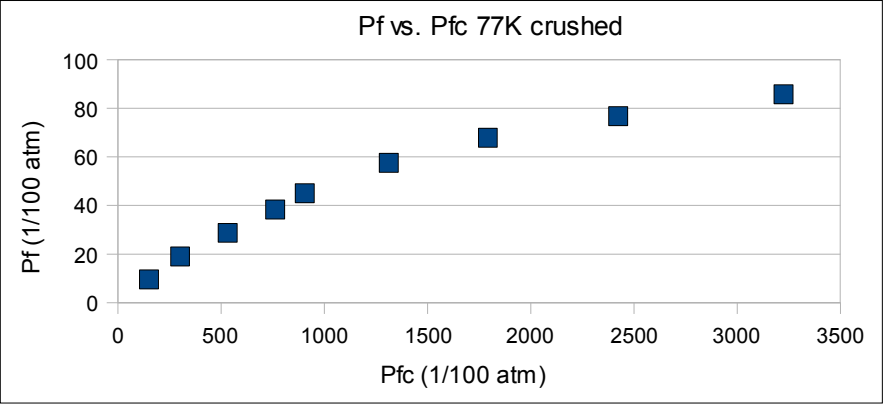


Figure 7. Adsorption of nitrogen in zeolite 13X crushed at 77K

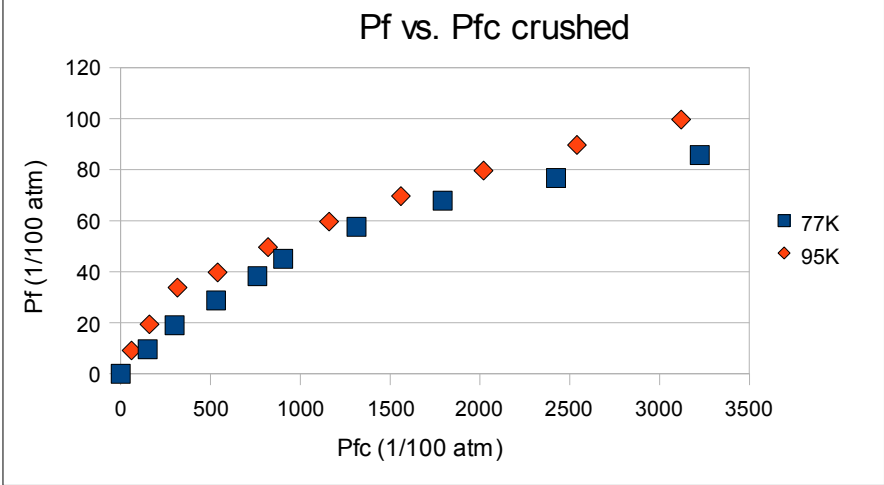


Figure 8. Comparison of adsorption of nitrogen in Zeolite 13X crushed at 95K and 77K

Results for Zeolite 5A

When I began working with 5A, I immediately prepared a crushed sample, intending to perform a later experiment with a sample in pellet form. I released nitrogen into the system starting at 0.02 atm, and continued until the point of saturation for 95K, obtaining the isotherm shown in Fig. 9.

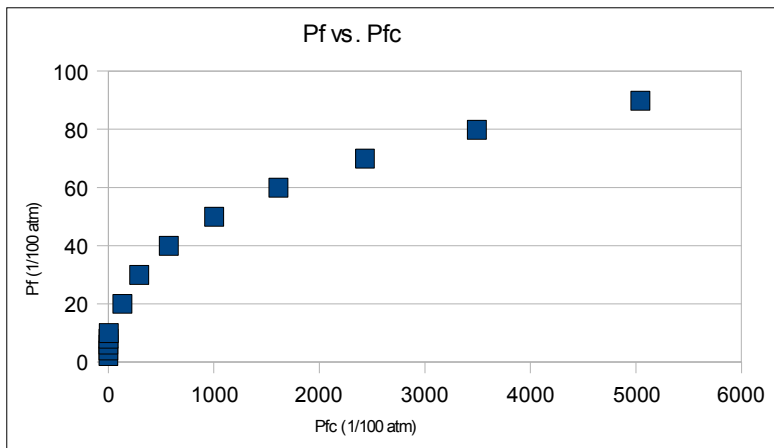


Figure 9. Adsorption isotherm for zeolite 5A at 95K

I then repeated the process at 77K and obtained the isotherm for this sample for this sample, shown in Fig. 10. A comparison of the 95K and 77K isotherms for 5A crushed is given in Fig. 11.

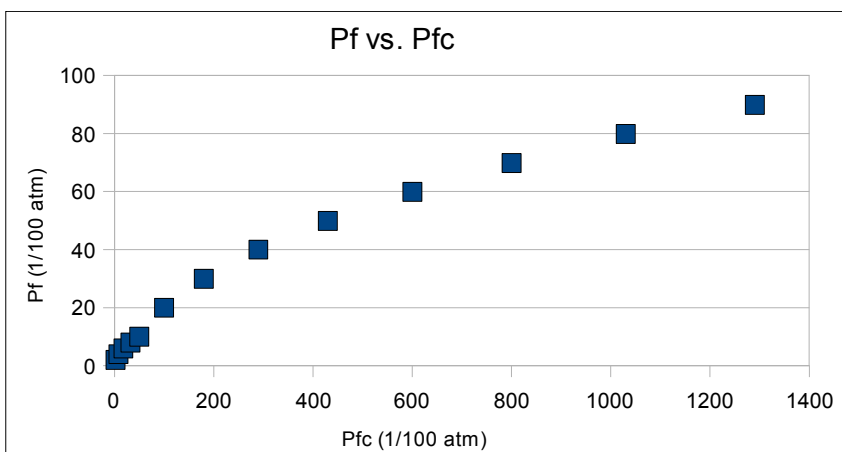


Figure 10. Adsorption isotherm for zeolite 5A at 77K

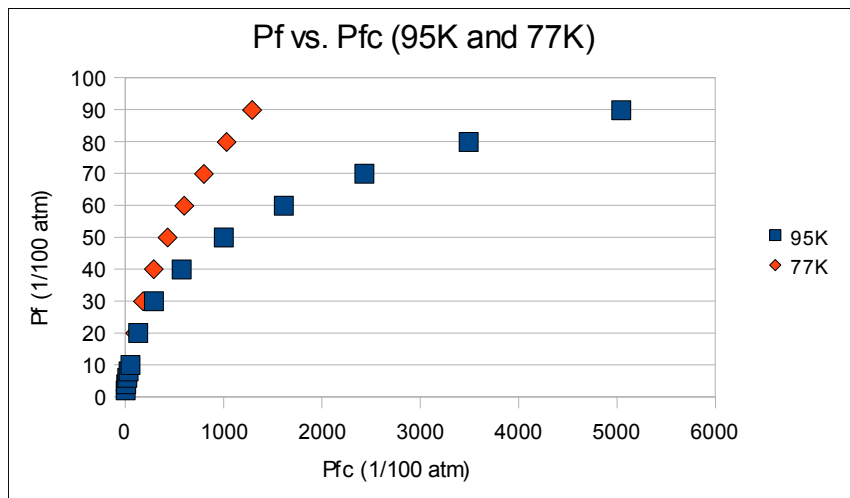


Figure 11. Comparison of 95K and 77K isotherms for zeolite 5A

Summary

From the isotherms for 13X, we observe that it is beneficial to crush the zeolite rather than use it in its pellet form. The comparison of 95K and 77K in Fig. 8 indicates that at warmer temperatures the saturation point of 13X is reached more quickly, but at a lower adsorption pressure (less nitrogen is taken into the zeolite). For the isotherm comparison of zeolite 5A (shown in Fig. 11), we deduced that the saturation point is reached more rapidly at a higher temperature. This indicates that (contrary to the kinetics of adsorption in 13X) the adsorption potential for 5A is larger at a lower temperature. In other words, the zeolite is able to adsorb more molecules at higher temperatures than at lower ones. We believe that 5A has such difficulty adsorbing large quantities of nitrogen because of the relative similarity between the pore diameter of 5A and the size of a nitrogen molecule.

From my work with zeolite 5A, I have learned that it is important to input gas in small units (particularly with this zeolite) because essential information that is contained in the beginning behavior of isotherm curves will be lost otherwise. Some possible sources of error in this particular experiment with 5A were that the sample was not kept sealed before hand in order to be isolated from moisture in the air (which zeolites will readily adsorb), and also that in the soldering process some chemical flux may have

been introduced inside the zeolite chamber. My efforts to redeem the sample consisted of vacuuming out the chamber while heating the zeolite chamber to a temperature that would adequately boil off any adsorbed moisture. I believe that this method sufficiently purified the sample.

Because of the ease with which zeolites adsorb moisture, a suggestion for future research is to purify the zeolite as much as possible *before* experimentation, either by desiccation (in case of water adsorption), or by heating the sealed zeolite chamber to evaporate any moisture trapped within the molecular cages, as was performed in this study.

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I am grateful to Dr. Sullivan for the mentoring he provided during the course of this research. His eagerness to teach and give advice was much appreciated, as was his patience. In addition to guiding me through some conundrums pertaining to this specific research, he was quite willing to answer any questions about areas not in the scope of this study, and for that I am grateful. Two other individuals of notable significance are Dr. Kevin Ingersent and Dr. Dianne Cothran for their suggestions and guidance in editing this report. I much appreciate their help in presenting this finished copy. I would also like to recognize Jay Horton for the instruction he provided on the machining and soldering that were necessary during the course of my research.

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