HYDROGEN ADSORPTION STUDIES OF ENGINEERED
AND CHEMICALLY MODIFIED ACTIVATED CARBONS

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Doctor of Philosophy

by
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MAY 2012
The undersigned, appointed by the Dean of the Graduate School, have examined the dissertation entitled

HYDROGEN ADSORPTION STUDIES OF ENGINEERED AND CHEMICALLY MODIFIED ACTIVATED CARBONS

Presented by Matthew Beckner,

A candidate for the degree of doctor of philosophy,

And hereby certify that, in their opinion, it is worthy of acceptance.

___________________________
Professor Peter Pfeifer

___________________________
Professor Carlos Wexler

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Professor Haskell Taub

___________________________
Professor Galen Suppes

___________________________
Professor Satish Jalisatgi
“Le mieux est l'ennemi du bien.”
-François-Marie Arouet de Voltaire
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<td>DOE</td>
<td></td>
<td>United States Department of Energy</td>
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<tr>
<td>MOF</td>
<td></td>
<td>Metal Organic Framework</td>
</tr>
<tr>
<td>COF</td>
<td></td>
<td>Covalent Organic Framework</td>
</tr>
<tr>
<td>SSA</td>
<td></td>
<td>Specific Surface Area</td>
</tr>
<tr>
<td>$T$</td>
<td>K or $^\circ$C</td>
<td>Temperature</td>
</tr>
<tr>
<td>$p$</td>
<td>bar</td>
<td>Pressure</td>
</tr>
<tr>
<td>$N$</td>
<td></td>
<td>Particle number</td>
</tr>
<tr>
<td>$V$</td>
<td>m$^3$ or cm$^3$</td>
<td>Volume</td>
</tr>
<tr>
<td>$\Theta(p, T)_s$</td>
<td>number adsorbed per number adsorption sites</td>
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<td>$q(T)$</td>
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<td>$\mu^0(T)$</td>
<td>J</td>
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<tr>
<td>$k$</td>
<td>J/K</td>
<td>Boltzmann’s Constant</td>
</tr>
<tr>
<td>$m$</td>
<td>g or kg</td>
<td>Mass</td>
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<tr>
<td>$h$</td>
<td>J · s</td>
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<tr>
<td>$\Lambda$</td>
<td>m</td>
<td>Thermal DeBroglie wavelength</td>
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<tr>
<td>Symbol</td>
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<td>$q_x, q_y, q_z$</td>
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<td>$U_{00}$</td>
<td>J</td>
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<td>$\nu_x, \nu_y, \nu_z$</td>
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<td>$\alpha(T)$</td>
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<td>$\frac{m_{\text{ex}}}{m_s}$</td>
<td>g/kg</td>
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<td>$\frac{m_{\text{st}}}{m_s}$</td>
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<td>$\rho_i$</td>
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<td>$\phi_i$</td>
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<td>$\Sigma$</td>
<td>m²/g</td>
<td>Specific surface area</td>
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<tr>
<td>$N_A$</td>
<td>particles/mol</td>
<td>Avogadro’s number</td>
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<td>TDP</td>
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<td>g$^2$/cm$^6$</td>
<td>Third virial coefficient</td>
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<td>$V_v$</td>
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<td>$f$</td>
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<td>$m^0_{res}$</td>
<td>g</td>
<td>Blank excess adsorption</td>
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\[
\frac{m_{\text{exc}}}{m_s} \quad \text{g/kg} \\
\delta V_s \quad \text{cm}^3 \\
PRT \quad \text{Platinum Resistance Thermometer} \\
PSD \quad \text{Pore Size Distribution} \\
QSDFT \quad \text{Quenched Solid Density Functional Theory} \\
NLDFT \quad \text{Non-Local Density Functional Theory} \\
A \quad \text{m}^2 \\
\Sigma'_{\text{hole}} \quad \text{m}^2/\text{g} \\
\chi_B \quad \text{Mass ratio of boron to carbon} \\
m'_C \quad \text{g} \\
X_C \quad \text{Molar mass ratio of carbon to boron} \\
\Sigma'_{\text{sub}} \quad \text{m}^2/\text{g} \\
A_R \quad \text{m}^2 \\
\Sigma'_{\text{end}} \quad \text{m}^2/\text{g} \\
\Sigma_R \quad \text{m}^2/\text{g} \\
X_R \quad \text{Molar mass ratio of boron to carbon}
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<td>Å</td>
<td>Carbon-carbon bond length in graphite</td>
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<td>$d_{b-c}$</td>
<td>Å</td>
<td>Boron-carbon bond length in boron-doped graphite</td>
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<td>$d_\Pi$</td>
<td>Å</td>
<td>Distance a substituted boron atom protrudes from the carbon plane</td>
</tr>
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<td>$d_\alpha$</td>
<td>Å</td>
<td>Distance a nearest-neighbor carbon atom protrudes from the carbon plane</td>
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<td>$d_\beta$</td>
<td>Å</td>
<td>Distance a next-nearest-neighbor carbon atom protrudes from the carbon plane</td>
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<td>Fourier Transform Infrared Microscopy</td>
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<tr>
<td>ppm</td>
<td></td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>$k_\Pi$</td>
<td>kg/Pa</td>
<td>Henry’s Law constant</td>
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<td>$E_\Pi$</td>
<td>kJ/mol</td>
<td>Binding energy; equivalent to $U_{0\Pi}$</td>
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<td>$w$</td>
<td>Å</td>
<td>Pore width</td>
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<td>$S$</td>
<td>System consisting with $N$ molecules in a volume $V$ at a pressure $p$ and temperature $T$ that includes an adsorbing solid and obeys Henry’s Law</td>
</tr>
<tr>
<td>$N_{exc}$</td>
<td>Excess adsorption (number of molecules)</td>
</tr>
<tr>
<td>$S'$</td>
<td>A subsystem of $S$ for which there is no adsorption potential</td>
</tr>
<tr>
<td>$V_{\text{observed}}$</td>
<td>cm$^3$</td>
</tr>
<tr>
<td>$V_0$</td>
<td>cm$^3$</td>
</tr>
<tr>
<td>$k_{H,V}$</td>
<td>cm$^3$/bar or m$^3$/Pa</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Pa $\cdot$ m</td>
</tr>
<tr>
<td>$S$</td>
<td>J/K</td>
</tr>
<tr>
<td>$\mu$</td>
<td>J</td>
</tr>
<tr>
<td>$\Xi$</td>
<td>Grand canonical partition function</td>
</tr>
<tr>
<td>$Q_N(V,T)$</td>
<td>Canonical Partition function</td>
</tr>
<tr>
<td>$z$</td>
<td>m$^{-2}$</td>
</tr>
<tr>
<td>$b_N$</td>
<td>m$^{-3}$</td>
</tr>
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</table>
ABSTRACT

In recent years, there has been a great emphasis on replacing fossil fuels with clean, renewable energy for use in vehicles. One potential solution is the use of hydrogen gas as a fuel source to power a fuel cell. Before a change from fossil fuels to hydrogen can occur, there must be significant progress in developing low pressure hydrogen storage systems. Activated carbons have the potential to be excellent storage systems for hydrogen gas because of their high surface areas and reversible hydrogen storage capabilities. However, limitations on the surface area and binding energy restrict their effectiveness as a potential storage material. There is significant interest in the properties of boron-doped activated carbons for their potential to improve hydrogen storage.

My research focuses on the production of boron-doped activated carbons and the evaluation of their adsorption and structural characteristics. Boron-doped activated carbons have been produced using a process involving the pyrolysis of decaborane \((B_{10}H_{14})\) and subsequent high-temperature annealing. Presented here is a systematic study of the undoped activated carbon precursor on the effect of activation temperature and KOH:C on pore structure. A second study of the effect of different boron-doping processes on the samples’ structure, hydrogen sorption, and surface chemistry is presented. Room temperature hydrogen adsorption experiments show a 20% increase in the hydrogen excess adsorption per surface area compared to the undoped material. Experimentally determined adsorption enthalpies showed that the boron-doped activated carbon had an enthalpy of \(\sim 9-10 \text{ kJ/mol}\) compared to \(6 \text{ kJ/mol}\) for the undoped precursor.
Chapter 1 - Introduction

In recent years, there has been a great emphasis on replacing fossil fuels with clean, renewable energy for use in vehicles. One potential solution is the use of hydrogen gas as a fuel source to power a fuel cell. For vehicular use, the United States Department of Energy (DOE) has identified three major challenges to implementing a hydrogen-powered solution [1]: (i) hydrogen production costs must be substantially lowered, (ii) there must be a substantial reduction in fuel-cell costs, and (iii) hydrogen storage systems capable of delivering a driving range of hundreds of kilometers without major detrimental effects to vehicle cost, safety, or cargo capacity, must be developed.

Arguably, the third challenge is the most daunting because of the strict restrictions placed on tank design (e.g. cost of materials, weight of the tank to meet safety requirements, size of the tank, etc.). Hydrogen has a mass energy density three times that of gasoline. The significant problem is that hydrogen occupies more than 30 times the volume of gasoline [2]. It is therefore necessary to increase the volumetric energy density of hydrogen before it can be considered a useful option.

While simply compressing the gas to a higher pressure seems to be an obvious solution, thicker tank walls are required to meet the safety requirements and such tanks limit storage and passenger space [3,4]. To solve this problem, many researchers are investigating new, innovative materials to reduce the internal pressure of the container while simultaneously storing more gas than compressed hydrogen tanks. Materials such
as metal hydrides, chemical hydrides, cryogenic hydrogen, and adsorbants such as carbonaceous materials, metal organic frameworks (MOFs), and covalent organic frameworks (COFs) have shown promise (cf. Fig. 1.1). However, none are currently able to fully meet the DOE’s requirements [5].

As we reach the current technological limit of such materials, it is absolutely imperative to understand fully the physical mechanisms behind the interaction of hydrogen with storage materials in order to develop new materials with an increased storage capacity. Here, we investigate adsorption-based materials as a potential solution because they do not require external heating to remove the hydrogen as is necessary with chemical and metal hydrides; and they have the potential to operate at ambient temperatures, thereby reducing the tank weight required for cryogenic systems.

![Figure 1.1. Current progress toward reaching the DOE storage goals [5]. All estimates include system weight and volume. Hollow data points were estimated by the author.](image)
One method of increasing storage capacity is to increase the specific surface area (SSA) of the material. In general, increasing the SSA increases the number of adsorption sites per mass of material and thereby increases the number of gas molecules adsorbed per unit mass (Fig. 1.2) [4,6].

However, there is a physical limit to how large the SSA may be. For graphene, the maximum theoretical surface area is 2,965 m²/g [7], although it has been theorized that by removing carbon atoms, a surface area as high as 7,000 m²/g may be achieved [8]. To go beyond this limit, we investigated altering the surface chemistry of the material to enhance its adsorption characteristics.

It has been shown theoretically that substitution of boron into the carbon surface can increase the hydrogen binding energy of the carbon material [9-12]. While much research has been accomplished in the theoretical realm, producing a real boron-doped material has proven to be a more challenging task. A few materials have been manufactured in various labs that have shown encouraging results.

Studies on boron nitride nanotubes have shown some promise [13,14]. Ma et al. [13] reported an excess adsorption of 2 wt% at 10 bar and room temperature measured gravimetrically. Chung et al. [14] reported approximately 3 wt% at 50 bar and 77 K for their sample B/C-II-600, which had a SSA of 780 m²/g. Their data is significantly above the value predicted by “Chahine’s rule” [8] for a carbon material of that surface area. Jin et al. [15] were able to produce boron-substituted carbon scaffolds with SSAs ranging from 600 to 900 m²/g that showed a higher adsorbed hydrogen concentration (wt% g/m²) than undoped carbon scaffolds. While these studies have shown that it is possible to
increase the adsorbed hydrogen concentration, their relatively low SSAs do not allow for these materials to solve the initial storage problem.

![Figure 1.2. "Chahine Plot" for various single walled carbon nanotubes (SWCNTs, ■), activated carbons (•, ○), and boron-doped carbons (▲, △). Solid data points indicate those from literature sources [6,14,16-18]. Hollow data points indicate data measured at MU for which the blank isotherm has been subtracted. Open circles with an “x” indicate data measured at MU for which the blank isotherm has not been subtracted. The black line represents the values predicted by the so-called “Chahine Rule” [8].]

It is the purpose of this project to produce new high-surface-area materials with increased binding energies via boron-doping to develop higher storage capacity materials and gain a better understanding of the material’s basic interaction with the hydrogen gas. In order to evaluate material performance, hydrogen storage was measured using an improved manometric technique (cf. Chapter 3). Using this method, we find that hydrogen adsorption is increased after boron doping and that the adsorption energy increases from 5-6 kJ/mol to 10-11 kJ/mol (cf. Chapter 6).
Physicists and chemists studying gas-solid interactions are concerned with three quantities: excess adsorption, absolute adsorption, and storage capacity. If one could explicitly measure the gas density at every point in the system, the task of determining these three quantities would be trivial. However, because “Maxwell’s demons” are not commercially available to count molecules for us, more ingenious methods of determining the adsorption properties are required.

Instruments used to measure adsorption of gases vary greatly in design and theory. Despite their differences, each instrument measures the same quantity, excess adsorption. Excess adsorption may be defined as follows [19]:

Consider two systems of equal volume. The first system is that of a free gas at a temperature $T^0$, pressure $p^0$, and contains $\bar{N}^0$ gas molecules (cf. Fig. 2.1(a)). The second system contains an external potential $U(\tau)$ due to an adsorbing surface outside of the system and the gas has a temperature $T$, pressure $p$ far from the adsorbing surface, and contains $\bar{N}$ gas molecules (cf. Fig. 2.1(b)). If both systems have the same temperature and pressure (i.e. $T = T^0$ and $p = p^0$), then the excess adsorption is given by $\bar{N} - \bar{N}^0$.

Excess adsorption is reported in the literature as either wt% or normalized to sample mass, referred to here as gravimetric excess adsorption. For adsorbents, excess adsorption is the only quantity that may be directly measured without theoretical assumptions [20].
Figure 2.1. Comparison of systems with (b) and without (a) an external potential due to an adsorbing surface [21]. Excess adsorption is found by calculating the number of particles in $V$ for system a ($\tilde{N}^a$) and system b ($\tilde{N}$) and is given by $\tilde{N} - \tilde{N}^a$. (c) Graphical representation of gas density vs. distance from adsorbent surface. The three regions indicated show excess adsorption (I), absolute adsorption (I + II), and total storage capacity (I + II + III) [22].

2.1 Langmuir Adsorption: Localized and Mobile Adsorption

Here we consider two distinct models of adsorption based on the Langmuir theory of adsorption [23]. Consider an adsorption potential that is periodic in the $x$ and $y$ directions (parallel to the adsorbent surface) as in Fig. 2.1. If the thermal energy of the
adsorbed gas is sufficiently low, the adsorbed gas is bound within the potential well
(localized adsorption). If the thermal energy is sufficient large, then the adsorbed gas is
free to move around the surface of the solid (mobile adsorption).

From Hill [19] (Eqs. (7) to (10), p. 128), the Langmuir isotherm for surface
coverage $\Theta (0 \leq \Theta \leq 1$ for monolayer adsorption) is given as a function of temperature $T$ and pressure $p$ by

$$
\Theta(p, T) = \frac{\chi(T)p}{1 + \chi(T)p}.
$$

The Langmuir constant $\chi(T)$ is given in terms of the partition function for one adsorbed
molecule $q(T)$ and the standard chemical potential $\mu^0(T) \equiv -kT \ln \left( \left( \frac{2\pi mkT}{\hbar^2} \right)^{3/2} kT \right)$.

$$
\chi(T) = q(T)e^{\mu_0(T)/kT}
= q(T)e^{-kT \ln[\Lambda^{-3/kT}]/(kT)}
= q(T)e^{\ln[\Lambda^3/kT]}
= \frac{q(T)\Lambda^3}{kT}.
$$

Here, $\Lambda$ is the thermal de Broglie wave length $\Lambda \equiv \hbar/(2\pi mkT)^{1/2}$ where $m$ is the mass
of a single gas molecule and $\hbar$ and $k$ are Plank’s and Boltzmann’s constants,
respectively. The partition function is given in terms of one-dimensional partition
functions in the harmonic oscillator approximation

$$
q(T) = q_xq_yq_ze^{-U_{00}/(kT)}
$$

where $U_{00}$ is the minimum of the adsorption potential $U(x, y, z)$ (cf. Fig. 2.2) and $q_x$, $q_y$, and $q_z$ are the one-dimensional partition functions. The choice of the one-dimensional
partition functions is where the distinction between localized and mobile adsorption is made.

![Diagram of adsorption potential and possible thermal energies for mobile and localized adsorption.]

**Figure 2.2.** Illustration of the adsorption potential and possible thermal energies for mobile and localized adsorption.

**Localized adsorption**

In the localized model, the adsorbed gas molecule is bound in all three directions x, y, and z. The one-dimensional partition functions $q_x$, $q_y$, and $q_z$ are the one-dimensional harmonic oscillator partition functions with vibrational frequencies $\nu_x$, $\nu_y$, and $\nu_z$,

$$q_i = \frac{e^{-\frac{1}{2}h\nu_i/(kT)}}{1 - e^{-h\nu_i/(kT)}}$$  \hspace{1cm} (2.4)

Beginning from Eq. (2.4):
Finally, combining Eqs. (2.3) and (2.5), the total partition function is

\[ q(T) = \frac{e^{-U_{00}/(kT)}}{8 \prod_{i=1}^{3} \sinh \left( \frac{\hbar \nu_i}{2kT} \right)} \]  \hspace{1cm} (2.6)

Substituting Eq. (2.6) into Eq. (2.2)

\[ \chi_{\text{local}}(T) = \frac{q(T) \Lambda^3}{kT} e^{-U_{00}/(kT)} \Lambda^3 = \frac{\prod_{i=1}^{3} \sinh \left( \frac{\hbar \nu_i}{2kT} \right)}{e^{-U_{00}/(kT)}} \frac{\Lambda^3}{8kT} \]

\[ = \frac{\prod_{i=1}^{3} \sinh \left( \frac{\hbar \nu_i}{2kT} \right)}{\prod_{i=1}^{3} \sinh \left( \frac{\hbar \nu_i}{2kT} \right)} \left( 2\pi m kT \right)^{(3/2)} 8kT \]

\[ \chi_{\text{local}}(T) = \frac{e^{-U_{00}/(kT)}}{\prod_{i=1}^{3} \sinh \left( \frac{\hbar \nu_i}{2kT} \right)} \sqrt{\frac{\hbar^6}{(8\pi m)^3 (kT)^{5}}} \]  \hspace{1cm} (2.7)

Mobile adsorption

For mobile adsorption, the adsorbed gas is allowed to move freely across the surface of the solid, but the adsorbed gas still oscillates within an adsorption potential in the z (perpendicular) direction. The z-direction partition function is the same as for localized adsorption (Eq. (2.4)), however the x and y directions partition functions are that of a free gas.
The partition function for an ideal (i.e. freely moving) gas is given by

\[ q(T) = V/\Lambda^3 \]  
where \( V \) is the volume of the gas [19] (Eqs. (4) to (10), p. 77). Again, the partition function may be expressed as a product of one-dimensional partition functions such that each is given by

\[ q_i = \frac{\sqrt[3]{V}}{\Lambda}. \]  

(2.8)

For mobile adsorption, we take the length of the volume element in the x and y directions to be equal to the square root of the area per adsorption site \( \alpha(T) \). In other words

\[ q_x = q_y = \frac{\sqrt{\alpha(T)}}{\Lambda}. \]  

(2.9)

Using these partition functions along with the harmonic oscillator partition function and Eq. (2.3), the full partition function for the case of mobile adsorption is

\[
q(T) = q_x q_y q_x e^{-U_{00}/(kT)} \]
\[
= \frac{\sqrt{\alpha(T)}}{\Lambda} \frac{\sqrt{\alpha(T)}}{\Lambda} \frac{1}{2 \sinh \left( \frac{\hbar \nu}{2kT} \right)} e^{-U_{00}/(kT)}
\]

\[
q(T) = \frac{\alpha(T) e^{-U_{00}/(kT)}}{2\Lambda^2 \sinh \left( \frac{\hbar \nu}{2kT} \right)}
\]  

(2.10)

This partition function substituted into Eq. (2.2) gives
The final form of the Langmuir constant for mobile adsorption is

\[
\chi_{\text{mobile}}(T) = \alpha(T) \frac{q(T) \Lambda^3}{kT} \\
= \frac{\alpha(T)e^{-\frac{U_{00}}{kT}}}{\sinh \left( \frac{\hbar \omega_0}{2kT} \right)} \frac{\Lambda^3}{2\Lambda^2 kT} \\
= \frac{\alpha(T)e^{-\frac{U_{00}}{kT}}}{\sinh \left( \frac{\hbar \omega_0}{2kT} \right)} \frac{\Lambda}{2kT} \\
= \frac{\alpha(T)e^{-\frac{U_{00}}{kT}}}{\sinh \left( \frac{\hbar \omega_0}{2kT} \right)} \frac{\hbar}{2kT} \sqrt{\frac{1}{2\pi mkT}}
\]

2.2 Derivation of Calculated Quantities: Gravimetric Storage Capacity, Volumetric Storage Capacity, and Gravimetric Absolute Adsorption

Recall from above the difference between excess adsorption, absolute adsorption, and storage capacity (cf. Fig. 2.1). In order to convert excess adsorption into absolute adsorption or storage capacity, it is necessary to know two things: (i) the gas density as a function of pressure and temperature and (ii) the total volume that the gas occupies. The gas density may be found using an equation of state or by referencing a data table (cf. Sec. 3.2). The task of determining the volume occupied by the gas is not so trivial. It is the purpose of this section to define the volumes required to calculate gravimetric storage capacity, volumetric storage capacity, and gravimetric absolute adsorption and use these definitions to derive a conversion from gravimetric excess adsorption to each quantity.
Consider a system of total volume \( V_{\text{system}} \) consisting of an adsorbent solid of undefined geometry and an adsorbing gas. We define several volumes such that sum of all defined volumes equals the total volume (cf. Fig. 2.3):

- **Solid Volume** – The volume occupied by the adsorbing solid.
- **Closed Pore Volume** – The volume occupied by pores inaccessible to gas.
- **Open Pore Volume** – The volume accessible to gas that is within a dead-end or caternary pore of the solid particle\(^1\).
- **External Void Volume** – The volume accessible to gas that is within the solid particle, but not within a pore.
- **Inter-Particle Void Volume** – The volume that exists between or outside of particles.

From these basic definitions, we define four quantities to be used in calculating gravimetric storage capacity, volumetric storage capacity, and gravimetric absolute adsorption (cf. Table 2.1) [24,25]:

- **Skeletal Volume** – The sum of the solid and closed pore volumes.
- **Particle Volume** – The sum of the skeletal and open pore volumes.
- **Apparent Volume** – The sum of the particle and external void volumes.
- **Bulk Volume** – The sum of the apparent and inter-particle void volumes.

It is important to note that the generic system considered for later calculation may or may not contain all of the volumes listed above.

---

\(^1\) A caternary pore is defined to be the volume occupied by an adsorbed gas at its normal boiling point. It is referred to as a caternary pore because it is bounded by the meniscus formed by the adsorbed liquid.
Gravimetric storage capacity and porosity

Gravimetric storage capacity is defined to be the total mass of gas in the system per mass of sample. To calculate the gravimetric storage capacity from excess
adsorption, it is necessary to add to the excess adsorption the amount of gas that would be present if there was no gas-solid interaction

\[
\frac{m_{st}}{m_s} = \frac{m_{exc}}{m_s} + \frac{\rho_{gas}(p,T)}{m_s} V_{gas}. \tag{2.12}
\]

Here, \(\frac{m_{st}}{m_s}\) is the gravimetric storage capacity and \(V_{gas}\) is the total volume occupied by the gas. In general, the volume occupied by the gas will be given by \(V_{system} - V_{skeletal}\). However, any volume defined in Table 2.1 may be used to define the total volume of the system\(^2\). It follows from Eq. (2.12) that

\[
\frac{m_{st}}{m_s} = \frac{m_{exc}}{m_s} + \rho_{gas}(p,T) \left( V_{system} - V_{skeletal} \right). \tag{2.13}
\]

\[
\frac{m_{st}}{m_s} = \frac{m_{exc}}{m_s} + \rho_{gas}(p,T) \left( \frac{1}{\rho_{system}} - \frac{1}{\rho_{skeletal}} \right). \tag{2.14}
\]

It is often convenient to consider gravimetric storage capacity in terms of porosity instead of system density. Porosity is defined to be the ratio of open pore volume to the volume of the entire system

\[
\phi_{system} \equiv \frac{V_{pores}}{V_{system}} = \frac{V_{pores}}{V_{pores} + V_{skeletal}}. \tag{2.15}
\]

where

\[
V_{pores} \equiv V_{system} - V_{skeletal}. \tag{2.16}
\]

is the total volume available to the gas\(^3\). Eq. (2.14) may be rewritten in terms of porosity.

\(^2\) Note that choosing the skeletal volume as the system volume is an inappropriate selection as it does not contain any gas.

\(^3\) Note that choosing the system volume to be the skeletal volume gives a porosity of zero.
Volumetric storage capacity

Volumetric storage capacity is the total amount of gas in the system normalized to the volume of the system $V_{\text{system}}$. Because the total mass of gas stored is the same as the gravimetric storage capacity, one needs to multiply gravimetric storage capacity by the density of the system to convert to volumetric storage capacity.

\[
\frac{m_{\text{st}}}{m_s} = \frac{m_{\text{exc}}}{m_s} + \frac{\rho_{\text{gas}} (p, T)}{\rho_{\text{skeletal}}} \left( \frac{V_{\text{skeletal}}}{\phi_{\text{system}} - 1} \right)
\]

\[
\frac{m_{\text{st}}}{m_s} = \frac{m_{\text{exc}}}{m_s} + \frac{\rho_{\text{gas}} (p, T)}{\rho_{\text{skeletal}}} \left( \frac{1}{\phi_{\text{system}} - 1} \right)^{-1}
\]

\[\text{(2.19)}\]

Experimentally, it is often easier to determine the porosity than the system density. The system density may be rewritten in terms of the porosity using Eqs. (2.16) and (2.17).

\[
V_{\text{system}} = V_{\text{skeletal}} + V_{\text{pores}}
\]

\[
V_{\text{system}} = V_{\text{skeletal}} + \frac{V_{\text{skeletal}}}{\phi_{\text{system}} - 1} \Rightarrow V_{\text{system}} = V_{\text{skeletal}} \left( \frac{1}{1 - \phi_{\text{system}}} \right)
\]

\[
\rho_{\text{system}} = \rho_{\text{skeletal}} (1 - \phi_{\text{system}})
\]

\[\text{(2.20)}\]

Substitution Eq. (2.20) into Eq. (2.19), we arrive at the final result

\[
\frac{m_{\text{st}}}{V_{\text{system}}} = \frac{m_{\text{st}}}{m_s} \rho_{\text{skeletal}} (1 - \phi_{\text{system}})
\]

\[\text{(2.21)}\]

\[\text{Note that if the system consists of only the skeletal volume, then } \phi_{\text{system}} = 0 \text{ (cf. Footnote 3) and we arrive at the trivial result } \rho_{\text{skeletal}} = \rho_{\text{skeletal}}.\]
Gravimetric absolute adsorption

To calculate gravimetric absolute adsorption, it is necessary to know the volume that the adsorbed gas occupies. However, the task of determining this experimentally is not simple.

Gravimetric absolute adsorption is proportional to the surface coverage and is given by

\[ \frac{m_{\text{abs}}}{m_s} = \frac{\sum M_{\text{gas}}}{\alpha(T)N_A} \Theta(p, T) \]  

(2.22)

where \( \Sigma \) is the specific surface area \((\text{m}^2/\text{g})\), \( \alpha(T) \) is the area per adsorption site \((\text{m}^2/\text{site})\), \( \Theta(p, T) \) is the surface coverage \(\text{(number adsorbed per number of adsorption sites)}\), \( N_A \) is Avogadro’s number, and \( M_{\text{gas}} \) is the molar mass of the adsorbing gas.

From inspection of Fig. 2.1, excess adsorption may be derived from Eq. (2.22) by subtracting the amount of gas present in the adsorbed film, if it were at the gas density far away from the surface. In other words

\[ \frac{m_{\text{exc}}}{m_s} = \frac{m_{\text{abs}}}{m_s} - \rho_{\text{gas}}(p, T)V_{\text{film}} \]

\[ \frac{m_{\text{exc}}}{m_s} = \frac{\sum M_{\text{gas}}}{\alpha(T)N_A} \Theta(p, T) - \rho_{\text{gas}}(p, T)V_{\text{film}} \]  

(2.23)

where \( V_{\text{film}} \) is the specific film volume \(\text{(SFV)}\) \((\text{cm}^3/\text{g})\). For supercritical gases, monolayer saturation occurs at high pressures. If one takes the case \( \lim_{p \to \infty} m_{\text{exc}}/m_s \Theta(p, T) = 1 \) and

\[ \frac{m_{\text{exc}}}{m_s} = \frac{\sum M_{\text{gas}}}{\alpha(T)N_A} - \rho_{\text{gas}}(p, T)V_{\text{film}} \]  

(2.24)
It is apparent from Eq. (2.24) that, at monolayer saturation, excess adsorption is a linear function of gas density whose slope is the SFV.

It would be convenient to use Eq. (2.24) to calculate SFVs for all samples using low temperature data. However, the linear region does not occur over a sufficient range of densities for all samples. For the purpose of this study, Eq. (2.24) was used to calculate a SFV for one sample, and it was then assumed that $V_{\text{film}} = \Sigma_{\text{BET}} t_{\text{film}}$ to calculate a characteristic film thickness $t_{\text{film}}$ using the BET surface area $\Sigma_{\text{BET}}$. Using this method, a film thickness of 5.7 Å was found (cf. Fig 2.4).

![Graph showing the linear fit to excess adsorption at high gas density.](image)

**Figure 2.4.** Graph showing the linear fit to excess adsorption at high gas density.
2.3 The Differential Enthalpy of Adsorption

Adsorption isotherms measured at different temperatures may be used to calculate the differential enthalpy of adsorption as a function of surface coverage using the Clausius-Clapeyron equation

\[
\Delta_{\text{ads}}H(\theta) = \frac{RT_1 T_2}{T_2 - T_1} \ln \left( \frac{p_2(T_2, \theta)}{p_1(T_1, \theta)} \right)
\]  

(2.25)

where \( p_1 \) and \( p_2 \) and \( T_1 \) and \( T_2 \) and the pressures and temperatures of the measured isotherms and \( R \) is the gas constant [22]. The differential enthalpy of adsorption is inherently negative. The magnitude of the adsorption enthalpy is referred to as the isosteric heat of adsorption.

Because the differential enthalpy of adsorption is a function of coverage, excess adsorption isotherms must be converted to absolute adsorption before the calculation may be performed. Calculation of the adsorption enthalpy from excess adsorption yields an unphysical rise in the adsorption enthalpy at high surface coverage (cf. Fig. 2.5).

Adsorption enthalpies were determined experimentally by measuring two excess adsorption isotherms and 273 K and 303 K. These isotherms were then converted to gravimetric absolute adsorption as described in Sec. 2.2. Because the two isotherms do not contain data points that are at the same gravimetric absolute adsorption, the 303 K isotherm was interpolated and this interpolated isotherm was used together with the 273 K isotherm data to calculate the adsorption enthalpy using Eq. (2.25). Six models were considered for data interpolation:
Linear Interpolation:
The 303 K isotherm was linearly interpolated and only 303 K data points that were with 0.1 g/kg to a corresponding 273 K data point were used.

Langmuir [23]:
The constant $b$ is the $\chi(T)$ as used for mobile or localized adsorption (cf. Sec. 2.1) and the constant $\alpha$ is a scaling factor.

\[
\frac{m_{abs}}{m_s} = \frac{\alpha bp}{1 + bp}
\]

The Redlich-Peterson Isotherm [26]:
$\alpha$, $b$, and $c$ are empirical constants. This model satisfies Henry’s Law (cf. Chapter 7).

\[
\frac{m_{abs}}{m_s} = \frac{\alpha p}{1 + bp^c}
\]

Modified Redlich-Peterson Isotherm:
$\alpha$, $b$, and $c$ are empirical constants. This model does not satisfy Henry’s Law and has no real physical significance.

Freundlich Equation [27]:
This is equation is known to be a poor fit for activated carbons at high pressures or low temperatures [22]. It is included for comparison only. $\alpha$ and $b$ are empirical constants.

\[
\frac{m_{abs}}{m_s} = \alpha p^{1/b}
\]

Ono-Kondo Model [28]:
This is the mono-layer Ono-Kondo model. It is the only model based on excess adsorption. The constant $b$ is the adsorbed film saturation pressure (i.e. the pressure at which $m_{exc}/m_s = 0$). The constant $c$ is the binding energy of the gas-solid interaction (cf. $U_{06}$ Sec. 2.1) and the constant $\alpha$ is a scaling factor. All constants were determined empirically.
Each isotherm model was fit to a characteristic activated carbon, sample 3K\textsuperscript{5}. The specific fitting parameters for 3K are shown in Table 2.2. There was a correlation between the reduced $\chi^2$ values and the closeness of each calculated adsorption enthalpy to the linear interpolation (cf. Fig. 2.6). Although all of the fits appear to be reasonable, the calculated adsorption enthalpies differ greatly at low values of absolute adsorption. Inspection of Eq. (2.25) reveals the ultimate reason for this discrepancy.

At low values of absolute adsorption, the pressures $p_1$ and $p_2$ are very near one another such that $p_2/p_1 \sim 1$. Since $\Delta_{\text{mic}}H$ depends on $\ln (p_2/p_1)$, any small change in either pressure results in a large change in enthalpy. Conversely, at high values of absolute adsorption, the pressures $p_1$ and $p_2$ differ greatly such that $p_2/p_1 \gg 1$. In this

\textsuperscript{5} For information regarding the genesis of sample 3K, see Chapter 5.

**Figure 2.5.** The enthalpy of adsorption as a function of gravimetric absolute adsorption for sample 3K calculated using different adsorbed film thicknesses. Isobars indicate the pressures of the 273 K isotherm. $t_{\text{film}} = 6.3 \ \text{Å}$ is equivalent to assuming the adsorbed film and open pore volumes are equal.
limit, small changes in $p_1$ or $p_2$ will not result in and large change in $\Delta_{sub} H$. As can be seen in Fig. 2.7, models which do not fit the data at low pressures tend to give enthalpies that are higher than the linear interpolation.

**Table 2.2.** Fitting parameters for different isotherm models. These fitting parameters were used to calculate the adsorption enthalpies shown in Fig. 2.5.

<table>
<thead>
<tr>
<th>Fitting Parameter</th>
<th>Langmuir</th>
<th>Redlich-Peterson</th>
<th>Modified Redlich-Peterson</th>
<th>Freundlich</th>
<th>Ono-Kondo</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>102.5</td>
<td>0.243</td>
<td>119.6</td>
<td>0.427</td>
<td>51.3</td>
</tr>
<tr>
<td>b</td>
<td>0.00225</td>
<td>0.00672</td>
<td>0.00176</td>
<td>0.817</td>
<td>3.06 x 10^6</td>
</tr>
<tr>
<td>c</td>
<td>---</td>
<td>0.823</td>
<td>0.0334</td>
<td>---</td>
<td>-2680</td>
</tr>
<tr>
<td>Reduced $\chi^2$</td>
<td>4x10^-3</td>
<td>3 x 10^-4</td>
<td>1 x 10^-4</td>
<td>0.09</td>
<td>4 x 10^-3</td>
</tr>
</tbody>
</table>

No one model investigated can completely describe the adsorption of any of the activated carbon samples presented in later chapters. With the exception of the Freundlich equation, all of the models also fit the data reasonably well. The difference in the calculated enthalpies result from the natural logarithm of the ratio of the pressures as described above. Because of this, we take the measured enthalpy of adsorption to be an average of all of the fitting models (Freundlich excluded) with an uncertainty describing the variance in the enthalpies calculated using all of the models. An additional uncertainty of 0.2 kJ/mol has also been added to account for uncertainties in the adsorbed film thickness (cf. Fig. 2.6)
Figure 2.6. Graph of adsorption enthalpies using several models.

Figure 2.7. Log-Log plot showing the fits to absolute adsorption.
Chapter 3 – Isotherm Measurement History, Techniques, and Sources of Uncertainty

Absolute adsorption and storage capacity are derived from the excess adsorption measurement using assumptions about the pore volume, adsorbed film thickness, or surface geometry (cf. Sec. 2.2). Because of this, the only way to improve the accuracy of absolute adsorption or storage capacity is to improve the accuracy of excess adsorption measurements.

There are three main methods for determining excess adsorption: thermal desorption spectroscopy, gravimetry, and manometry (also known as volumetry). Here we outline the basic principles and sources of uncertainty of the three methods and provide a comparison of adsorption measurements taken in different laboratories. For monometry in particular, we show methods for reducing the uncertainty.

3.1 Methods of Measurement

Thermal desorption spectroscopy

The use of spectroscopy to study gas adsorption has been employed as early as 1960 [29]. In the modern sense, thermal desorption spectroscopy (TDS), also known as temperature programmed desorption (TPD), involves the heating of an adsorbent at a specified rate and using a mass spectrometer [30,31], mass flow meter [32], or pressure transducer [33] to measure the amount of gas removed from the surface as a function of temperature (cf. Fig. 3.1). The use of a quadrupole or time-of-flight mass spectrometer is particularly useful because it allows individual gas species to be counted separately. TDS
therefore allows for a variety of uses other than hydrogen gas analysis such as investigating the effectiveness of outgassing procedures or determining the gas separating efficiency of molecular sieves.

While TDS can provide information about desorption kinetics, it is not particularly useful for adsorbents. TDS requires a non-adsorbing carrier gas to transport desorbed hydrogen from the sample to the mass spectrometer. For adsorbants, the gas kinetics are simply too fast at temperatures above 80 K to allow for any measurement (cf. Fig. 3.1) [34,35]. Because of the gas kinetics, TDS is not used to analyze our materials.

Gravimetry

In 1921, Bakr and King published the designs and initial results for a gravimetric method for determining the “reverse” adsorption of solvents on solid materials [36]. Five years later with an improved design, McBain and Bakr employed the first entirely self-
contained, spring-based microbalance for measuring adsorption of solvents on activated carbons [37]. This new design (cf. Figs. 3.2(a) and 3.2(b)) became the earliest ancestor of today’s commercially available gravimetric adsorption analyzers.

While the basic method of determining adsorption has not changed since McBain and Bakr’s second design, early instruments did not contain balances accurate enough to measure small molecules such as hydrogen. Advances in the design of microbalance in the last 85 years have eventually made this possible (cf. Figs. 3.2(c) and 3.2(d)).

Gravimetric adsorption instruments measure excess adsorption by making three mass measurements [38]. For the first measurement, the system is evacuated and the mass of the sample and sample holder $m_0$ is measured. The system is then pressurized with helium or other non-adsorbing gas and the mass $m_1$ is measured. This mass corresponds to

$$m_1 = m_0 - \rho_{\text{He}} V_0$$

where the helium density $\rho_{\text{He}}$ times the volume of the sample and sample holder $V_0$ represents the buoyant force on the sample. The helium is removed by outgassing and the sample chamber is pressurized with a gas. Once thermal equilibrium is reached, the final mass measurement $m_2$ is taken

$$m_2 = m_0 + m_{\text{abs}} - \rho_{\text{gas}} (V_0 + V_{\text{film}})$$

Again, the product of the gas density $\rho_{\text{gas}}$ with the volume of the sample and sample holder $V_0$ represents the buoyant force on the sample. The product of the gas density and adsorbed film volume $V_{\text{film}}$ represents the buoyant force attributed to the

---

6 Di Giovanni et al. incorrectly define excess adsorption as $m_{\text{exc}} = m_{\text{abs}} - \rho_{\text{gas}} V_0$, but their method is ultimately correct.
adsorbed film [38,39]. Combining Eqs. (3.1) and (3.2) and using the basic definition for excess adsorption \( m_{\text{exc}} = m_{\text{abs}} - \rho_{\text{gas}} V_{\text{film}} \), the gravimetric excess adsorption for a gravimetric measurement is given by

\[
\frac{m_{\text{exc}}}{m_s} = \frac{1}{m_s} \left[ m_2 - m_0 + \frac{\rho_{\text{gas}}}{\rho_{\text{He}}} (m_0 - m_1) \right].
\]  

(3.3)

Additional data points are measured by increasing or decreasing the gas pressure and recalculating Eq. (3.3) using a new measurement for \( m_2 \).

An alternative method for gravimetry was described by Burress that was used to measure methane adsorption [40]. Because hydrogen has a much smaller mass compared to methane \( m_{\text{CH}_4} \approx 16 m_{\text{H}_2} \), this method is not applicable to hydrogen.

Manometry

Volumetric methods for determining excess adsorption have been used for more than 80 years [41]. True volumetric measurements are often referred to as “BET volumetric” measurements because it was the type of measurement used by Emmitt and Brunauer [22]. Their original setup used a mercury burette to measure volume changes. Current instruments have replaced Emmitt and Brunauer’s measurement of volume changes for a measurement of pressure change called Sieverts’ method, named for German chemist Adolf Sierverts [41]. Though Sieverts’ method is technically manometric, because pressure changes are measured, the volumetric label is still used colloquially.
Figure 3.2. A picture (a) and diagram (b) of a gravimetric instrument c. 1948 based on McBain and Bakr's design used to study the adsorption of solvents [42]. Diagram of hydrogen gravimetric sorption instruments from 1967 (c) [43] and 2006 (d) [44].

The Sieverts’ type instrument consists of two known volumes, referred to here as the dosing volume $V_d$ and reactor volume $V_r$, separated by a valve (cf. Fig. 3.3). Initially,
the entire system is outgassed. The dosing volume is pressurized with an adsorptive gas and is allowed to equilibrate. The temperature and pressure is measured and the mass density $\rho_{11}$ is calculated using an appropriate equation of state. Here, the first subscript indicates the step in the procedure and the second indicates the data point in the isotherm. Once equilibrium has been reached, the valve separating the dosing volume and reactor volume is opened and the gas is allowed to expand freely. Again, equilibrium is reached and the gas density $\rho_{21}$ is calculated based on pressure and temperature measurements.

The excess adsorption is given by

$$m_{\text{exc}} = \rho_{11} V_d - \rho_{21} (V_d + V_r - V_s)$$

where $V_s$ is the sample skeletal volume which may be determined using a non-adsorbing gas or a known skeletal density. If two or more data points are to be measured, the valve is closed and a third density $\rho_{31}$ is determined. This third measurement is used to determine how much gas remains in the reactor volume $m'_1$ at the end of the measurement

$$m'_1 = \rho_{11} V_d - \rho_{31} V_d$$

and is necessary to avoid double counting of gas molecules.

The process is repeated for as many data points as are required. The excess adsorption for all data points is calculated by taking the total amount of gas that has been added into the system during measurement of the isotherm minus the amount of that would be present if there was no adsorption. In general for the $k^{th}$ data point, the excess adsorption will be given by

$$m_{\text{exc}} = \sum_{i=1}^{k} \left[ \rho_{1i} V_d - \rho_{2i} (V_d + V_r - V_s) + \rho_{2(i-1)} (V_d + V_r - V_s) - \rho_{3(i-1)} V_d \right]$$

and finally the gravimetric excess adsorption is
One immediate consequence of Eq. (3.5) is that every data point in an isotherm depends on all previous data points. This does result in an accumulation of uncertainties. However, uncertainties do not strictly add from data point to data point. For example, if the total uncertainty when measuring \( \rho_1 \), \( \rho_2 \), and \( \rho_3 \) is one percent, then the uncertainty for the 2\(^{nd} \) data point is not 2\% nor is the 3\(^{rd} \) data point 3\% etc. The uncertainties do not strictly add from data point to data point because all of the terms with \( \rho_2 \), cancel from the previous data points. Additionally, because this is the only term with the sample temperature, thermal fluctuations in the sample do not propagate errors to later data points.

\[
\frac{m_{\text{exc}}}{m_a} = \frac{1}{m_a} \sum_{i=1}^{k} \left[ \rho_{1i} V_d - \rho_{2i} (V_d + V_r - V_s) + \rho_{2(i-1)} (V_d + V_r - V_s) - \rho_{3(i-1)} V_d \right] \tag{3.5}
\]

Figure 3.3. Adolf Sieverts’ original setup from 1929 [41]. English translations are shown in parenthesis.
3.2. Sources of uncertainty

Removing sources of uncertainty is essential to measuring hydrogen adsorption isotherms accurately. Improper considerations can lead to unrealistic results. A perfect example is from initial reports that claimed 10 wt% hydrogen storage on carbon nanotubes [45] and other reports of 67 wt% on graphite nanofibers [46].

Gas purity

Gravimetric measurements are particularly susceptible to the effects of gas purity because any adsorbed molecule is measured indiscriminately and heavy molecules will lead to a higher observed gravimetric excess adsorption (Table 3.1). The effect on volumetric measurements is more difficult to quantify. It depends greatly on the adsorption properties of the trace gases in the mixture. Using a higher purity source is the easiest way to eliminate gas purity issues. The International Union of Pure and Applied Chemistry (IUPAC) recommends a 99.9% purity for nitrogen measurements [39]. At least 99.999% purity should be used for hydrogen measurements [47].
Table 3.1. The effect of gas purity on a gravimetric hydrogen adsorption experiment. It is assumed in these calculations that the gas mixture consists of the indicated percentage of hydrogen and the remainder is atmosphere. Percent difference indicates difference from the real gravimetric excess adsorption.

<table>
<thead>
<tr>
<th>Hydrogen Gas Purity</th>
<th>Observed Gravimetric Excess Adsorption (g/kg)</th>
<th>Percent Difference from 100% Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>99.9999</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>99.999</td>
<td>1.00</td>
<td>0.03</td>
</tr>
<tr>
<td>99.99</td>
<td>1.00</td>
<td>0.28</td>
</tr>
<tr>
<td>99.9</td>
<td>1.03</td>
<td>2.77</td>
</tr>
<tr>
<td>99.0</td>
<td>1.28</td>
<td>27.74</td>
</tr>
<tr>
<td>98.0</td>
<td>1.55</td>
<td>55.48</td>
</tr>
<tr>
<td>97.0</td>
<td>1.83</td>
<td>83.22</td>
</tr>
<tr>
<td>96.0</td>
<td>2.11</td>
<td>110.96</td>
</tr>
</tbody>
</table>

Sample mass

Properly determining the sample mass is crucial to making an accurate adsorption measurement. To measure the sample mass, the sample must be outgassed at an elevated temperature to remove any adsorbed gases, particularly water. We have observed differences between the mass before and after high temperature outgassing, the wet and dry-mass, respectively, as high as twenty percent.

Recall the equations for gravimetric excess for manometric methods (Eq. 3.5). For manometric measurements, the sample mass is only used when normalizing the measured adsorption. In this case, using the wet-mass will result in an observed value that is lower than the true excess adsorption value. The sample mass may also be used to calculate the sample volume using a known density. If the sample volume is calculated from a known density \( V_s = m_s/\rho_{\text{skeletal}} \), this will actually slightly increase the gravimetric excess adsorption compared to the wet-mass with a measured skeletal density (cf. Fig. 3.4). This increase is apparent from Eq. (3.5) because the product of the sample
volume and the density $\rho_2$, is added for each data point. The difference in the two isotherms is more apparent at high pressures because of this product $\rho_2 V_e$.

**Figure 3.4.** The effect of using a wet-mass that is 20% higher than the dry mass using both a calculated and measured skeletal density. The measured skeletal density isotherm uses the dry-mass and a skeletal density of 2.0 g/cm$^3$ when calculating the skeletal volume.

**Equation of state**

Manometric measurements are completely dependent on the proper measurement of system volumes and determination of gas density as is clearly apparent in Eq. (3.5). We first consider the effect of the equation of state (EOS) used to calculate the densities. The densities may be derived from actual density data such as experiments performed by Leachman *et al.* [48] or an EOS such as the ideal gas law, van der Waals EOS, or virial expansion.

Another alternative is to calculate a compressibility factor based on actual density data. The compressibility factor is given by
\[ Z \equiv \frac{PV}{nRT} \]
such that

\[ \rho_{\text{gas}}(p, T) = \frac{p}{ZRT}. \]  

The compressibility factor may also be written in terms of the virial coefficients

\[ Z = 1 + B_2(T)\rho + B_3(T)\rho^2 + \cdots. \]  

Fig. 3.5 shows the difference between isotherms calculated using the ideal gas law and the compressibility factor derived from experimental density data. As expected, the isotherms only overlap at low pressures where hydrogen-hydrogen interactions are negligible.

Figure 3.5. Comparison of isotherms calculated using different equations of state. The ideal gas law, van der Waals equation of state, and a compressibility factor derived from experimental density data at 77 K (left) and 303 K (right).

### 3.3 Volume Calibration and Background Subtraction

Volume calibration for a manometric system is generally performed by making two measurements without an adsorbing sample. The first measurement consists of
taking individual, independent data points without a sample. It is important that the
dosing volume and the reactor volume are at the same temperature to avoid thermal
gradients in the system. Using conservation of particle number, this measurement gives
the equation

\[ \rho_{d1} V_d = \rho_{d1} (V_d + V_r + V_v) \] (3.7)

where \( \rho_{d1} \) and \( \rho_{d1} \) is the gas density before and after the valve separating the reactor and
dosing volumes is opened, and \( V_v \) is the volume displace by the valve when it is closed
(cf. Fig. 3.7).

The second measurement is identical to the first, except that a non-adsorbing
sample of known volume \( V_{\text{dis}} \) is placed in the reactor. This gives a second equation

\[ \rho_{d2} V_d = \rho_{d2} (V_d + V_r + V_v - V_{\text{dis}}) \] (3.8)

Solving Eqs. (3.7) and (3.8) for the dosing and reactor volumes gives

\[ V_d = \frac{\rho_{d1} \rho_{d2}}{\rho_{d2} \rho_{d1} - \rho_{d1} \rho_{d2}} V_{\text{dis}} \] (3.9)

\[ V_d = \frac{\rho_{d2} (\rho_{d1} - \rho_{d1}) V_{\text{dis}} - V_v}{\rho_{d1} \rho_{d2} - \rho_{d2} \rho_{d1}} \] (3.10)

The valve volume may then be found empirically by taking a third measurement,
generally a blank isotherm (one with no sample).

To test for the quality of a volume calibration, a blank isotherm is measured at
room temperature. An example of a blank isotherm measured for an HTP-1 Volumetric
Analyser (cf. Sec. 4.2) is shown in Fig. 3.6. For these instruments, the manufacturer
considers any value at or below 100 \( \mu \text{mol} \) to be a good calibration [34]. The decrease in
the blank isotherm at high pressures is thought to be caused by non-linearity in the pressure transducer [34].

![Graph of a blank isotherm at 303 K.](image)

**Figure 3.6.** Graph of a blank isotherm at 303 K. The maximum deviation from zero excess adsorption is one fifth the value recommended by the manufacturer.

**Thermal gradients**

If an isotherm is to be measured at a temperature other than room temperature, Eq. (3.5) must be modified to account for thermal gradients within the reactor volume. To accomplish this, we introduce the volume fraction \( f \). The purpose of the volume fraction \( 0 \leq f \leq 1 \) is to divide the reactor into two volumes, one assumed to be at the same temperature as the dosing volume and the other at the sample temperature. The volume fraction is determined empirically at each temperature by measuring blank isotherms and adjusting \( f \) until the total excess adsorption is as close to zero as possible. The warm reactor volume is now given by \( V_t(1 - f) \) and the cold reactor volume is given
by $V_r f$. Including the volume fraction in Eq. (3.5), the final working equation for calculating the excess adsorption for the $i^{th}$ data point is given by

$$\frac{m_{\text{exc}}}{m_s} = \frac{1}{m_s} \sum_{i=1}^{k} \left[ \rho \left( p_{v1}, T_{11i} \right) V_d - \rho \left( p_{v2}, T_{21i} \right) (V_d + V_v + V_r (1 - f)) - \rho \left( p_{v2}, T_{22i} \right) (V_r f - V_s - V_v) + \rho \left( p_{v2(i-1)}, T_{21(i-1)} \right) (V_d + V_v + V_r (1 - f)) + \rho \left( p_{v2(i-1)}, T_{21(i-1)} \right) (V_r f - V_s - V_v) - \rho \left( p_{v3(k-1)}, T_{31(k-1)} \right) V_d \right]. \quad (3.11)$$

It is important to note that if the volume fraction is zero (no thermal gradient), then Eq. (3.11) reduces to Eq. (3.5). In fact, if the reactor and dosing volumes are at the same temperature, any value of $f$ will yield the same results. An example of a blank hydrogen isotherms measured at 80 K calculated with different volume fractions is shown in Fig. 3.8.

**Figure 3.7.** Schematic representation of the volumes associated with manometric instruments.
Even with choosing a proper volume fraction, the gravimetric excess adsorption will still behave abnormally at high pressures (cf. Fig. 3.9) due to the steep rise in the blank isotherm at high pressures. To remove this unphysical rise in the gravimetric excess adsorption $m_{\text{exc}}/m_s$, the blank isotherm $m_{\text{exc}}^0$ must be subtracted from the measured isotherm (cf. Fig. 3.10)

$$\frac{m_{\text{exc}}'}{m_s} = \frac{m_{\text{exc}}}{m_s} - \frac{m_{\text{exc}}^0}{m_s}. \tag{3.12}$$

From Eq. (3.12), it is clear the contribution of the blank isotherm to the observed excess adsorption is dependent upon the mass of sample used. The greater the sample mass, the less of a contribution from the blank isotherm.

One unexpected consequence of blank isotherm subtraction is the effect on the thermal gradient. As is shown if Fig. 3.11, if the blank isotherm is subtracted, the choice of the volume fraction becomes essentially arbitrary. So long as both the blank isotherm and the original data were calculated using the same volume fraction, the resulting subtracted isotherm will be the same well within the uncertainty of the measurement.
Figure 3.9. 80 K isotherm calculated using various volume fractions. (left) An example of data with the correct volume fraction and (right) an example of data calculated with varying volume fractions.

Figure 3.10. Demonstration of blank isotherm subtraction. For this example, 0.098 g of sample was used.

Figure 3.11. The subtracted isotherm’s dependence on the volume fraction. (left) A graph showing the difference between a rough blank subtraction (one for which the blank isotherm data points are simply used) compared to a blank subtraction in which a polynomial fit to the blank isotherm was used. (right) Different subtracted isotherms calculated with varying volume fractions.
3.4 Round Robin Results

Round robin studies such as those done by Zlotea et al. show that hydrogen adsorption measurements can vary from lab to lab for reasons outlined in the previous sections [49]. Fig. 3.12 shows a typical range of values from such an experiment. It is generally considered good agreement if two isotherms measured in different labs are within 10% of one another.

![Graph showing hydrogen adsorption measurements at 77 K and ambient temperature.](image)

**Figure 3.12.** Results from a blind test conducted by Zlotea et al. in 2009 [49]. Measurements of an unknown activated carbon sample were performed at 77 K (left) and 303 K (right) at various labs.

To test the calibration of our manometric instrument, we measured a commercially available activated carbon sample, MSC-30 manufactured by Kansai Coke and Chemicals Co. Ltd. (Amagasaki, Japan). We then compared our measurements to values in the literature. The results are shown in Fig. 3.13 and agreement at both 77 K and 303 K is well within 10%.
Figure 3.13. Comparison of hydrogen adsorption measurements performed at different labs at (a) 77 K and (b) 303 K [17,50-52].
Chapter 4 – Experimental Methods

4.1 Dry-mass Determination

As discussed in Sec. 3.2, it is critical to correctly determine the dry sample mass before measurement of a hydrogen isotherm. The sample mass was determined using the following procedure:

1. The sample cell (with glass wool) was placed in an empty steel pressure vessel. The steel vessel was outgassed at room temperature to approximately 0.1 mbar.
2. The steel vessel was sealed under vacuum and the mass of the cell \( m_c \) was measured using a Metler-Toledo PB503-S mass balance accurate to 1 mg.
3. The sample cell was removed from the steel vessel and sample was added to the sample cell.
4. The steel vessel was outgassed at room temperature to approximately 0.1 mbar to minimize the amount of oxygen in the vessel prior to heating.
5. The steel vessel was outgassed continuously for two hours at 400 °C.
6. The steel vessel was allowed to cool to room temperature and was then sealed under vacuum.
7. The mass of the sample and the cell \( m_{c,s} \) was measured using the mass balance in number two above.

The sample mass was given by \( m_s = m_{c,s} - m_c \). This sample mass was used for all subsequent calculations of the sample volume, sample densities, and excess adsorption.

The uncertainty in the sample volume of the sample was given by

\[
\delta V_s = \left( \frac{0.002 \ [g]}{m_s} + \frac{0.2 \ [g/cm^3]}{2.0 \ [g/cm^3]} \right) V_c
\]

For a typical sample mass of 100 mg, the sample volume was 0.050 ± 0.007 cm³. For samples in which 300 mg was used, the sample volume was 0.15 ± 0.02 cm³.
4.2 Measurement of Excess Adsorption

The hydrogen gravimetric excess adsorption isotherms (excess adsorption) were measured using the HTP-1 Volumetric Analyser manufacture by Hiden Isochema, Warrington, UK. The HTP-1 is an amanometric instrument capable of measuring hydrogen isotherms at pressures ranging from 0.001 mbar to 1 bar using a set of two low-pressure Baratron capacitance manometers and from 1 bar to 200 bar using a 200 bar Baratron manometer. The system consisted of a dosing volume $V_d$ and a reactor volume $V_r$, which contained the sample, separated by a pneumatic valve whose diaphragm displaced a volume $V_v$ when closed. The dosing and pneumatic valve volumes were contained within a temperature controlled cabinet that was maintained at 30.0 ± 0.1 °C. The reactor volume was partially contained in this cabinet and the remainder was exposed to the lab environment. The sample temperature was controlled using a combination of a heating element and a continuous flow of liquid nitrogen. This combination allowed for measurement of isotherms at any temperature between 77 K and 773 K. The cabinet or dosing volume temperature was measured using two platinum resistance thermometers (PRTs) surrounding the dosing volume. The sample or reactor volume temperature was measured using a k-type thermocouple inserted directly into the sample.

For each measurement, glass wool was used to prevent elutriation of the sample into the instrument. The volume of this glass wool $V_g$ was determined using high pressure hydrogen pycnometry at 30 °C. The volume was determined using Eq. (3.5), assuming that glass wool did not adsorb hydrogen, i.e. $m_{\text{exc}} / m_s = 0$. 


After the sample mass was determined (cf. Sec. 4.1), the sample was loaded into the reactor. Before every isotherm was measured, the sample was outgassed at 200 °C for 2 hours using the built-in Pfeiffer Vacuum turbomolecular pump to a pressure of approximately $10^{-6}$ mbar. Once outgassed, the isotherm was measured according to the procedure for Sievert’s method outlined in Sec. 3.1.

### 4.3 Nitrogen Adsorption Measurements: Surface Area and Pore Volume

Specific surface areas (SSA) and pore size distributions (PSD) of all carbon samples were determined from nitrogen adsorption at subcritical conditions. The measurements were performed using the Autosorb-1-C (Quantachrome Instruments, Boynton Beach, FL USA). Specific surface areas were determined using the Brunauer-Emett-Teller (BET) theory [22] in the pressure range of 0.01 – 0.03 $P/P_0$, where $P_0$ is the saturation pressure of nitrogen at the experimental temperature (77 K). The open pore volume was determined at a relative pressure of 0.995 $P/P_0$ assuming that nitrogen has condensed in the pores at this pressure. The porosity was calculated using the open pore volume using Eq. (2.20). A skeletal density of 2.0 g/cm$^3$ was used.

The quenched solid density function theory (QSDFT) data reduction software, provided by Quantachrome [53], was used for all PSD calculations. QSDFT is a modified version of the non-local density functional theory (NLDFT) that takes into consideration the influence of surface roughness and heterogeneity on the adsorption mechanism [54,55], making it suitable for activated carbons.
Chapter 5 - Undoped Activated Carbons

5.1 Materials Synthesis and Naming Conventions

Nanoporous carbons were fabricated by a controlled pyrolysis of ground corncob using a proprietary multistep method [56]. All samples under consideration were prepared in granular form.

For each sample, a mixture of ground corncob and phosphoric acid (H₃PO₄) was pyrolyzed at 490 °C for several hours. Once pyrolyzed, the remaining material, known as carbon char, was washed and then mixed with potassium hydroxide (KOH). The KOH and char mixture was heated under nitrogen in a stainless steel reaction vessel at an elevated temperature (≥ 700 °C) for several hours. This is known as the activation step. Once, activated, the carbon was washed with water and dried.

Otawa et al. [57] described the activation process by the following reactions. Below 700 °C, the main products are hydrogen (H₂), water (H₂O), carbon monoxide (CO), carbon dioxide (CO₂), potassium oxide (K₂O), and potassium carbonate (K₂CO₃). The dehydration of KOH to K₂O (a) results in carbon consumption through the reaction of CO₂, produced in reactions (b) and (c), with K₂O to form K₂CO₃:

\[
\begin{align*}
2\text{KOH} & \rightarrow \text{K}_2\text{O} + \text{H}_2\text{O} & \text{(a)} \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 & \text{(b)} \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 & \text{(c)} \\
\text{CO}_2 + \text{K}_2\text{O} & \rightarrow \text{K}_2\text{CO}_3 & \text{(d)}
\end{align*}
\]
Above 700 °C, however, an important activation mechanism occurs alongside the formation of metallic potassium. This mechanism, described in (e) and (f), is directly related to the formation of sub-nanometer pores:

\[
\begin{align*}
K_2O + H_2 & \rightarrow 2K + H_2O \\
K_2O + C & \rightarrow 2K + CO
\end{align*}
\]  

(e) 
(f)

In this work, charred carbon is activated above 700 °C, where metallic potassium penetrates between graphitic layers. The removal of intercalated potassium results in the expansion of the pore structure [58].

**Naming conventions**

Samples were named based on the method of activation. The first half of a sample name indicates the mass ratio of KOH to carbon used. For instance, a ratio of 3:1 KOH:C was known as 3K. A ratio of 4:1 KOH:C was known as 4K, etc. The second half of the sample name indicates the temperature of activation. If a sample 3K was activated at 900 °C, its full name would be 3K 900 °C. If no activation temperature is given in the sample name, the sample was activated at 790 °C.

**5.2 Materials’ Structure Characterization**

A systematic study was carried out to investigate the effect of KOH:C (mass ratio) and activation temperature on the activated carbon structure and hydrogen adsorption characteristics. Structural information was obtained by measuring subcritical nitrogen isotherms as described in Sec. 4.3. Surface area and porosity data for these samples are given in Table 5.1 below. Individual pore size distributions may be found in Appendix 1.
Table 5.1. List of specific surface areas and porosities for KOH activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5K 700 °C</td>
<td>1500</td>
<td>0.58</td>
</tr>
<tr>
<td>2.5K 800 °C</td>
<td>1900</td>
<td>0.69</td>
</tr>
<tr>
<td>2.5K 900 °C</td>
<td>2000</td>
<td>0.70</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
</tr>
</tbody>
</table>

From these data, we may conjecture the following:

1. The porosity increases with increasing activation temperature and KOH:C (Fig. 5.2 Right).
2. The specific surface area increases with increasing activation temperature at low KOH:C and with increasing KOH:C at temperatures higher than 800 °C (Fig. 5.1 Left).
3. The micropore volume (< 20 Å) increases with increasing activation temperature and with increasing KOH:C at low KOH:C (Fig. 5.2 left).
4. The mesopore (> 20 Å, < 50 Å) and nanopore volumes (< 10 Å) increase as both the rate of reaction of potassium carbonate with the carbon char and the initial ratio of KOH to carbon (Fig. 5.2 right and Fig. 5.3).
Figure 5.1. 3D plots of surface area (left) and porosity (right) as a function of activation temperature and KOH:C. Bars with the same color were activated at the same temperature.

Figure 5.2. 3D plot of nanopore volume (< 10 Å) as a function of activation temperature and KOH:C. Bars with the same color were activated at the same temperature.

Figure 5.3. 3D plots of micropore volume (left) and mesopore volume (right) as a function of activation temperature and KOH:C. Bars with the same color were activated at the same temperature.
5.3 Room Temperature (303 K) Hydrogen Data

Now that we have identified the ways to engineer different pore structures, it is necessary to observe how different pore characteristics affect hydrogen storage. We begin here with a room temperature analysis.

Gravimetric excess adsorption isotherms of 2.5K, 3K, 3.5K, 4K, 5K, and 6K at various activation temperatures were measured at room temperature (303 K) with the Hiden HTP-1 Volumetric Analyser. Gravimetric and volumetric storage capacities were calculated as described in Sec. 2.2 using the porosities in Table 5.1. A summary of the room temperature data is given in Table 5.2. Individual isotherms may be found in Appendix 1.

Table 5.2. Summary of gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at room temperature (303 K).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²/g)</th>
<th>Porosity</th>
<th>Room Temp. Grav. Excess Adsorption (100 bar) (g/kg)</th>
<th>Room Temp. Grav. Storage Capacity (100 bar) (g/kg)</th>
<th>Room Temp. Vol. Storage (100 bar) (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 K 800 °C</td>
<td>1900</td>
<td>0.69</td>
<td>5.3</td>
<td>13.2</td>
<td>8.2</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
<td>6.7</td>
<td>13.3</td>
<td>9.3</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
<td>9.3</td>
<td>21.8</td>
<td>9.6</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
<td>7.5</td>
<td>19.4</td>
<td>8.5</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>8.3</td>
<td>20.9</td>
<td>9.2</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
<td>6.0</td>
<td>18.5</td>
<td>8.1</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
<td>6.3</td>
<td>14.6</td>
<td>8.8</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
<td>8.5</td>
<td>19.6</td>
<td>9.8</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>7.5</td>
<td>20.7</td>
<td>9.1</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
<td>5.6</td>
<td>20.6</td>
<td>7.8</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
<td>6.5</td>
<td>21.5</td>
<td>8.2</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
<td>7.7</td>
<td>21.8</td>
<td>8.7</td>
</tr>
</tbody>
</table>
From the graphs in Fig. 5.4 below, we find that gravimetric excess adsorption depends upon the micropore volume and is insensitive to the mesopore volume. This is consistent with a model of adsorption in which, at room temperature, the thermal energy of the hydrogen gas is sufficiently large to prevent the formation of a complete monolayer of gas at pressures lower than 100 bar. We therefore reason that at room temperature only the highest binding energy sites (i.e. those in the narrowest pores where the interaction potential from opposite pores walls constructively overlap) contribute to the adsorption at pressures less than 100 bar.

Additionally, we find that the gravimetric storage capacity increases as both the micro and mesopore volume increases. However, it is clear that the micropore volume plays a more important role than the mesopore volume. While increases in both the micro and mesopore volume will result in additional hydrogen gas in the pores and thus an increase in storage capacity, increases in the mesopore volume will lead to an increase in lower binding energy sites. Increases in micropore volume are not detrimental to volumetric storage capacity because even though the total pore volume increases, the number of adsorbed hydrogen molecules also increases. It follows that increasing the mesopore volume results in a larger pore volume with hydrogen stored only in gas phase and reduces the volumetric storage capacity. In short, increasing the micropore volume is more advantageous to gravimetric and volumetric hydrogen storage at room temperature than increasing the mesopore volume.
Figure 5.4. Graphs showing the effect of micropore volume (< 20 Å) (left) and mesopore volume (> 20 Å, < 50 Å) (right) on gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at room temperature (303 K). The arrows here are a guide to the eye.

Increasing the porosity has no effect on gravimetric excess adsorption, increases the gravimetric storage capacity, and decreases the volumetric storage capacity (Fig. 5.5 left). These results were to be expected. Increasing the porosity has no effect on the number of adsorption sites and therefore should not affect the excess adsorption. However, increasing the porosity does add to the number of hydrogen molecules in the gas phase and should increase the gravimetric storage capacity because more gas molecules are counted without increasing the sample mass. The volumetric storage capacity should decrease because a larger porosity equates to a lower sample density (cf. Eq. (2.20)).

Specific surface area, on the other hand, does affect the gravimetric excess adsorption (Fig. 5.5 right). Increasing the specific surface area results in more adsorption sites per gram of material and an increase in excess adsorption. At very high surface
areas, however, the excess adsorption decreases again. This decrease is attributed to an increase in the surface sites attributed to high diameter pores. We reason that although the surface area is very large, the surface sites have a lower binding energy on average.

**Figure 5.5.** Graphs showing the effect of porosity (left) and specific surface area (right) on gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at room temperature (303 K). The arrows here are a guide to the eye.

From this parametric study, we conclude the following regarding the hydrogen storage at room temperature of KOH-activated carbons:

1. The ideal surface area for these activated carbons is 2600 m$^2$/g.

2. An ideal sample should have a large micropore volume and high porosity due to micropores because the micropore volume is not significantly detrimental to volumetric storage capacity.

While we may use this study to identify experimentally which parameters may be optimized to increase hydrogen storage capacity, we have not developed a material that
can achieve the DOE goals at room temperature. It may be impossible to produce a material with a large micropore volume and high specific surface area using KOH as an activation agent, but we may be able to create the effect of a larger micropore volume by altering the surface chemistry of the material and thereby increasing the binding energy of the adsorption sites. Modification of the surface chemistry is discussed in Chapter 6. Another way to increase the number of adsorbed hydrogen molecules is to decrease the temperature. We now look at cryogenic hydrogen storage and investigate the effect of material properties on hydrogen adsorption at 80 K.

5.4 Cryogenic (80 K) Hydrogen Data

A typical set of adsorption isotherms (excess adsorption, gravimetric storage, and volumetric storage) are shown in Fig. 5.6. One immediate difference between 80 K hydrogen isotherms and those at room temperature is the presence of a maximum in the excess adsorption isotherms. At pressures higher than the pressure at which the maximum occurs $p_{\text{max}}$, the gas density increases faster with pressure than the adsorbed gas density. Because of this maximum, we find it useful to examine the effects of porosity, specific surface area, etc. at three points in the hydrogen isotherms: at 100 bar (where storage is maximum), at $p_{\text{max}}$, and at 10 bar (where the highest binding energy sites are being filled).
Figure 5.6. Gravimetric excess adsorption (left), gravimetric storage capacity (center) and volumetric storage capacity (right) of samples 3K, 4K, 5K, and 6K activated at 790 °C and measured at 80 K.

We find the same trends at 80 K and all three pressures as we did at 303 K as a function of porosity (cf. Fig. 5.7). As the porosity increases, the excess adsorption does not change, the gravimetric storage capacity increases, and the volumetric storage capacity decreases. The same trends also appear in terms of surface area at 80 K as at 303 K (cf. Fig. 5.8). One exception is the storage capacity for the highest surface area measured. For this sample (5K), the storage capacity does not increase compared to lower surface area samples until 100 bar. Also, the volumetric storage capacity decreases with increasing surface area. This is more obvious at 80 K than room temperature because, in general, as surface area increases, so does the porosity. Because the gas density at a given pressure is greater at 80 K than 303 K, it results in a greater loss in volumetric storage at 80 K compared to 303 K.
Figure 5.7. Graphs showing the effect of porosity on gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at 10 bar (left), $P_{\text{MAX}}$ (center), and 100 bar (right) and 80 K. The arrows here are a guide to the eye.

Figure 5.8. Graphs showing the effect of specific surface area on gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at 10 bar (left), $P_{\text{MAX}}$ (center), and 100 bar (right) and 80 K. The arrows here are a guide to the eye.
We also find the same trends in terms of micro (cf. Fig. 5.9) and mesopore volume (cf. Fig. 5.10) at 80 K as were observed at 303 K. Again, the sample with the highest micropore volume is an exception (5K).

**Figure 5.9.** Graphs showing the effect of micropore volume on gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at 10 bar (left), $P_{\text{max}}$ (center), and 100 bar (right) and 80 K. The arrows here are a guide to the eye.

**Figure 5.10.** Graphs showing the effect of mesopore volume on gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at 10 bar (left), $P_{\text{max}}$ (center), and 100 bar (right) and 80 K. The arrows here are a guide to the eye.
As with the measurements at 303 K, we draw the same conclusions at 80 K:

1. The ideal surface area for these activated carbons is 2600 m$^2$/g.
2. An ideal sample should have a large micropore volume and high porosity due to micropores because the micropore volume is not significantly detrimental to volumetric storage capacity.

We have now investigated the effect of activation temperature and KOH:C on hydrogen storage at 80 and 303 K. We have found essentially the same trends for the effect of porosity, specific surface area, micropore volume, and mesopore volume at both temperatures. From an engineering perspective, room temperature storage in these carbons is insufficient to meet the DOE goals and while 80 K is sufficient to exceed the gravimetric storage goals, the additional physical cost system volume and system weight and the monetary cost of maintaining a cryogenic system on-board a real vehicle makes 80 K storage a nonrealistic approach.

To conclude our discussion of activated carbons, we now look at an intermediate temperature that may have success in increasing the storage capacity while not adding a large volume or weight to a potential gas delivery system.

### 5.5 Dry-Ice Temperature (194 K) Hydrogen Data

For our final investigation, we look at hydrogen storage at the sublimation temperature of dry-ice (194 K). A summary of all 194 K data is given in Table 5.3.
Table 5.3. Summary of gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at dry-ice temperature (194 K).

N/A: not available.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²/g)</th>
<th>Porosity</th>
<th>Dry Ice Temp. Grav. Excess Adsorption (100 bar) (g/kg)</th>
<th>Dry Ice Temp. Grav. Storage Capacity (100 bar) (g/kg)</th>
<th>Dry Ice Temp Vol. Storage (100 bar) (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 K 800 °C</td>
<td>1900</td>
<td>0.69</td>
<td>16.4</td>
<td>29.0</td>
<td>18.0</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
<td>20.5</td>
<td>31.0</td>
<td>13.6</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
<td>21.7</td>
<td>40.4</td>
<td>17.8</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>23.2</td>
<td>43.3</td>
<td>19.0</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
<td>18.3</td>
<td>38.2</td>
<td>16.8</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
<td>18.8</td>
<td>32.0</td>
<td>19.2</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
<td>22.3</td>
<td>38.9</td>
<td>19.4</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>22.7</td>
<td>43.6</td>
<td>19.2</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Fig. 5.11 shows the isotherms of samples activated with a KOH:C of three. 3K 800 °C and 3K 900 °C are essentially indistinguishable. At 100 bar, 3K 900 °C has a gravimetric storage capacity of 43 ± 3 g/kg. This is sufficiently high to meet the DOE 2010 gravimetric storage target of 45 g/kg within uncertainty. Essentially, we have shown here that we may modestly decrease the temperature to increase the storage capacity by a factor of two.
Figure 5.11. Gravimetric excess adsorption (left), gravimetric storage capacity (center) and volumetric storage capacity (right) of sample 3K activated at 700, 800, 900, and 1000 °C and measured at dry-ice temperature (194 K).
Chapter 6 – Boron-doped Activated Carbons

One potential pathway to achieving higher hydrogen binding energies in carbonaceous materials is by substituting a fraction of the carbon atoms in the carbon matrix with boron (1:10 B:C mass ratio)[9,10,14] and thus achieving a higher storage capacity [9]. Substitution of a carbon with a boron atom results in an electron deficiency (empty p\textsubscript{z} orbital) in the carbon matrix which increases the depth of the gas-solid interaction potential [9,59,60]. Boron doped single-walled carbon nanotubes [61] and boron substituted carbon scaffolds [15] have been fabricated in other labs. However, these materials have very low specific surface areas (~400 m\textsuperscript{2}/g in the case of carbon nanotubes [62] and 900 m\textsuperscript{2}/g in the case of boron substituted carbon scaffolds [15]). Although these materials have been shown to increase the hydrogen binding energy, they still have storage capacities much lower than the 2015 DOE target of 4.5 wt% [63].

Here, we outline a process by which a high-surface-area activated carbon ($\Sigma = 2600$ m\textsuperscript{2}/g) may be doped using the unique properties of a boron containing compound (decaborane – B\textsubscript{10}H\textsubscript{14}). For this process, vapor deposition of decaborane on the carbon surface followed by pyrolysis and high temperature annealing is used to create the necessary boron substitution. Preliminary calculations show that in order to achieve the 1:10 ratio of B:C, it is necessary to repeat the process several times. Additionally, boron doping results in a reduction of the pore volume, but the pore volume should still be a significantly higher than previously manufactured boron-doped carbons. However,
theoretical estimates of the doped pore volume show that doping alone is insufficient to explain an observed reduction in pore volume.

6.1 Theoretical Predictions

The doping mechanism and activated carbon structure

Boron may be incorporated into a carbon structure by heating the carbon material to a high temperature (> 1000 °C), as shown by Endo et al. and Lowell [64,65]. Lowell found that the solubility limit for boron in graphite was around 2.5 atomic percent (at%) and that the solubility at 1000 °C was around 0.1 at% (cf. Fig. 6.1). Although activated carbons will not fully graphitize at these temperatures [66] unless under high pressure [67], 2.5 at% is not enough boron to adequately increase the hydrogen-carbon binding energy [9].

Harris et al. showed the presence of hexagonal and pentagonal carbon rings as well as holes in activated carbon using aberration corrected high-resolution transmission electron microscopy (cf. Fig. 6.2) [66]. These images showed activated carbon as a disordered grouping of roughly graphitic sheets. While boron-doping of graphite will not yield the required boron concentration, activated carbon may be suitable to incorporate boron atoms into the holes and on the edge of individual graphene sheets.
Figure 6.1. Boron solubility in graphite. Solid data points are experimental data. Hollow data points are from an extrapolation of experimental data using log[solubility] vs. $1/Temperature$.

Estimation of the expected specific surface area

From the previous section, there are three situations in which a boron atom may be properly incorporated into the carbon surface: (i) the boron is placed in a hole in the carbon surface; (ii) the boron atom substitutes a carbon atom; or (iii) a boron atom is placed at the end of a carbon sheet. For situation (i), the total surface area of the material $A$ is assumed not to change provided that the hole is too small for any gas to pass.
through. In this case, the specific surface area will decrease because of the additional mass of the boron atoms. For situation (ii), the total surface area of the material is assumed not to change. The specific surface area will increase because boron has a smaller mass than carbon. For situation (iii), the total surface area will increase because of the addition of the boron molecule. If one assumes that the total surface area per carbon atom is identical to the total surface area per boron atom, then the doped specific surface area will decrease (cf. Fig. 6.3).

First, we consider case (i). The doped specific surface area $\Sigma'_{\text{hole}}$ (SSA) will vary based on the un-doped SSA $\Sigma$ and the mass of boron $m_B$ used to dope the carbon material of mass $m_C$. Using that the total surface area of the carbon is given by

$$A = \Sigma m_C,$$

$$\Sigma'_{\text{hole}} = \frac{A}{m_C + m_B} = \frac{\Sigma m_C}{m_C + m_B} = \frac{\Sigma}{1 + \frac{m_B}{m_C}}$$

$$\Sigma'_{\text{hole}} = \frac{\Sigma}{1 + \chi_B}$$

(6.1)

where $\chi_B$ is the mass ratio of boron to carbon.

Next, we consider the case in which a boron substitutes for a carbon atom. In this case, the total mass of the sample is in terms of the mass of boron plus a new mass of carbon $m'_C$ which is given by

$$m'_C = m_C - m_B \frac{M_C}{M_B} = m_C - m_B \chi_C$$

(6.2)
where $M_C$ and $M_B$ is the molar mass of carbon and boron respectively and $X_C$ is the molar mass ratio of carbon to boron ($X_C \approx 1.1$). The doped specific surface area $\Sigma'_{\text{sub}}$ will be given by

$$
\Sigma'_{\text{sub}} = \frac{A}{m'_C + m_B} = \frac{A}{m_C - m_B X_C + m_B} = \frac{\Sigma}{1 - \frac{m_B X_C}{m_C} + \frac{m_B}{m_C}} = \frac{\Sigma}{1 - \chi_B X_C + \chi_B}
$$

$$
\Sigma'_{\text{sub}} = \frac{\Sigma}{1 + \chi_B (1 - X_C)} \quad \text{(6.3)}
$$

For the third case, the total surface area of the doped carbon will be the sum of the total surface area of the un-doped carbon $A$ and the surface area attributed to the boron atoms $A_B$. The doped specific surface area $\Sigma'_{\text{end}}$ will be given by

$$
\Sigma'_{\text{end}} = \frac{A + A_B}{m_C + m_B} = \frac{\Sigma m_C + \Sigma_B m_B}{m_C + m_B} = \frac{\Sigma + \Sigma_B m_B}{1 + \frac{m_B}{m_C}}
$$

$$
\Sigma'_{\text{end}} = \frac{\Sigma + \Sigma_B \chi_B}{1 + \chi_B} \quad \text{(6.4)}
$$

where $\Sigma'_{\text{end}}$ is the SSA of an equivalent structure consisting of boron atoms.

If the carbon structure has a SSA $\Sigma$ is replaced entirely with boron atoms and assuming that the total surface area does not change, the boron SSA $\Sigma''$ is given by

$$
63
$$
\[ \Sigma_B = \Sigma X_B \]  

(6.5)

where \( X_B \) is the molar mass ratio of boron to carbon (\( X_B = 0.9 \)). Substituting Eq. (6.5) into Eq. (6.4) gives the final equation for the doped SSA for the case in which a boron atom is added to the end of a carbon sheet

\[ \Sigma'_{\text{end}} = \frac{\Sigma (1 + X_B \chi_B)}{1 + \chi_B} \]  

(6.6)

where \( \Sigma \) is the SSA for the undoped graphene and \( \Sigma_{\text{end}}' \) is the SSA for the doped graphene when a boron atom is added to the end of a carbon sheet. The term \( (1 + X_B \chi_B) \) accounts for the increase in the SSA due to the addition of boron, and \( 1 + \chi_B \) is a correction factor to account for the change in the density of the graphene due to the addition of boron.

\[ \chi_B \]

Estimation of the expected pore volume

We now must consider how the boron is being incorporated into the carbon structure and how this affects the pore volume and porosity. There are two possibilities for the inclusion of boron: (i) the boron fits in a hole, substitutes a carbon, or is on the end of a carbon sheet and is in the plane of the carbon surface (sp\(^2\) hybridization); or (ii) the boron is bound on the surface, not replacing a carbon atom, and is out of the plane of the carbon surface (sp\(^3\) hybridization).

We consider the first possibility where a boron atom replaces a carbon atom and is situated in the plane of the graphene surface. Shown experimentally using Scanning
Tunneling Microscopy by Endo et al. [65], inclusion of the boron distorts the graphene plane because the boron-carbon bond length $d_{b,c}$ is longer than the carbon-carbon bond length $d_{c,c}$ ($d_{b,c} = 1.59 \text{ Å}; d_{c,c} = 1.42 \text{ Å}$). As a result, the borons are located $d_B = 0.395 \text{ Å}$ above the graphene plane, the nearest-neighbor carbon atoms ($\alpha$-carbons) are located $d_\alpha = 0.175 \text{ Å}$ above the graphene plane, and the next-nearest-neighbor carbon atoms ($\beta$-carbons) are located $d_\beta = 0.01 \text{ Å}$ above the graphene plane as observed by Endo et al. Fig. 6.4(a) shows a model of a 6 Å boron-doped pore with these characteristics. Because the boron and neighboring carbon atoms lay above the graphene plane, the pore volume will be reduced after doping.

We now consider the scenario that the boron has not substituted a carbon but is attached to the graphene surface out of the graphene plane. The valence electrons of carbon in graphene are $sp^2$ hybridized. Carbons may also be $sp^3$ hybridized which results in single $\sigma$-bonds between the carbon and four neighboring atoms. The electrostatic repulsion will tend to try to bend these five bonded atoms into a tetragonal geometry. As a result, a boron that has bonded to an $sp^3$ hybridized carbon atom will pull the carbon atom that it is bound to out of the graphene plane, as well as that carbon atom’s nearest-neighbors ($\alpha$-carbons), and next-nearest-neighbors ($\beta$-carbons) (cf. Fig. 6.4(b)).

The height of the atoms above the graphene plane was calculated using Avogadro [68] which used a force model based on the electronegativity of each atom. The results are taken to be only an estimate of the true result and are not very reliable (Table 6.1).

To estimate the amount that the pore volume has been reduced, we consider the pore space to be a hexagonal prismatic honeycomb structure. Each individual hexagonal prism is such that the height of the prism is the pore width above a specific atom and the
base area consists of a regular hexagon formed by bisecting the projection of the three carbon-carbon (or carbon-boron) bonds onto the graphene plane (cf. Fig. 6.5). Since the C-C bond lengths (and the projection of the out of plane bonds) are 1.4 Å, the base area of such a hexagon is given by \( A = \frac{3}{2\sqrt{3}} d_{c-c}^2 \) where \( d_{c-c} \) is the C-C bond length.

### Table 6.1. Distance above the graphene plane for each type of atom.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Distance above graphene plane (Å) (In-plane Model) [65]</th>
<th>Distance above graphene plane (Å) (Out of Plane Model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>0.395</td>
<td>2.17</td>
</tr>
<tr>
<td>α-Carbon</td>
<td>0.175</td>
<td>0.15</td>
</tr>
<tr>
<td>β-Carbon</td>
<td>0.01</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Figure 6.4.** Model of a boron doped slit shaped pore (carbon center to carbon center width \( w = 6 \) Å) with the boron in the graphene plane (a) and the boron bound out of the graphene plane (b). A hydrogen molecule (white) and nitrogen molecule (blue) are included for size comparison.
Figure 6.5. A representation of the allotment of pore volume to each atom. The colors of the hexagonal prisms represent the boron atom (orange), the α-carbons (red), the β-carbon (green), and the center of the hexagonal rings (blue).

For every boron atom substituted into the graphene sheet, 10 atoms will contribute to a reduction in the total specific pore volume $V'_{\text{pore}}$: 1 boron, 3 α-carbons, and 6 β-carbons. There are 3 additional hexagonal prism-shaped volumes attributed to the center of the three carbon rings around the boron atom. We take these to be analogous to nearest-neighbor atoms and are considered to contribute the same volume as the α-carbons. The pore volume will be reduced by the hexagonal area described above multiplied by the distance of each atom above the graphene plane. The doped specific pore volume $V'_{\text{pore}}$ is given by

$$V'_{\text{pore}} = V_{\text{pore}} - \frac{3}{2\sqrt{3}} d_{\text{c-c}}^2 \chi_B \frac{N_A}{M_B} (d_B + 6d_\alpha + 6d_\beta)$$  \hspace{1cm} (6.7)

where $V_{\text{pore}}$ is the undoped specific pore volume and $d_B$, $d_\alpha$, and $d_\beta$ is the distance of the boron, alpha, and beta carbons respectively above the graphene plane. Fig. 6.6 shows the predicted pore volumes for a typical undoped pore volume of 1.6 cm$^3$/g. At 0.1 B:C, the
change in pore volume is within the uncertainty of the nitrogen adsorption measurement. Therefore, there should not be a measureable reduction in pore volume.

![Image](image.png)

**Figure 6.6.** Doped specific pore volume as a function of boron to carbon mass ratio for (left) a generic surface and for (right) a representative undoped specific pore volume.

### 6.2 Decaborane Phase Diagram

Before doping experiments were conducted, it was necessary to develop a phase diagram for the doping material, decaborane, from literature sources, as shown in Fig. 6.7 [69-71]. The solid-gas and liquid-gas coexistence curves were fit to the experimental data using a function of the form

$$p = \exp \left[ a + bT + cT^2 \right]$$

(6.8)

where $p$ has units of bar and $T$ has units of Celsius. Table 6.2 is a list of the fitting parameters used. Miller [70] provides a fit for his solid-gas coexistence data by using a linear fit to $\log p$ vs. $1/T$. This fit is in good agreement with higher pressure data measured by Furukawa and Park [69]. Furukawa and Park additionally provided the following equation for their liquid-gas vapor pressure data:
Here, temperature has units of Kelvin. Table 6.3 provides a comparison between Miller and Furukawa and Park’s experimental fits and those fit with Eq. 6.8. An important observation is that the fit provided by Furukawa and Park differs by 30% at the boiling point. From the data presented in Table 6.3, we conclude that below the triple point, either our fit or that given by Miller is sufficient to describe the solid-gas coexistence curve, but that Furukawa and Park’s equation for data above the triple point is not sufficient because it does not predict the boiling point accurately.

The liquid-solid coexistence curve in Fig. 6.7 was produced using a linear interpolation between the melting point [71] and the triple point [69]. The parameters used for this curve can also be found in Table 6.2.

\[ \log p(\text{mm Hg}) = -4225.345/T - 0.0107975T + 16.63911 \] (6.9)
Table 6.2. Fitting parameters for the solid-gas, liquid-solid, and liquid-gas coexistence curves. Here pressure has units of bar and temperature has units of Celsius.

<table>
<thead>
<tr>
<th>Fitting Parameter</th>
<th>Solid-Gas Coexistence ( p = \exp[a + bT + cT^2])</th>
<th>Liquid-Solid Coexistence ( p = a(T - b) + c)</th>
<th>Liquid-Gas Coexistence ( p = \exp[a + bT + cT^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-12.74902</td>
<td>1.24302</td>
<td>-8.89085</td>
</tr>
<tr>
<td>B</td>
<td>0.12516</td>
<td>98.37</td>
<td>0.06179</td>
</tr>
<tr>
<td>C</td>
<td>-3.38999x10^{-4}</td>
<td>0.0243</td>
<td>-9.38498x10^{-5}</td>
</tr>
</tbody>
</table>

Table 6.3. Comparison of fitting methods

**Solid-Gas Coexistence**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Experimental Data (bar)</th>
<th>MU fit (bar)</th>
<th>Difference - MU (bar)</th>
<th>Diff. - MU (%)</th>
<th>Miller fit (bar)</th>
<th>Difference - Miller (bar)</th>
<th>Diff. - Miller (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-33.15</td>
<td>3.25015x10^{-8}</td>
<td>3.1x10^{-8}</td>
<td>2x10^{-9}</td>
<td>6</td>
<td>3.2x10^{-8}</td>
<td>5x10^{-10}</td>
<td>0.2</td>
</tr>
<tr>
<td>-23.15</td>
<td>1.4856 x10^{-7}</td>
<td>1.3x10^{-7}</td>
<td>2x10^{-8}</td>
<td>13</td>
<td>1.5E-07</td>
<td>-1x10^{-9}</td>
<td>0.7</td>
</tr>
<tr>
<td>-13.15</td>
<td>6.05206 x10^{-7}</td>
<td>5.2x10^{-7}</td>
<td>8x10^{-8}</td>
<td>13</td>
<td>6.0E-07</td>
<td>5x10^{-9}</td>
<td>0.8</td>
</tr>
<tr>
<td>-3.15</td>
<td>1.40218 x10^{-6}</td>
<td>1.9x10^{-6}</td>
<td>-5x10^{-7}</td>
<td>36</td>
<td>2.2E-06</td>
<td>-5x10^{-7}</td>
<td>36</td>
</tr>
<tr>
<td>72.29</td>
<td>0.00488</td>
<td>0.0042</td>
<td>7x10^{-4}</td>
<td>14</td>
<td>0.0035</td>
<td>1x10^{-3}</td>
<td>21</td>
</tr>
<tr>
<td>81.96</td>
<td>0.00807</td>
<td>0.0085</td>
<td>-4x10^{-4}</td>
<td>5</td>
<td>0.0071</td>
<td>1x10^{-3}</td>
<td>12</td>
</tr>
<tr>
<td>88.65</td>
<td>0.01344</td>
<td>0.013</td>
<td>&lt;1x10^{-2}</td>
<td>&lt;7</td>
<td>0.011</td>
<td>2x10^{-3}</td>
<td>15</td>
</tr>
<tr>
<td>98.37</td>
<td>0.0243</td>
<td>0.024</td>
<td>&lt;1x10^{-2}</td>
<td>&lt;4</td>
<td>0.022</td>
<td>2x10^{-3}</td>
<td>8</td>
</tr>
<tr>
<td>(Triple Point)</td>
<td>0.0243</td>
<td>0.024</td>
<td>&lt;0.001</td>
<td>&lt;4</td>
<td>0.023</td>
<td>0.001</td>
<td>&lt;4</td>
</tr>
</tbody>
</table>

** Liquid-Gas Coexistence**

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Experimental Data (bar)</th>
<th>MU fit (bar)</th>
<th>Difference - MU (bar)</th>
<th>Diff. - MU (%)</th>
<th>Furukawa fit (bar)</th>
<th>Difference - Furukawa (bar)</th>
<th>Diff. - Furukawa (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>98.37</td>
<td>0.0243</td>
<td>0.024</td>
<td>&lt;0.001</td>
<td>&lt;4</td>
<td>0.023</td>
<td>0.001</td>
<td>&lt;4</td>
</tr>
<tr>
<td>(Triple Point)</td>
<td>0.0243</td>
<td>0.024</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
<td>0.042</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
</tr>
<tr>
<td>111.75</td>
<td>0.04269</td>
<td>0.042</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
<td>0.052</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
</tr>
<tr>
<td>116.92</td>
<td>0.05237</td>
<td>0.052</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
<td>0.063</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
</tr>
<tr>
<td>121.92</td>
<td>0.06347</td>
<td>0.063</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
<td>0.063</td>
<td>&lt;0.001</td>
<td>&lt;2</td>
</tr>
<tr>
<td>213</td>
<td>1.01325</td>
<td>1.01</td>
<td>&lt;0.01</td>
<td>&lt;0.9</td>
<td>0.66</td>
<td>0.3</td>
<td>30</td>
</tr>
<tr>
<td>(boiling point)</td>
<td>1.01325</td>
<td>1.01</td>
<td>&lt;0.01</td>
<td>&lt;0.9</td>
<td>0.66</td>
<td>0.3</td>
<td>30</td>
</tr>
</tbody>
</table>

\( ^a \) Data taken from Miller [70]; \( ^b \) Data taken from Furukawa and Park [69]; \( ^c \) Data taken from Hawley’s Chemical Dictionary [71];

\( ^7 \) The number of significant digits in the experimental data is highly suspect, but values here are directly quoted from the original papers. An exception is data from Hawley’s Chemical Dictionary where the pressure indicated is exactly 1 atmosphere.
6.3 Boron Doping Methods

The boron doping procedure consisted of two parts: (i) deposition of the boron containing compound (decaborane –B_{10}H_{14}) onto the surface of the carbon and (ii) high-temperature annealing to decompose the decaborane and incorporate the boron into the surface of the carbon. During the deposition phase, it was critical to heat the decaborane past its boiling point so that gaseous decaborane may infiltrate the pore space.

Three methods were used for the deposition of decaborane throughout the pore space. Method I (Fig. 6.8(a)) consisted of the following procedure:

i. The carbon-decaborane mixture was placed in a Schlenk flask (V \approx 120 \text{ cm}^3) and was initially under Argon at atmospheric pressure and room temperature.

ii. The carbon-decaborane mixture was cooled to -68 °C using a dry ice and acetone bath to prevent sublimation of the decaborane. The mixture was outgassed at this temperature for one hour to a pressure of approximately 40 mbar.

iii. The flask was sealed under vacuum and allowed to return to room temperature.

iv. The sealed flask was heated to 120 °C for 1 hour. The flask was then allowed to return to room temperature and the decaborane solidified in the pores.

v. The sample was transferred to a steel vessel (V \approx 25 \text{ cm}^3) under argon at atmospheric pressure at room temperature.

vi. The sample was heated to 600 °C. At 300 °C the sample reached the decomposition temperature of decaborane.

vii. The sample temperature was maintained at 600 °C for 12 hours and then cooled to room temperature. In producing Fig. 6.8(a), it was assumed that hydrogen formation from the decaborane decomposition contributes to additional pressure within the vessel above 300 °C.

Method II (Fig. 6.8(b)) consisted of the following procedure:

i. The carbon-decaborane mixture was placed in a Schlenk flask (V \approx 120 \text{ cm}^3) and was initially under Argon at atmospheric pressure and room temperature.

ii. The carbon-decaborane mixture was cooled to -68 °C using a dry ice and acetone bath. The mixture is outgassed at this temperature for one hour to a pressure of approximately 40 mbar.

iii. The flask was sealed under vacuum and allowed to return to room temperature.

iv. The sealed flask was heated to 250 °C for 1 hour. Upon cooling, the decaborane condensed in the pores and glass walls as a solid.

v. The sample was transferred to a steel vessel (V \approx 25 \text{ cm}^3) under argon at atmospheric pressure at room temperature.
vi. The sample was heated to 600 °C. At 300 °C the sample reaches the decomposition temperature of decaborane. At this point approximately 50% of the decaborane is still in the liquid phase.

vii. The sample temperature was maintained at 600 °C for 12 hours and then cooled to room temperature. In producing Fig. 6.8(b), it was assumed that hydrogen formation from the decaborane decomposition contributes to addition pressure within the vessel above 300 °C.

Method III was a slightly modified variation of Method I. In Method III, the decaborane and carbon were placed in separate Schlenk flasks that were connected by at 90° elbow joint. Both flasks were heated to 120 °C for 4 hours.

![Figure 6.8](image)

**Figure 6.8.** Method I (a) and Method II (b) phase diagrams calculated assuming a carbon mass of 1.975 g and a decaborane mass of 0.160 mg. The roman numerals at each point correspond to the steps in the procedures outlined above.

The important thing to note is that in all three methods, the decaborane returned to the solid phase after the deposition process and was then annealed. During the annealing process, the decaborane was in both the liquid and gas phase when it reached the decomposition temperature.
6.4 Results

Sixteen samples were initially fabricated using Methods I, II, and III above using activated carbon that was not outgassed as a precursor. Samples for which nitrogen data was measured are found in Table 6.4. Sample names have the form “x – Hy (z,w)” where x is the undoped precursor, y is a number indicating the order in which the samples were fabricated, z is the doping method used (I, II, or III), and w indicates the annealing temperature (A = 600 °C; B = 1000 °C). Boron content was determined using prompt gamma neutron activation analysis (PGAA) at the University of Missouri Research Reactor (MURR). Hydrogen data for these samples were measured using a mass that was not determined by the procedure in Sec. 4.1. The uncertainty in the sample mass was too large for any useful conclusions to be drawn from this data.

Specific surface areas (SSA) and specific pore volumes (SPV) for these samples were significantly lower than expected for boron-doped material (cf. Sec. 6.1 and Fig. 6.9). If a boron is to incorporate properly into the carbon structure, an electron deficiency in the carbon structure is helpful for the formation of boron-oxygen bonds. These boron-oxygen bonds have been observed in samples that were exposed to air using Fourier-Transform Infrared-Microscopy (FTIR) (cf. Fig. 6.10) [74]. This B-O bond formation is likely responsible for the blocking of pores in the material which result in a loss of surface area and porosity [75].

Because of this pore blocking effect, all subsequent samples were fabricated using a precursor that was outgassed at an elevated temperature for more than 24 hours and were stored in an argon glove box (< 10 ppm oxygen, < 0.5 ppm water).
Table 6.4. B-doped sample information for samples fabricated with a non-outgassed precursor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>B:C [g/g] (PGAA)</th>
<th>Specific Surface Area [m²/g]</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3K</td>
<td>N/A</td>
<td>2600</td>
<td>0.76</td>
</tr>
<tr>
<td>4K</td>
<td>N/A</td>
<td>2600</td>
<td>0.81</td>
</tr>
<tr>
<td>3K-H5 (III,A)</td>
<td>0.008</td>
<td>2800</td>
<td>N/A</td>
</tr>
<tr>
<td>3K-H6 (II,A)</td>
<td>0.014</td>
<td>2400</td>
<td>0.77</td>
</tr>
<tr>
<td>3K-H7 (I,A)</td>
<td>0.074</td>
<td>2300</td>
<td>0.73</td>
</tr>
<tr>
<td>3K-H7 (I,B)</td>
<td>0.062</td>
<td>1300</td>
<td>0.62</td>
</tr>
<tr>
<td>3K-H8 (I,A)</td>
<td>0.075</td>
<td>2500</td>
<td>0.75</td>
</tr>
<tr>
<td>4K-H11 (I,A)</td>
<td>0.084</td>
<td>2200</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Figure 6.9. Graph of reduced specific surface area (doped SSA/undoped SSA) vs. boron content.

Figure 6.10. FTIR microscopy spectra of sample 3K-H31 (III,A). **Red**: large aperture (100 µm). **Blue**: small aperture (20 µm).
Two samples (3K-H30 (I,A) and 3K-H31 (III,A)) were fabricated using a precursor that was outgassed at 250 °C for 48 hours (3K-200C). Eight samples were fabricated using a precursor that was outgassed at 600 °C for more than 48 hours (3K 600-C). Additionally, five samples were fabricated using a multiple doping process. None of the samples were exposed to air once the precursor was outgassed. A summary of the structural characteristics is given in Table 6.5.

Table 6.5. Structural data for samples doped using previously outgassed carbon as a precursor.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>B:C [g/g] (PGAA)</th>
<th>Specific Surface Area [m²/g]</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3K-250C</td>
<td>N/A</td>
<td>N/A</td>
<td>2700</td>
<td>0.77</td>
</tr>
<tr>
<td>3K-H30 (I,A)</td>
<td>3K-250C</td>
<td>0.084</td>
<td>2300</td>
<td>0.75</td>
</tr>
<tr>
<td>3K-H31 (III,A)</td>
<td>3K-250C</td>
<td>0.100</td>
<td>2000</td>
<td>0.73</td>
</tr>
<tr>
<td>3K-600C</td>
<td>N/A</td>
<td>N/A</td>
<td>2600</td>
<td>0.76</td>
</tr>
<tr>
<td>3K-H60 (I,A)</td>
<td>3K-600C</td>
<td>0.086</td>
<td>2100</td>
<td>0.74</td>
</tr>
<tr>
<td>3K-H60 (I,B)</td>
<td>3K-600C</td>
<td>0.067</td>
<td>2100</td>
<td>0.72</td>
</tr>
<tr>
<td>3K-H75 (I,A)</td>
<td>3K-600C</td>
<td>0.018</td>
<td>2400</td>
<td>0.80</td>
</tr>
<tr>
<td>3K-H79 (I,A)</td>
<td>3K-H78 (I,A)</td>
<td>0.071</td>
<td>2200</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Fig. 6.11 shows the pore size distributions for the samples in Table 6.5. For all non-multiply-doped samples, the nanopore volume (< 10 Å) and the micropore volume (< 20 Å) was reduced, but there was a negligible effect on the mesopore volume (> 20 Å, < 50 Å). The multiply-doped samples showed a decrease in the nanopore volume, but showed an increase in the micro and mesopore volumes. Additionally, the total pore volume increased by 20%.

Fig. 6.12 shows the 303 K and 80 K gravimetric excess adsorption and areal excess adsorption (excess adsorption normalized to the surface area) isotherms for 3K-600C, 3K-H60 (I,A), and 3K-H60 (I,B). At 303 K, the boron doped samples have an equal or greater gravimetric excess adsorption as the undoped precursor despite a 20% reduction in surface area and a reduction in the micropore volume (the number of highest
binding energy sites). At 80 K, the three samples are experimentally indistinguishable, except in the pressure range of 25 bar to 75 bar. Again, the boron-doped samples have either greater or equal gravimetric excess adsorption in spite of the loss of surface area. It is a reasonable conclusion from this data alone that the binding energy of hydrogen to the carbon sample has increased due to this boron doping.

Figure 6.11. Pore size distributions for oxygen-free boron-doped activated carbons.
In order to determine if the binding energy has actually increased, two isotherms were measured at 273 K and 303 K for samples 3K-600C and 3K-H60 (I,A). We then applied the process for using the Clausius-Clapeyron equation outlined in Sec. 2.3. As shown in Fig. 6.13, the 3K-H60 (I,A) has a higher adsorption enthalpy than 3K-600C.
Figure 6.13. Adsorption enthalpies for the undoped and boron-doped carbons.
Chapter 7 – Proposed Experiments: Applications of Henry’s Law

At high temperatures and low pressures, the excess adsorption isotherm is linear according to Henry’s Law

\[ m_{\text{exc}} = k_H p \]  

(7.1)

where \( k_H \) is the Henry’s Law constant. In terms of the gravimetric excess adsorption, Eq. 7.1 is (cf. Appendix 2)

\[ \frac{m_{\text{exc}}}{m_s} = \frac{\Sigma M_{\text{gas}} p}{N_A k T} \int (e^{u(z)/(kT)} - 1) \, dz \]  

(7.2)

where \( \Sigma \) is the specific surface area, \( M_{\text{gas}} \) is the molar mass of the gas, \( k \) is Boltzmann’s constant, \( N_A \) is Avogadro’s number, and \( u(z) \) is the gas-solid interaction potential. By comparing Eqs. 7.1 and 7.2, the Henry’s Law constant is

\[ k_H = \frac{\Sigma M_{\text{gas}}}{N_A k T} \int (e^{u(z)/(kT)} - 1) \, dz \]  

(7.3)

The Henry’s Law constant may be determined at low pressures and high temperatures from the slope of the gravimetric excess adsorption.

### 7.1 Estimating the binding energy

Using Eq. 7.3 and the experimentally determined Henry’s law constant, the binding energy may be estimated using a suitable adsorption potential \( u(z) \). Here we
consider two models for the adsorption potential: (i) a constant potential \( u(z) = E_B \) and (ii) a harmonic oscillator potential.

**Constant potential**

We evaluate Eq. 7.3 for a constant potential in a pore

\[
u(z) = \begin{cases} 
\infty & z < 0 \\
E_B & 0 < z < w \\
\infty & w < z 
\end{cases}
\] (7.4)

where \( w \) is the width of a pore. Using this potential in Eq. 7.3

\[
k_H = \frac{\Sigma M_{\text{gas}}}{N_A kT} \int_0^w \left( e^{-E_B/(kT)} - 1 \right) \, dz
\] (7.5)

The integrand in this case is simply a constant, so Eq. 7.5 is evaluated to be

\[
k_H = \frac{\Sigma M_{\text{gas}}}{N_A kT} w \left( e^{-E_B/(kT)} - 1 \right)
\] (7.6)

\[
k_H = \frac{V_{\text{pore}} M_{\text{gas}}}{N_A kT} \left( e^{-E_B/(kT)} - 1 \right)
\] (7.7)

where \( V_{\text{pore}} \) is the specific pore volume (m\(^3\)/g).

The specific pore volume can be written in terms of the porosity using

\[
\phi = \left[ 1 + (\rho_{\text{skeletal}} V_{\text{pore}})^{-1} \right]^{-1}
\] or, for the pore volume as a function of the porosity

\[
V_{\text{pore}} = \left[ \rho_{\text{skeletal}} (\phi^{-1} - 1) \right]^{-1}
\]

This gives

\[
k_H = \frac{M_{\text{gas}} \left( e^{-E_B/(kT)} - 1 \right)}{\rho_s (\phi^{-1} - 1) N_A kT}
\] (7.8)

Eq. 7.8 can be solved for the binding energy

\[
M_{\text{gas}} e^{-E_B/(kT)} - 1 = k_H \rho_{\text{skeletal}} (\phi^{-1} - 1) N_A kT
\]

\[
e^{-E_B/(kT)} = M_{\text{gas}}^{-1} \left[ k_H \rho_{\text{skeletal}} (\phi^{-1} - 1) N_A kT + 1 \right]
\]

\[
E_B(k_H) = -kT \ln \left( M_{\text{gas}}^{-1} \left[ k_H \rho_{\text{skeletal}} (\phi^{-1} - 1) N_A kT + 1 \right] \right)
\] (7.9)
Because only the highest binding energy sites are filled at low pressures (corresponding to the narrowest pores), the porosity in Eq. 7.9 should be calculated from the volume of nanopores

\[
E_B(k_H) = -kT \ln \left( M_{\text{gas}}^{-1} \left[ k_H \rho_{\text{skeletal}} \left( \phi_{\text{nanopores}}^{-1} - 1 \right) N_A kT + 1 \right] \right).
\] (7.8)

**Harmonic oscillator potential**

Here we consider two harmonic oscillator adsorption potentials. The first corresponds to mobile adsorption

\[
u(z) = E_B + 2\pi^2 m \nu_z^2 (z - z_{\text{min}})^2
\] (7.9)

where \( m \) is the mass of one gas molecule, \( \nu_z \) is the vibrational frequency perpendicular to the surface, and \( z_{\text{min}} \) is the distance from the surface of the minimum of the potential.

The Henry’s law constant is given by Steele [76]

\[
k_H = e^{-E_B/kT} \left( \frac{1}{2\pi mkT \nu_z^2} \right)^{1/2}
\] (7.10)

Solving for the binding energy gives

\[
E_B = -kT \ln \left[ k_H \sqrt{2\pi mkT \nu_z^2} \right]
\] (7.11)

The other adsorption potential corresponds to localized adsorption

\[
u(x, y, z) = E_B + 2\pi^2 m \nu_x^2 (z - z_{\text{min}})^2 + 2\pi^2 m \nu_y^2 x^2 + 2\pi^2 m \nu_z^2 y^2
\] (7.12)

where \( \nu_x \) and \( \nu_y \) are the vibrational frequencies parallel to the surface. Again, the Henry’s law constant is given by Steele [76]

\[
k_H = e^{-E_B/kT} \left( \frac{kT}{(2\pi m)^3 \nu_x^2 \nu_y^2 \nu_z^2} \right)^{1/2}
\] (7.13)
where \( \alpha(T) \) is the area per adsorption site and solving for the binding energy gives

\[
E_B = -kT \ln \left( \alpha(T) k_H \sqrt{\frac{(2\pi m)^{3/2} \mu_x^2 \mu_y^2 \mu_z^2}{kT}} \right).
\] (7.14)

### 7.2 Estimating the Skeletal Density

Up to this point, all of the theoretical calculations regarding adsorption have been concerned with gas molecules close to the surface. We now consider the adsorption process from the point of view of a molecule far away from the surface that experiences no external potential due to the adsorbing surface.

Consider a system \( S \) of \( N \) molecules in a volume \( V \) at a pressure \( \rho \) and temperature \( T \) that includes an adsorbing solid. In the low pressure and high temperature limit, \( S \) obeys Henry’s law

\[
N_{\text{exc}} = k_H \rho
\] (7.15)

where \( N_{\text{exc}} \) is the number of molecules contributing to excess adsorption.

We now consider a subsystem of \( S, S' \), of \( N' \) gas molecules in a volume \( V' \) at a pressure \( \rho \) and temperature \( T \) in which gas molecules are allowed to freely move in and out of the system. Inherently, \( N > N' \) and \( V > V' \). From the point view of \( S' \), adsorption is equivalent to a change in the number of gas molecules.

Let us take the largest possible volume of \( S' \) in which \( V' \) is the entire portion of \( V \) that is at a constant gas density, i.e. region III in Fig. 7.1. Consider that there is no adsorption potential and that at some time, the adsorption potential is simply switched on. In \( S' \), the number of molecules decreases and the pressure decreases. A gas molecule in \( S' \) would infer that the total system volume \( V \) must be increasing and that the change in
volume is directly proportional to the number of gas molecules that have left $S'$ (from the ideal gas law).

If Henry’s law is valid, then the apparent change in system volume must also be a linear function of pressure

$$V_{\text{observed}} - V_0 = k_{\text{H,V}} p$$

$$V_{\text{observed}} = k_{\text{H,V}} p - V_0.$$  \hspace{1cm} (7.16)

where $k_{\text{H,V}}$ is a constant with units of volume per pressure and $V_0$ is the observed volume of the system at zero pressure.

![Figure 7.1. Schematic of gas density as a function of distance from the adsorbent surface.](image)

By measuring adsorption isotherms at low pressure and high temperature (~303 K), it must be possible to graph the sample volume (calculated assuming no adsorption) as a function of pressure. If Henry’s Law is valid for the experimental data, then the observed sample volume will be linear with respect to pressure and may be extrapolated to zero pressure. Once the sample volume is determined at zero pressure, the mass may be measured and the true skeletal density determined. In principle, the true skeletal density...
density should depend upon the size of the molecules used to measure it. With accurate enough experiments, this difference should be observed.

The significance of this proposed measurement cannot be understated, because every adsorption measurement depends on knowledge of the volume or density of the sample. Recalling from Eq. 3.5, the measurement of excess adsorption depends upon the sample volume, and the sample volume for all measurements presented here was determined using a presumed skeletal density of 2.0 g/cm$^3$. If the skeletal density is found to be less than 2.0 g/cm$^3$, then the true excess adsorption is higher than those presented here. Additionally, gravimetric storage capacity (cf. Eq. 2.14) and volumetric storage capacity (cf. Eq. 2.21) depend on the skeletal density.
Chapter 8 – Conclusions

In this study, we investigated the interaction of hydrogen gas with activated carbons with the ultimate goal of using activated carbon as a hydrogen storage material. One method of increasing storage capacity is to increase the specific surface area (SSA) of the material [4,6]. However, there is a physical limit to how large the SSA may be (2,965 m²/g for graphene [7]). It has been shown theoretically that substitution of boron into the carbon surface can increase the hydrogen binding energy of the carbon material [9-12]. Because of this predicted increase in binding energy, we have additionally studied boron-doped activated carbons.

In Chapter 2, we outlined the theoretical background of adsorption physics required to understand the remaining chapters. Excess adsorption, absolute adsorption, and storage capacity were defined. It was shown that gravimetric storage capacity, volumetric storage capacity, and absolute adsorption may be derived from excess adsorption using Eqs. (2.14), (2.19), and (2.23), respectively. Adsorption enthalpies were calculated using two isotherms, one at 273 K and another at 303 K. We showed that the calculated enthalpy depended on the interpolation of the 303 K isotherm. We determined that an average of the interpolation models used is the best option for calculating the adsorption enthalpies.

We gave an overview of gas adsorption measurement techniques in Chapter 3. Thermal Desorption Spectroscopy (TDS), Gavimetry, and Manometry were presented. TDS was found to not be suitable for adsorbents while the gravimetric instruments in our
lab were also insufficient to measure hydrogen adsorption. Several sources of
uncertainty in manometric measurements were presented. It was shown that the equation
of state used to calculate gas densities only has a significant impact on the measured
adsorption isotherm at high pressures. Additionally, we showed that our manometric
instrument was able to reproduce results in other labs.

Experimental details were outlined in Chapter 4. We introduced the method for
determining the dry mass of a sample before adsorption measurement, the manometric
instrument used to perform hydrogen isotherms (HTP-1 Volumetric Analyser, Hiden
Isochema), and the nitrogen adsorption instrument (Autosorb 1-C, Quantachrome
Instruments). Specific surface areas were calculated using the BET theory and pore size
distributions were determined using quenched solid density functional theory.

Experimental results for undoped carbons were presented in Chapter 5. From the
nitrogen adsorption data and the proposed reaction for KOH activated carbons, we
concluded the following:

1. The porosity increases with increasing activation temperature and KOH:C.
2. The specific surface area increases with increasing activation temperature at low
   KOH:C and with increasing KOH:C at temperatures higher than 800 °C.
3. The micropore volume (< 20 Å) increases with increasing activation temperature
   and with increasing KOH:C at low KOH:C.
4. The mesopore (> 20 Å, < 50 Å) and nanopore volumes (< 10 Å) increase as both
   the rate of reaction of potassium carbonate with the carbon char and the intial
   ratio of KOH to carbon.
From 80 and 303 K hydrogen data, we concluded that the ideal surface area for these activated carbons was 2600 m²/g and that an ideal sample should have a large micropore volume because the micropores are not significantly detrimental to volumetric storage capacity. We additionally showed data at 194 K as an intermediate temperature option for hydrogen storage.

In Chapter 6, we showed results from boron-doped activated carbons. Although it is not likely feasible to substitute 10% boron into the carbon structure, it is possible for boron to bind into holes in the carbon or onto the end of carbon sheets. We developed a series of expected results based on simple calculations. We expect the surface area to be reduced if there is no carbon substitution (cf. Fig. 8.1), but we do not expect a measurable change in the pore volume.

Boron-doped samples produced using a precursor that was not outgassed before doping showed a decrease in the surface area beyond what was predicted (cf. Fig. 8.1). Samples that were fabricated from pre-outgassed carbon still showed a reduction in surface area and pore volume. However, the gravimetric excess adsorption and areal excess adsorption were significantly higher than the undoped precursor (cf. Fig. 8.2). Additionally, the adsorption enthalpy for the doped material was higher at room temperature.

Finally, we outlined an experiment for an alternative method of determining the binding energy by gas adsorption instruments. By measuring low pressure, high temperature isotherms, the binding energy may be estimated using either a constant potential model or a harmonic oscillator potential. This method may also be used to measure the skeletal density of a material using an adsorbing gas. In the Henry’s Law
region of an isotherm, an observed volume for the sample must also be a linear function of pressure.

**Figure 8.1.** (Left) Expected and (Right) observed specific surface areas for boron-doped carbon materials.

**Figure 8.2.** (Left) Gravimetric excess adsorption and (Right) adsorption enthalpies of boron-doped activated carbons.
Appendix 1 – Nitrogen and Hydrogen Data

A1.1 Nitrogen Data

Table A1.1. List of specific surface areas and porosities for KOH activated carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific Surface Area [m²/g]</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5K 700 °C</td>
<td>1500</td>
<td>0.58</td>
</tr>
<tr>
<td>2.5K 800 °C</td>
<td>1900</td>
<td>0.69</td>
</tr>
<tr>
<td>2.5K 900 °C</td>
<td>2000</td>
<td>0.70</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Figure A1.1. Pore size distributions for 2.5K activated at 700, 800, and 900 °C (left), 3K activated at 700, 800, 900, and 1000 °C (center), and 3.5 K activated at 700, 800, and 900 °C (right). In all cases, increasing the activated temperature reduced the micropore volume (pores < 20 Å) and increased the mesopore volume (pores > 20 Å, < 50 Å).
Figure A1.2. Pore size distributions for 2.5K, 3K, and 3.5K activated at 700 °C (left), 2.5K, 3K, and 3.5K activated at 800 °C (center), and 2.5K, 3K, and 3.5K activated at 900 °C (right). In all cases, increasing the KOH:C resulted in an increase in mesopore volume (> 20 Å, < 50 Å) but had a negligible effect on the micropore volume (pores < 20 Å).

A1.2 Room Temperature Hydrogen Data

Table A1.2. Summary of gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at room temperature (303 K), all measured on the Hiden instrument. For briquettes, a small piece of the monolith was analyzed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area [m²/g]</th>
<th>Porosity</th>
<th>Room Temp. Grav. Excess Adsorption (100 bar) [g/kg]</th>
<th>Room Temp. Grav. Storage Capacity (100 bar) [g/kg]</th>
<th>Room Temp. Vol. Storage (100 bar) [g/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 K 800 °C</td>
<td>1900</td>
<td>0.69</td>
<td>5.3</td>
<td>13.2</td>
<td>8.2</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
<td>6.7</td>
<td>13.3</td>
<td>9.3</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
<td>9.3</td>
<td>21.8</td>
<td>9.6</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
<td>7.5</td>
<td>19.4</td>
<td>8.5</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>8.3</td>
<td>20.9</td>
<td>9.2</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
<td>6.0</td>
<td>18.5</td>
<td>8.1</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
<td>6.3</td>
<td>14.6</td>
<td>8.8</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
<td>8.5</td>
<td>19.6</td>
<td>9.8</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>7.5</td>
<td>20.7</td>
<td>9.1</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
<td>5.6</td>
<td>20.6</td>
<td>7.8</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
<td>6.5</td>
<td>21.5</td>
<td>8.2</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
<td>7.7</td>
<td>21.8</td>
<td>8.7</td>
</tr>
</tbody>
</table>
Figure A1.3. Gravimetric excess adsorption (left), gravimetric storage capacity (center), and volumetric storage capacity (right), all at 303 K, of sample 3K activated at 790, 800, 900, and 1000 °C.

Figure A1.4. Gravimetric excess adsorption (left), gravimetric storage capacity (center) and volumetric storage capacity (right), all at 303 K, of sample 3.5K activated at 700, 800, 900 °C.
## A1.3 80 K Hydrogen Data

Table A1.3. Summary of gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at 80 K and 10 bar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area [m²/g]</th>
<th>Porosity</th>
<th>80 K Grav. Excess Adsorption [g/kg]</th>
<th>80 K Grav. Storage Capacity [g/kg]</th>
<th>80 K Vol. Storage [g/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 K 800 °C</td>
<td>1900</td>
<td>0.69</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
<td>49.5</td>
<td>55.6</td>
<td>24.4</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
<td>37.1</td>
<td>51.6</td>
<td>21.1</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>47.2</td>
<td>53.5</td>
<td>23.6</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
<td>39.2</td>
<td>45.5</td>
<td>20.0</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
<td>45.1</td>
<td>49.0</td>
<td>29.4</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
<td>48.6</td>
<td>53.6</td>
<td>26.8</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>47.6</td>
<td>53.6</td>
<td>23.6</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
<td>46.8</td>
<td>54.0</td>
<td>20.5</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
<td>40.7</td>
<td>47.9</td>
<td>18.2</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
<td>43.5</td>
<td>50.3</td>
<td>20.1</td>
</tr>
</tbody>
</table>

Table A1.4. Summary of gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at 80 K and \( p_{\text{max}} \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area [m²/g]</th>
<th>Porosity</th>
<th>( p_{\text{max}} ) [bar]</th>
<th>80 K Grav. Excess Adsorption [g/kg]</th>
<th>80 K Grav. Storage Capacity [g/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 K 800 °C</td>
<td>1900</td>
<td>0.69</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
<td>35</td>
<td>52.4</td>
<td>72.3</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
<td>35</td>
<td>54.2</td>
<td>74.1</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>35</td>
<td>45.4</td>
<td>65.0</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
<td>35</td>
<td>51.0</td>
<td>63.8</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
<td>35</td>
<td>56.6</td>
<td>82.7</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
<td>64</td>
<td>57.0</td>
<td>87.7</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>64</td>
<td>56.3</td>
<td>87.9</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
<td>47</td>
<td>47.1</td>
<td>68.8</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
<td>33</td>
<td>52.4</td>
<td>85.1</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
<td>52</td>
<td>52.4</td>
<td>85.1</td>
</tr>
</tbody>
</table>
Table A1.5. Summary of gravimetric excess adsorption, gravimetric storage capacity, and volumetric storage capacity at 80 K and 100 bar.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area [m²/g]</th>
<th>Porosity</th>
<th>80 K Grav. Excess Adsorption [g/kg]</th>
<th>80 K Grav. Storage Capacity [g/kg]</th>
<th>80 K Vol. Storage [g/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 K 800 °C</td>
<td>1900</td>
<td>0.69</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 700 °C</td>
<td>2200</td>
<td>0.65</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3K 790 °C</td>
<td>2600</td>
<td>0.78</td>
<td>58.7</td>
<td>110.0</td>
<td>48.2</td>
</tr>
<tr>
<td>3K 800 °C</td>
<td>2600</td>
<td>0.78</td>
<td>46.8</td>
<td>92.4</td>
<td>40.7</td>
</tr>
<tr>
<td>3K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>49.0</td>
<td>99.3</td>
<td>43.7</td>
</tr>
<tr>
<td>3K 1000 °C</td>
<td>2000</td>
<td>0.78</td>
<td>42.2</td>
<td>92.4</td>
<td>40.7</td>
</tr>
<tr>
<td>3.5K 700 °C</td>
<td>2000</td>
<td>0.70</td>
<td>46.2</td>
<td>80.5</td>
<td>48.3</td>
</tr>
<tr>
<td>3.5K 800 °C</td>
<td>2500</td>
<td>0.75</td>
<td>54.3</td>
<td>98.2</td>
<td>49.1</td>
</tr>
<tr>
<td>3.5K 900 °C</td>
<td>2500</td>
<td>0.78</td>
<td>54.7</td>
<td>106.6</td>
<td>46.9</td>
</tr>
<tr>
<td>4K 790 °C</td>
<td>2600</td>
<td>0.81</td>
<td>52.9</td>
<td>114.1</td>
<td>43.4</td>
</tr>
<tr>
<td>5K 790 °C</td>
<td>3200</td>
<td>0.81</td>
<td>42.0</td>
<td>103.2</td>
<td>39.2</td>
</tr>
<tr>
<td>6K 790 °C</td>
<td>2700</td>
<td>0.80</td>
<td>50.9</td>
<td>108.4</td>
<td>43.4</td>
</tr>
</tbody>
</table>

Figure A1.5. Gravimetric excess adsorption (left), gravimetric storage capacity (center) and volumetric storage capacity (right), all at 80 K, of sample 3K activated at 800, 900, and 1000 °C.

Figure A1.6. Gravimetric excess adsorption (left), gravimetric storage capacity (center) and volumetric storage capacity (right), all at 80 K, of sample 3.5K activated at 700, 800, and 900 °C.
Appendix 2 – Derivation of the Henry’s Law Isotherm

The thermodynamic equation for a single component gas-solid system is

\[ dE = TdS - \varphi dA - pdV + \mu dN \]  \hspace{1cm} (A2.1)

where \( A \) is the surface area of the gas, \( \varphi \) is known as the spreading pressure, and \( p \) is the gas pressure far away from the adsorbent [19]. The spreading pressure term arises from assuming that the pressure of the adsorbed film is not isotropic and consists of perpendicular \( (p_\perp) \) and parallel \( (p_\parallel) \) components. The spreading pressure is defined to be [76]

\[ \varphi \equiv (p_\parallel - p_\perp) t, \]

where \( t \) is the thickness of the adsorbed film. The spreading pressure has units of force per unit length.

We now consider two nearly identical systems as was shown by Hill (Fig. A2.1) [19,21,77]. The first is a diffuse, one-component gas in the presence of an external field. This system represents the adsorption of gas molecules at low pressures and high temperatures. The second is an identical system with no external field. The variables of this system are denoted by a superscript 0. The goal here is to use the grand canonical ensemble to develop an equation for excess adsorption (i.e. \( \tilde{N} - \tilde{N}^0 \)) for the case of a diffuse gas.

The entropy of such a gas system in the grand canonical ensemble is given by

\[ S = \frac{E}{T} - \frac{\tilde{N} \mu}{T} + k \ln \Xi. \]  \hspace{1cm} (A2.2)
Here $\bar{E}$ and $\bar{N}$ and the ensemble averages of the internal energy and particle number respectively and $\Xi$ is the grand canonical partition function. From Eq. (A2.1), the entropy is also

$$S = \frac{E}{T} + \frac{\varphi A}{T} + \frac{pV}{T} - \frac{N\mu}{T}. \quad \text{(A2.3)}$$

Equating Eqs. (A2.2) and (A2.3) gives the grand canonical partition function

$$\Xi = e^{(\varphi A + pV)/(kT)} = \sum_N Q_N(V, A, T)\lambda^N. \quad \text{(A2.4)}$$

where $Q_N(V, A, T)$ is the canonical partition function and $\lambda = e^{p/(kT)}$. By an equivalent line of thought, the partition function for the non adsorbing gas is

$$\Xi^0 = e^{pV/(kT)} = \sum_N Q_N(V, T)\lambda^N. \quad \text{(A2.5)}$$

**Figure A2.1.** Comparison of systems with (b) and without (a) an external potential due to an adsorbing surface [19]. Excess adsorption is found by calculating the ensemble average of the number of particles in $V$ for system a ($\bar{N}^0$) and system b ($\bar{N}$) and is given by $\bar{N} - \bar{N}^0$. 

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The canonical partition function for both systems is given by

\[ Q_N^0 = \frac{Z_N^0}{N!\Lambda^3 N} \] and \[ Q_N = \frac{Z_N}{N!\Lambda^3 N} \] (A2.6)

where

\[ Z_N^0 = \int_V e^{-U_N^0/(kT)} d\vec{r}_1 \cdots d\vec{r}_N \text{ and } Z_N = \int_V e^{-(U_N^0 + U_N)/(kT)} d\vec{r}_1 \cdots d\vec{r}_N. \] (A2.7)

The potential energy of the gas-solid system is the sum of the energy of the empty system \( U_N^0 \) and the external potential \( U_N \) where \( U_N \) is the sum of the individual contributions from a points in the solid \( u(\vec{r}) \).

In terms of the activity \( z = Q_1^0 \lambda/V = \lambda/\Lambda^3 \), the grand canonical partition functions are

\[ \Xi^0 = \sum_N \frac{Z_N^0}{N!} z^N \text{ and } \Xi = \sum_N \frac{Z_N}{N!} z^N. \] (A2.8)

Recalling from statistical mechanics that

\[ \bar{N} = kT \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T} = z \left( \frac{\partial \ln \Xi}{\partial z} \right)_{V,T}, \] (A2.9)

it follows that

\[ \bar{N}^0 = z \left( \frac{\partial \ln \Xi^0}{\partial z} \right)_{V,T} = z \left( \frac{\partial \sum_N V b_N^0 z^N}{\partial z} \right)_{V,T} = z \left( \frac{\partial \sum_N V b_N z^N}{\partial z} \right)_{V,T} = z \left( \sum_N V N b_N z^{N-1} \right) = V \sum_N N b_N^0 z^N \]

\[ \bar{N} = z \left( \frac{\partial \ln \Xi}{\partial z} \right)_{V,T} = z \left( \frac{\partial \sum_N V b_N z^N}{\partial z} \right)_{V,T} = z \left( \sum_N V N b_N z^{N-1} \right) = V \sum_N N b_N z^N \]
The \( b_N \) and \( b_N^0 \) are Thiele Semi-Invariants divided by the system volume \( V \)

\[
\begin{align*}
\bar{N} - \bar{N}^0 &= V \sum_N \bar{N}(b_N - b_N^0) z^N. \\
\end{align*}
\] (A2.10)

where the first sum is over all positive integers such that \( \sum_i i n_i = j \) \[77\]. At very low gas pressures, \( z = p/(kT) \) and

\[
\begin{align*}
\bar{N} - \bar{N}^0 &= V (b_1 - b_1^0) z \\
&= V (b_1 - 1) \frac{p}{kT} \\
&= (Z_1 - V) \frac{p}{kT} \\
&= \frac{p}{kT} \int_V \left( e^{u/(kT)} - 1 \right) \, d^3 \mathbf{r}.
\end{align*}
\] (A2.11)

If the external potential is dependent only on the distance from the solid surface, then we arrived to the equation shown by Hill \[19,77\]

\[
\bar{N} - \bar{N}^0 = \frac{A_p}{kT} \int (e^{u(z)/(kT)} - 1) \, dz. 
\] (A2.12)

In terms of the gravimetric excess adsorption, Eq. (A2.12) is

\[
\frac{m_{\text{exc}}}{m_s} = \frac{\Sigma M_{\text{gas}} p}{N_A kT} \int (e^{u(z)/(kT)} - 1) \, dz. 
\] (A2.13)

It should be evident from the steps in Equation A2.11 that the \(-1\) portion of the integrand of Eq. (A2.13) is the ideal gas contribution to the excess adsorption. If one removes this contribution, an equation for absolute adsorption is obtained

\[
\frac{m_{\text{abs}}}{m_s} = \frac{\Sigma M_{\text{gas}} p}{N_A kT} \int (e^{u(z)/(kT)}) \, dz. 
\] (A2.14)
References


[34] D. Broom. private communication, 2010.


VITA

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