

Measuring the Extent of Helium Adsorption in Highly Microporous Carbon Materials

Hans Swenson, Nicholas P. Stadie
Montana State University, Bozeman, MT 59717, United States

Undergraduate
Scholars Program

Overview

Accuracy of gas adsorption measurements are dependent upon reliable estimations of the void space of a sample, usually obtained via expansion of helium gas into the sample container. This method relies on the assumption that helium does not adsorb in significant amounts. This experiment set out to determine the efficacy of measuring void space with helium, and to calculate the propensity of helium to adsorb onto high surface area ($>3000 \text{ m}^2/\text{g}$) carbon powders.

Methods

The primary instrument used for this project was a Micromeritics® 3-Flex apparatus. MSC-30, an industrial super-activated carbon and N051, a novel zeolite templated carbon were used as the analytes for the project. These carbon powders were loaded into sample tubes, and the tubes were evacuated to 10^{-9} mbar of pressure under heat to remove atmospheric adsorbates. Helium gas was then slowly introduced to each sample to calculate the free space of the sample tube. Helium adsorption isotherms were collected at temperatures from 77 K to 491 K, and each isotherm was normalized to the highest temperature free space. In this way, an array of isotherms bearing resemblance to a Henry's Law curve were obtained.

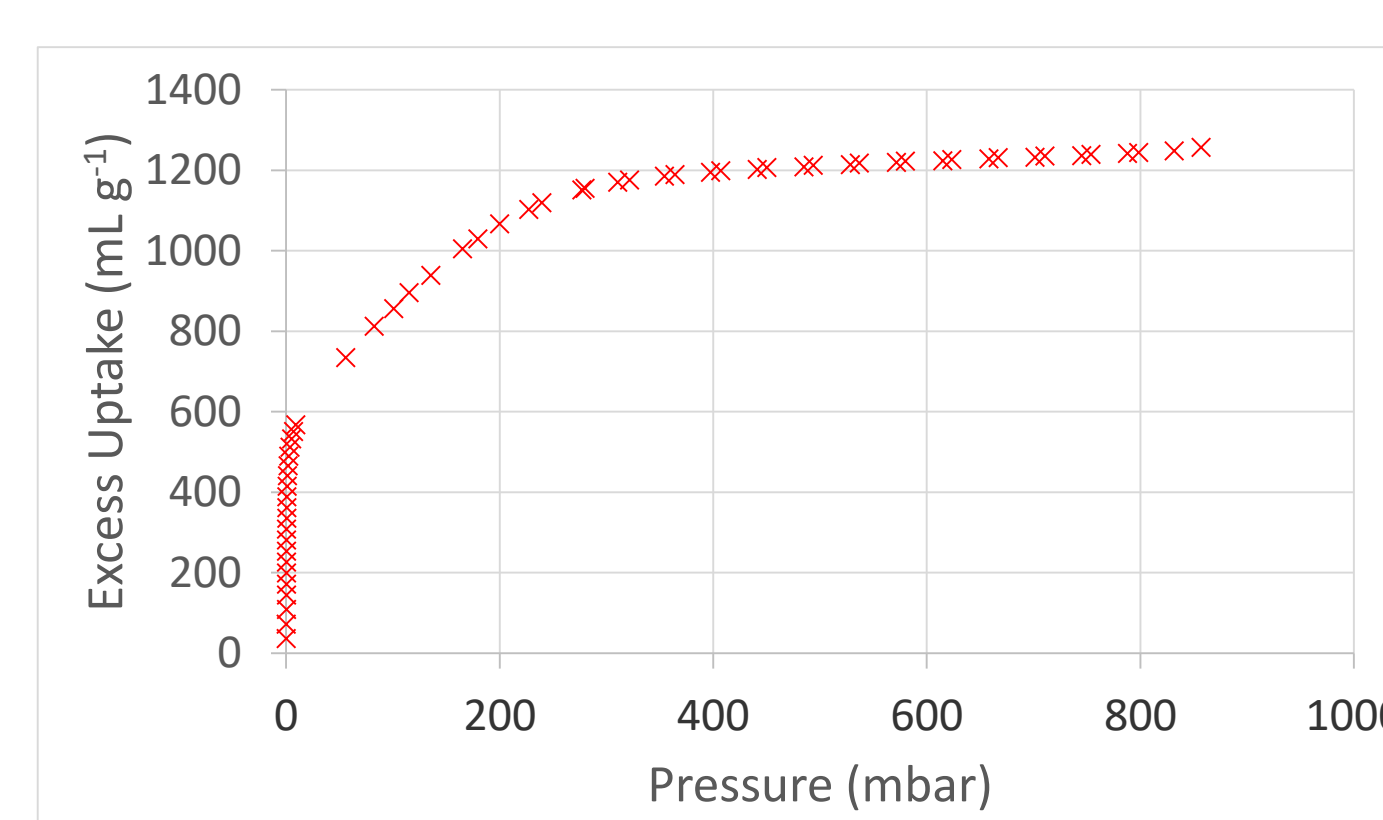


Figure 1. A 77 K Nitrogen Isotherm of MSC-30

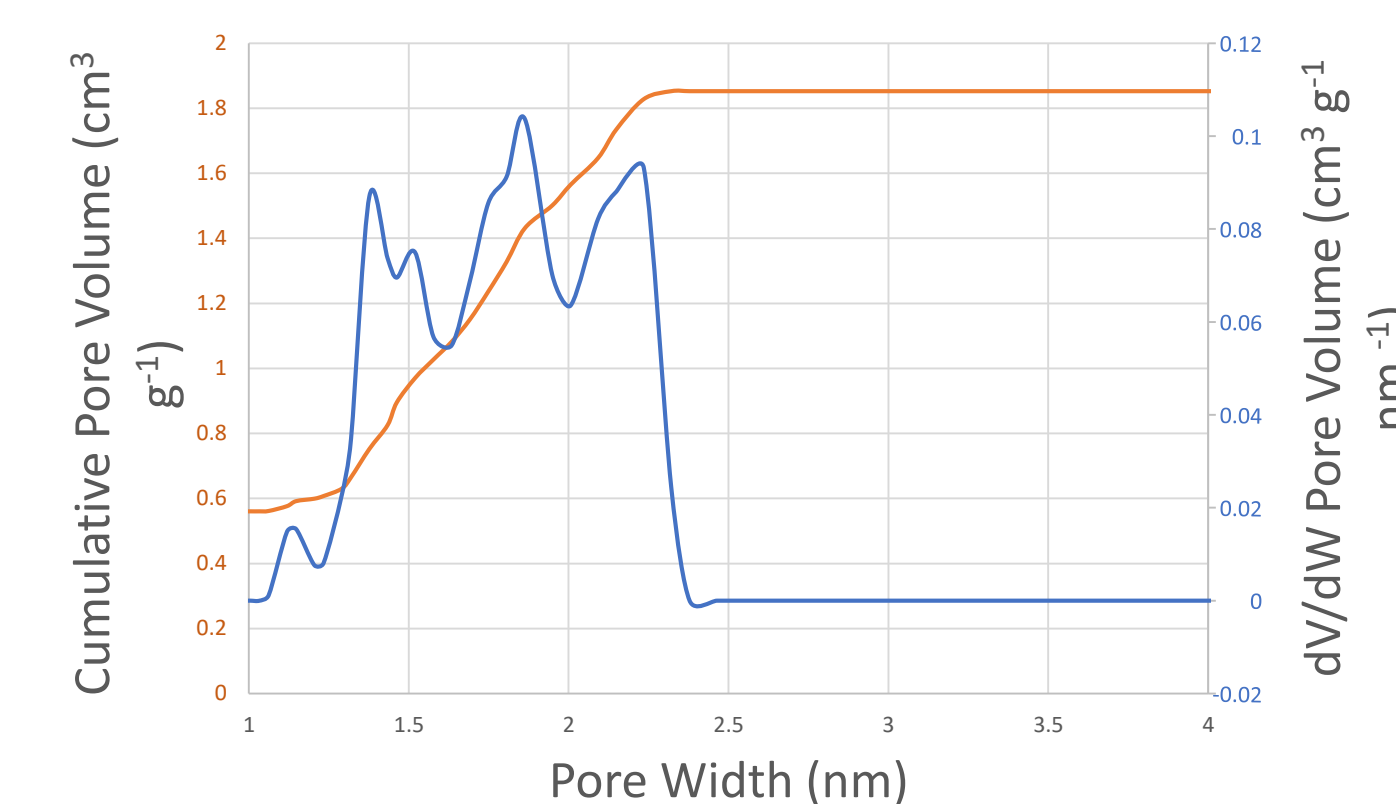


Figure 2. Pore Size Distribution of MSC-30

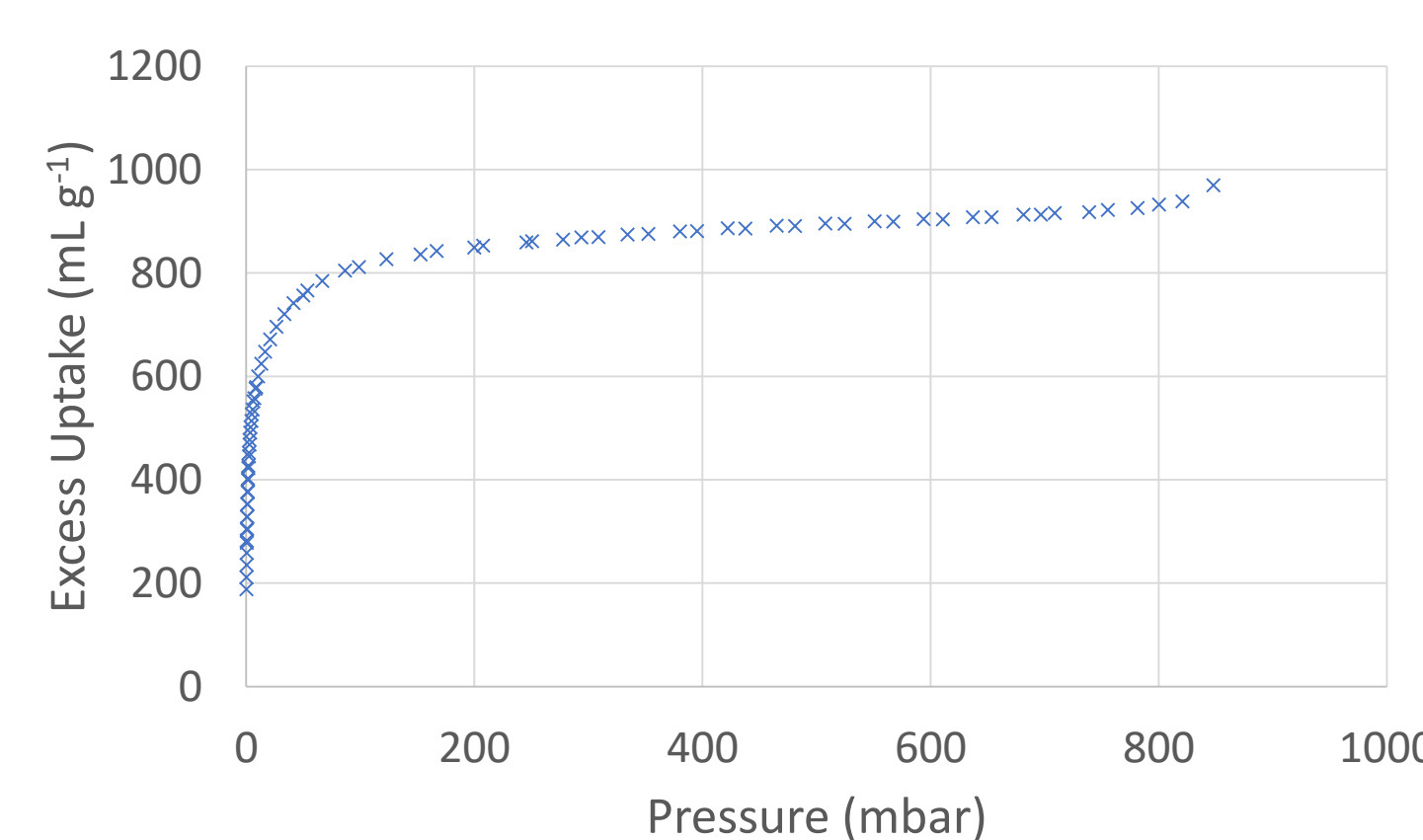


Figure 3. A 77 K Nitrogen Isotherm of N051

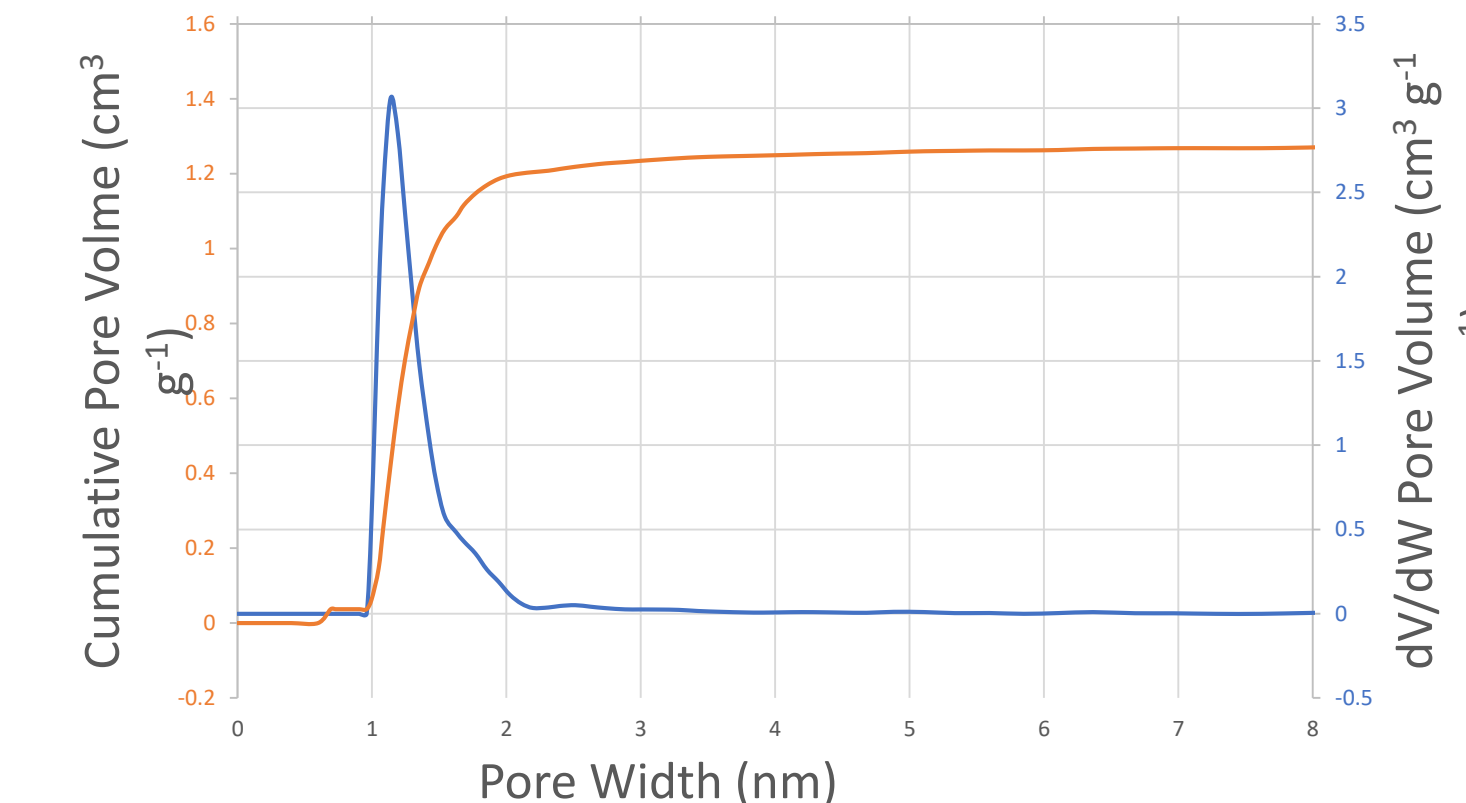


Figure 4. Pore Size Distribution of N051

Adsorption Theory

Adsorption, specifically gas adsorption, is defined as the adherence of gas molecules to a solid surface due to Van der Waals forces. The magnitude of adsorption is directly proportional to the surface area of the solid.

One of the fundamental principles of gas adsorption is the theory of the monolayer. As shown by Figure 5, when a gas molecule becomes close enough to a solid surface, Van der Waals forces cause the molecule to 'stick', or adsorb onto the surface in one of a finite number of binding sites. When every binding site is occupied, the gas can only adsorb onto a layer of already adsorbed gas, and the system is said to have a saturated monolayer.

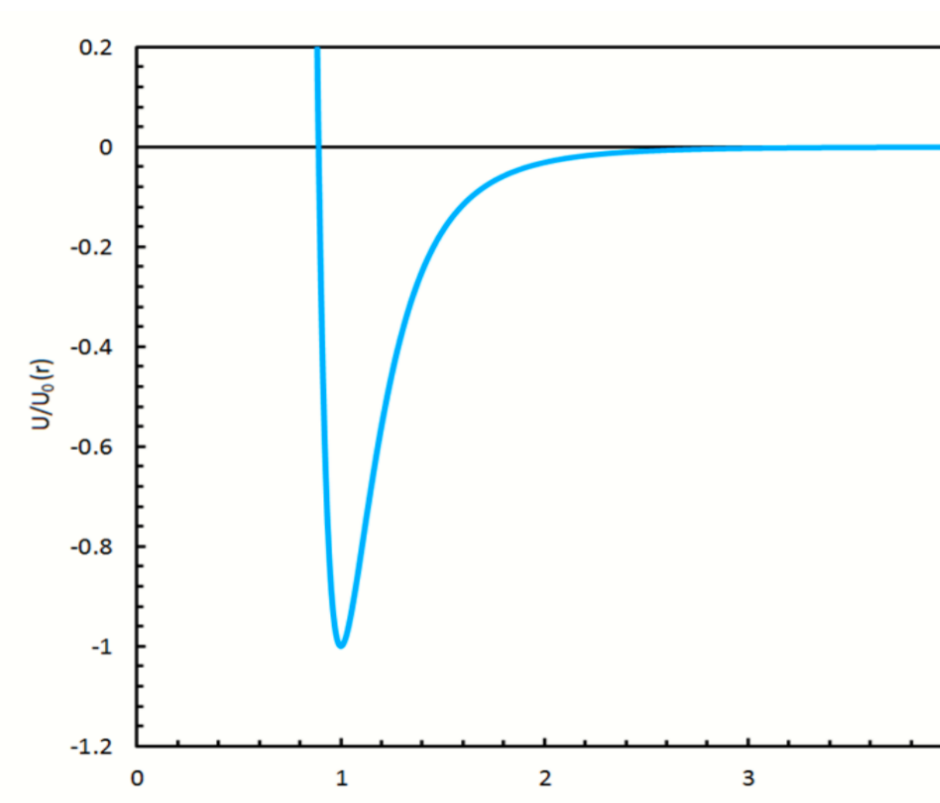


Figure 5. The Lennard-Jones 6-12 potential, with r/r_0 as the equilibrium distance between the and the gas [2]

Material Characterization

Standard physisorption analyses were taken of both carbon samples prior to experimentation. This involved creating isotherms at 77 K with N_2 gas. Figure 1 and Figure 3 are the results of these isotherms. From the isotherms, BET surface area was determined to be $3474 \pm 36 \text{ m}^2 \text{ g}^{-1}$ for MSC-30, and $3147 \pm 19 \text{ m}^2 \text{ g}^{-1}$ for N051. Figure 2 and Figure 4 show DFT pore size distributions of the two carbons. MSC-30 has a variety of micropores ranging from 1 nm to 2.5 nm in diameter, while N051 has a very narrow distribution, with the vast majority of micropores at 1 nm.

Thermodynamic Calculations

Every isotherm was fit to a linear curve, and a horizontal line was drawn at 0.01 mmol g^{-1} . Pressure corresponding to this amount of Uptake was recorded for every isotherm to create a plot of pressure vs temperature. By taking the log of the y-axis and inverting the x-axis, a Van't Hoff plot was created (Figure 8). The isosteric enthalpy of adsorption was found by linearizing the plot, and multiplying the slope of this line by R. The isosteric heat of adsorption of Helium gas was found to be 2640 J mol^{-1} .

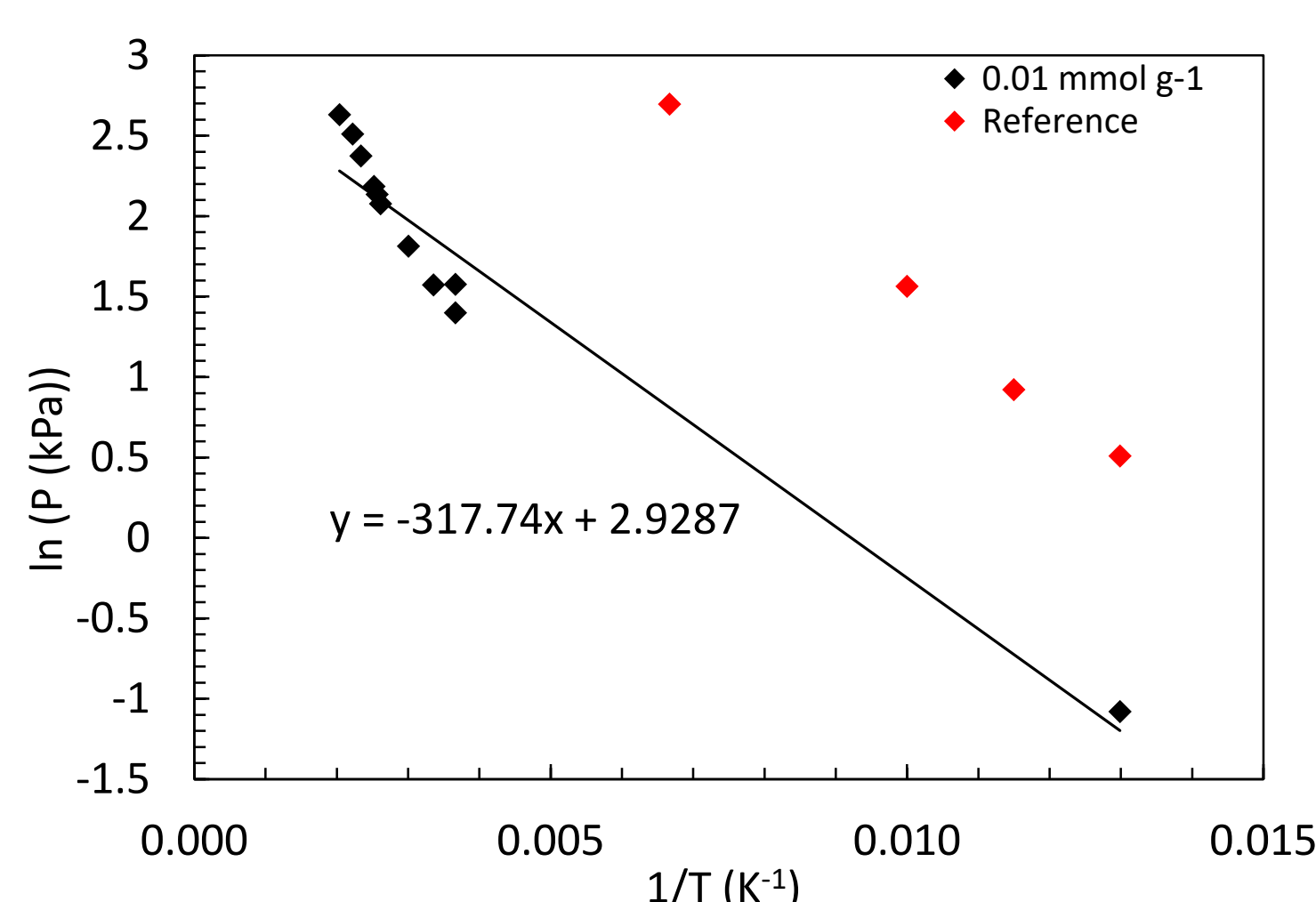


Figure 8. Van't Hoff Plot of MSC-30 data, compared to values from the literature (red) [1].

Future Work

- Because the *real free space* accepted for this project was an extrapolation from experimental data, future measurements would have to be taken at temperatures higher than 500 K to determine the accuracy of this estimate.
- N051 exhibited much higher helium adsorption than MSC-30. Future work would involve analyzing materials of different compositions and pore distributions to determine the effect of surface character on the extent of helium adsorption.

Implications

Helium is the standard for both industrial and research applications of physisorption analysis. The results of this project imply that error is implicit in these measurements, and that these errors can be both proactively and retroactively adjusted for, provided that accurate isosteric heats of adsorption for helium can be obtained.

Free Space Analysis

Because free space is generally measured with helium, obtaining accurate volume measurements were difficult. As Figure 6 shows, every initial isotherm consisted of a plot which was 'zeroed' with itself, leading to no estimated adsorption and a large amount of noise. Because physisorption of gases decreases with increased temperature, the next technique used was to normalize every isotherm to the free space of the highest temperature isotherm ($\sim 500 \text{ K}$). If helium adsorption became negligible at 500 K, the higher temperature isotherms should asymptotically converge to zero. This was not the case, leading to a third method, which involved curve-fitting a plot of free space vs temperature to find the asymptotic limit. Figure 7 shows the final array of isotherms, standardized to the calculated *real free space*.

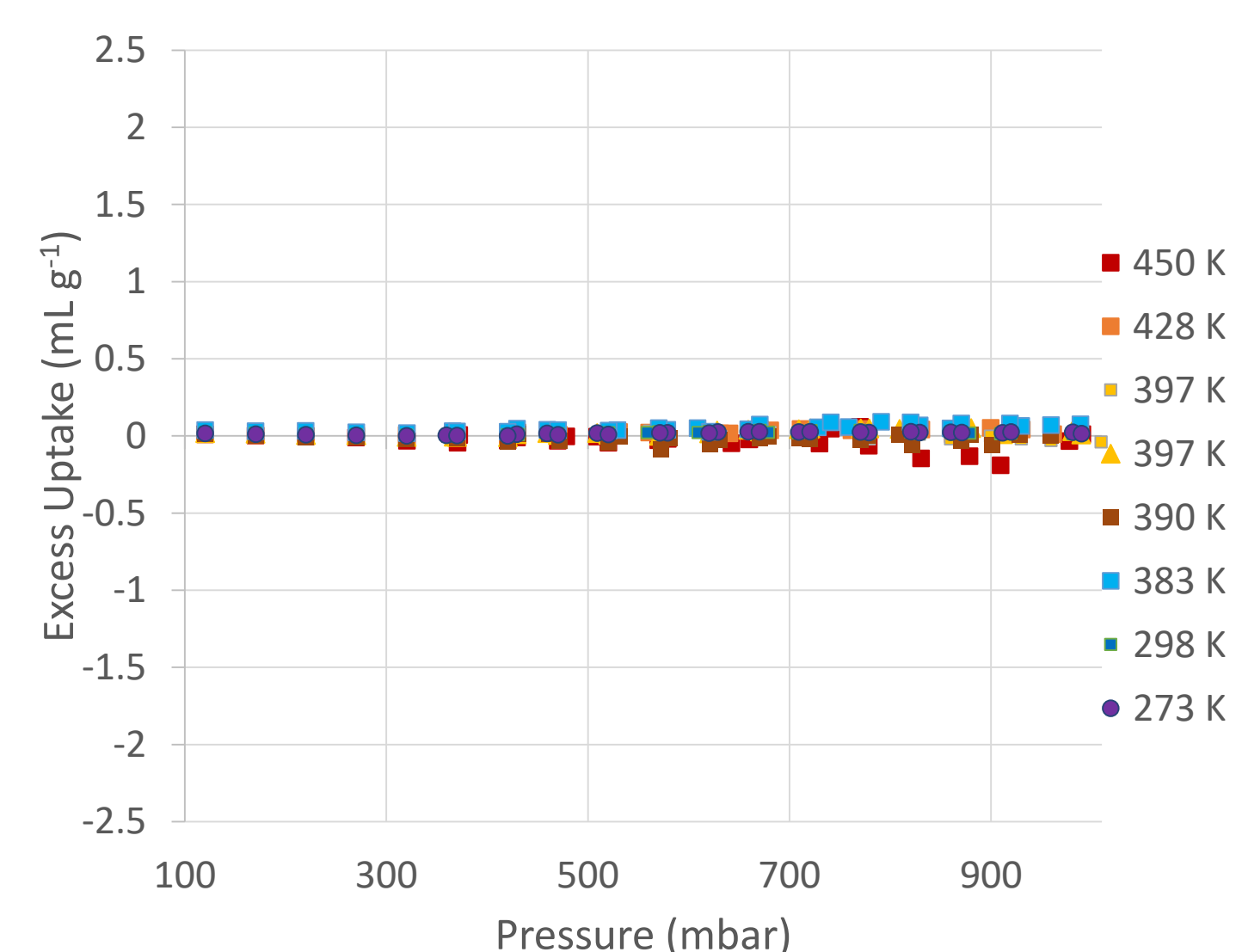


Figure 6. Unadjusted MSC-30 Isotherms

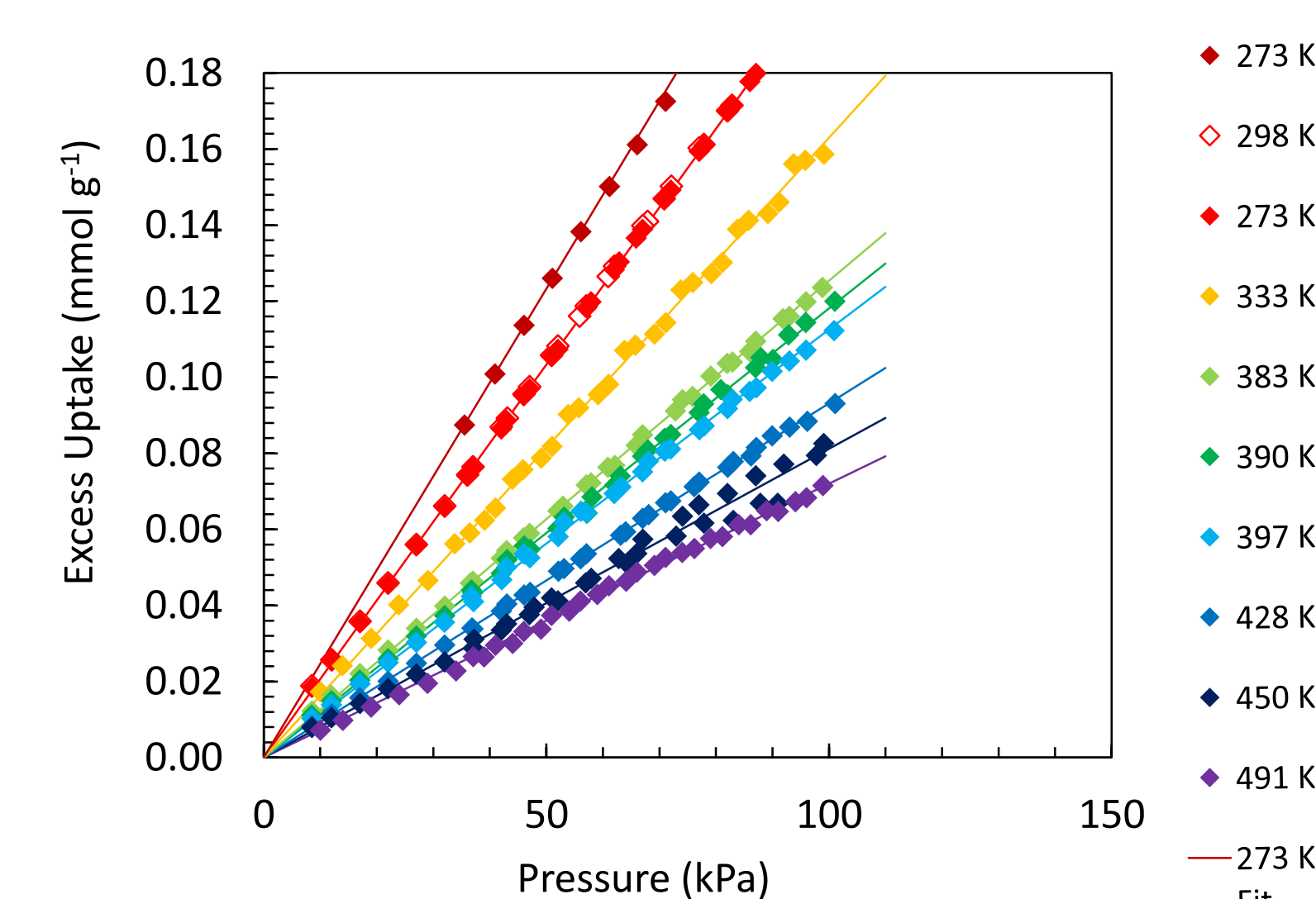


Figure 7. MSC-30 Isotherms adjusted to the *real free space*

[1] Sircar, S. (2001). Role of helium void measurement in estimation of Gibbsian surface excess. *Proceedings of Fundamental of Adsorption*, 7, 656-663.

[2] Stadie, N. P. (2013). Synthesis and thermodynamic studies of physisorptive energy storage materials (Unpublished master's thesis). Caltech.