The purpose of this experiment is to study the adsorption of gases on solid surfaces and to introduce you to some aspects of vacuum technique. To prepare for the laboratory you must:

1. Read Ch. XIX, Vacuum Techniques, in SGN. (Omit “Pumping Speed for a System,” p. 616-620, on first reading). Especially read the section on thermocouple vacuum gauges and capacitance manometers.
2. Submit a Matlab program to calculate various parameters from the data given in the exercise at the end of the chapter.

Adsorption of Gases on Solids

Attractive forces between gas molecules are responsible for the liquefaction of all gases; similar forces between surfaces and gas molecules are responsible for the phenomenon of gas adsorption on surfaces. This adsorption tends to be classified as physical adsorption (physisorption) or chemical adsorption (chemisorption) depending on the strength of the bonding. Physisorption energies are less than $\approx 20 \text{ kJ/mole}$, whereas chemisorption energies can be comparable to those of real chemical bonds $\approx 50-100 \text{ kJ/mole}$. These phenomena are of great practical use in catalysis, of course.

The Langmuir Isotherm

Adsorption is usually described in terms of how much gas is adsorbed as a function of pressure, the adsorption isotherm. The simplest of these is the Langmuir adsorption isotherm which is based on the following assumptions:

1. The surface contains a fixed number of adsorption sites. $\theta = \text{fraction of sites covered}; 1-\theta = \text{fraction of sites not covered}$.
2. Each site can hold one adsorbed molecule. A monolayer is the maximum amount which can be adsorbed.
3. The sites are independent and have no interaction.
4. The binding energy is the same for each site and does not depend on $\theta$.

With these assumptions, consider the rate of adsorption, $R_a$, which is proportional to the number of impacts with uncovered surface sites and is

$$ R_a = k_a P (1-\theta) N $$

(1)

---

1This experiment is similar to Experiment 26, Ch. XI in SGN, p. 300-9, and you may find that helpful. It is modeled closely after that reported by B. W. Davis, G. H. Saban, and T. F. Moran, *J. Chem. Ed.* 50 219 (1973)
where \( k_a \) is the rate constant for adsorption, \( P \) is the gas pressure, \((1 - \theta)\) is the fraction of sites not covered, and \( N \) is the total number of sites. The rate of desorption, \( R_d \), is

\[
R_d = k_d \theta N
\]

(2)

where \( k_d \) is the rate constant for desorption. At equilibrium, the two rates are equal and

\[
k_a P (1 - \theta) = k_d \theta
\]

(3)

\[
\theta = \frac{KP}{1+KP} \quad K = \frac{k_a}{k_d}
\]

(4)

If \( V_\infty \) denotes the volume\(^2 \) adsorbed for complete coverage (\( \theta = 1 \)) then in general \( \theta = V/V_\infty \)

and

\[
\frac{V}{V_\infty} = \frac{KP}{1+KP}
\]

(5)

or

\[
V_\infty/V = 1/KP + 1
\]

(6)

so plot of \( 1/V \) vs. \( 1/P \) is linear with slope \( 1/KV_\infty \) and intercept \( 1/V_\infty \)

**Example:**

for the adsorption of CO on charcoal at 273K

\[
\begin{align*}
P(\text{torr}) &\quad 100 \quad 200 \quad 300 \quad 400 \quad 500 \quad 600 \quad 700 \\
V(\text{cc}) &\quad 10.2 \quad 18.6 \quad 25.5 \quad 31.5 \quad 36.9 \quad 41.6 \quad 46.1 \\
\end{align*}
\]

From the slope and intercept of the plot of \( 1/V \) vs. \( 1/P \) we conclude that \( V_\infty = 107 \text{ cc} \) and \( K = 1.05 \times 10^{-3}V_\infty \).

\(^2\)It is customary to express the volume adsorbed as the volume at STP (1 atm & 273K).
Chapter 6. Adsorption of N₂

**BET isotherm**

The Langmuir isotherm makes no provision for more than one layer of gas adsorbing on the surface. Frequently however, the amount of gas adsorbed continuously increases as the pressure is increased indicating that gas sticks to the substrate and to gas already adsorbed. Allowance for multilayer adsorption was introduced by Brunauer, Emmett, and Teller (BET) and despite some rather drastic assumptions, it survives as the most useful theory of physical adsorption to date.

The BET isotherm was a generalization of the Langmuir isotherm and assumes the following:

1. The surface is uniform and all sites are equivalent. (i.e., no pores, steps, etc.)
2. Molecules adsorbed on the surface sites are localized.
3. Each molecule in the first layer provides a site for adsorption of a second layer, each molecule in the second layer provides a site for adsorption of a third layer, and so on.
4. There is no interaction between molecules in a given layer.
5. Molecules in the second and higher layers are held together by the forces in the bulk liquid whereas molecules in the first layer are different by virtue of being bound to the surface. For the layer bound to the substrate, \( k_a \) and \( k_d \) are the rate constants for adsorption and desorption; for the other layers, \( k_{a'} \) and \( k_{d'} \) are the respective rate constants.

Proceeding in a fashion similar to that for the Langmuir isotherm, we have the rate of adsorption for various layers as

\[ R_{a0} = k_a P N_0 \]  \hspace{1cm} (7)

\[ R_{a1} = k_a' P N_1 \]  \hspace{1cm} (8)

etc.

The rate of desorption for various layers is

\[ R_{d0} = k_d N_1 \]  \hspace{1cm} (9)

\[ R_{d1} = k_d' N_2 \]  \hspace{1cm} (10)

etc.

At equilibrium the rates of a/d must be the same, so

\[ k_a P N_0 = k_d N_1 \]  \hspace{1cm} (11)

\[ k_a' P N_1 = k_d' N_2 \]  \hspace{1cm} (12)

etc.

---

Chapter 6. Adsorption of N\textsubscript{2}

In terms of the molecules in the first layer,

\[ N_1 = \frac{k_a}{k_d} PN_0 = cKP N_0 \quad (13) \]

\[ N_2 = \frac{k_a'}{k_d'} PN_1 = KPN_1 = c(KP)^2 N_0 \quad (14) \]

etc.

where \( k_a'/k_d' = K \) and \( k_a/k_d = cK \)

The total number of gas molecules adsorbed, \( N \), is obtained by summing the number in the monolayer, plus twice the number in the double layer, plus three times the number in the triple........ (because a monolayer site contributes one, a double layer site two, etc.)

\[ N = [N_1 + 2N_2 + 3N_3...] = \sum_{i=1}^{\infty} i N_i \quad (15) \]

The volume adsorbed is \( NQ \) where \( Q \) is a constant. In a complete monolayer each site contributes one molecule and

\[ V_m = Q \sum_{i=0}^{\infty} N_i \quad (16) \]

\[ \theta = \frac{V}{V_m} = \frac{Q \sum_{i=1}^{\infty} i N_i}{Q \sum_{i=0}^{\infty} N_i} = \frac{\sum_{i=1}^{\infty} i N_i}{N_0 + \sum_{i=1}^{\infty} N_i} \quad (17) \]

now let \( N_i = N_{i-1} c (KP)^i \)

\[ \theta = \frac{cN_0 \sum_{i=1}^{\infty} i (KP)^i}{N_0 + cN_0 \sum_{i=1}^{\infty} (KP)^i} = \frac{\frac{KP}{cN_0(1-KP)^2}}{\frac{KP}{N_0 + cN_0 (1-KP)}} \quad (18) \]

\[ = \frac{cKP}{(1-KP + cKP)(1-KP)} \quad (19) \]
(Eq 19 results using the relations $\sum y^i = \frac{y}{1-y}$ and $\sum iy^i = \frac{y}{(1-y)^2}$.)

Finally, consider the equilibrium between the gas and a sample with all of the surface sites completely covered. (i.e., the substrate is covered completely with gas and this surface now looks like a liquid)

then

$$k_a P^0 N = k_d N \quad (20)$$

and

$$k_a' P = k_d' \quad \text{so } K = k_a' / k_d' = 1 / P^0 \quad (21)$$

where $P^0$ is the vapor pressure of the liquid. We finally have

$$\theta = \frac{V}{V_m} = \frac{cZ}{(1-Z+cZ)(1-Z)} \quad (22)$$

where $Z = KP = P/P^0$. Rearrangement gives

$$\frac{V_m}{V} = \frac{(1-Z+cZ)(1-Z)}{cZ} \quad (23)$$

or

$$\frac{Z}{V(1-Z)} = \frac{1}{cV_m} + \frac{Z(1-c)}{cV_m} \quad (24)$$

so a plot of $\frac{Z}{V(1-Z)}$ vs. $Z$ gives $\frac{1}{cV_m}$ as intercept and $\frac{(1-c)}{cV_m}$ as slope.

Equivalently, $\theta = \frac{n_{\text{ads}}}{n_m}$, where $n_{\text{ads}}$ is the number of moles adsorbed and $n_m$ is the number of moles adsorbed when the adsorbent is covered by a monolayer. The analog of eq (24) then becomes

$$\frac{Z}{n_{\text{ads}}(1-Z)} = \frac{1}{cn_m} + \frac{Z(1-c)}{cn_m} \quad (24a)$$

Both eq (24) and (24a) are of the form $Y = ZX + b$. (24b)

### Heats of Adsorption & Desorption

By definition,

$$c = \frac{k_a / k_d}{k_a' / k_d'} = \frac{P^0}{k_d / k_a} = \frac{P^0}{P'} \quad (25)$$

where $P'$ would be the equilibrium pressure of the adsorbate if only monolayer adsorption is allowed. The vapor pressure of a liquid is generally given by the equation

$$\Delta G^0 = - RT \ln P$$
where $\Delta G^0$ is the standard Gibbs free energy of vaporization. Eq (25) can be rewritten as

\[
c = \exp\left(\frac{\Delta G_{\text{vap}}^0 - \Delta G_m^0}{RT}\right) \approx \exp\left(-\frac{\Delta H_{\text{vap}}^0 - \Delta H_m^0}{RT}\right)
\]

(26)

where $\Delta G_m$, $\Delta H_m$ refer to the monolayer. The second expression is true because the entropies of vaporization or desorption will be very similar. Thus if $\Delta H_{\text{vap}}$ is known, an estimate for $\Delta H_m$ may be obtained from eq (26).

**Example**

for adsorption of $\text{N}_2$ on 1 gram of TiO$_2$ at low temp (75K)

\[
\begin{align*}
p(\text{torr}) & \quad 1.2 & 14 & 45.8 & 87.5 & 127.7 & 164.4 & 204.7 \\
V(\text{cc}) & \quad 601 & 720 & 822 & 935 & 1046 & 1146 & 1254 \\
P_0 & = 570 \quad (V \text{ corrected to } 273K)
\end{align*}
\]

Fig 2. Adsorption of $\text{N}_2$  Left: (1/v vs. 1/P). Right: $Z/[V(1-Z)]$ vs. $Z$

thus $cV_m = 2.47 \times 10^5$

and $\frac{c-1}{2.47e5} = .001225$ so $c=304$ and $V_m = 813 \text{ cc}$

the density of $\text{N}_2$ (liq) = .81 g/cc so $1.75 \times 10^{22}$ molecules occupy a cube 1 cm/side. If these are little cubes of side a, a=3.9 Å; the cube$^4$ has cross section 15 Å$^2$. Assuming $V_m$ corresponds to a perfect gas at 273K, 813cc corresponds to $813/22.4 = .036$ moles $=2.18 \times 10^{22}$ molecules so the area of the solid $= 3.2 \times 10^7 \text{ cm}^2 = 3200 \text{ m}^2$

**EXPERIMENTAL**

**PRINCIPLES**

$^4$ Different assumptions for how the molecules are packed will give different numbers here.
The amount of N₂ adsorbed on a sample of silica gel is measured at several pressures to determine the adsorption isotherm. A vacuum line of known volume is filled with nitrogen and the pressure is measured. A sample of silica gel contained in another known volume is connected, the gas is allowed to adsorb on the silica gel, and the resulting lower pressure is measured. Knowledge of the initial and final pressures and the appropriate volumes allow one to use the perfect gas law to calculate the amount of gas adsorbed on the silica gel.

The appropriate volumes are obtained in a preliminary set of measurements. Helium gas, which is not adsorbed on the silica gel, is admitted to a glass bulb of known volume attached to the vacuum line. The pressure is measured, and then a sequence of gas expansions and pressure measurements allow one to calculate various other volumes in the apparatus.

**Vacuum Line**

The vacuum system is shown below and consists of two interconnected manifolds: a primary manifold consisting of valves 1 through 5, and a secondary manifold of valves 6, 7, 8, 9 and 3 (In this and succeeding discussions of various stopcocks, you should refer to the figure to see what function is played by the opening or closing of a given stopcock.)

Valve 1 allows the main vacuum line to be evacuated.
Valve 2 allows N₂ or He to be bled into the system at about 5 psi.
Valve 3 connects the primary manifold to the secondary manifold.
Chapter 6. Adsorption of N\textsubscript{2}

Valves 4, 5, 8 and 9 allow one to isolate, evacuate, or fill with gas the two storage bulbs, the calibrated bulb, and the silica gel container, respectively. If gases are adsorbed on the silica gel contained in the bulb at 9 at liquid N\textsubscript{2} temperature, it must be evacuated BEFORE removal of the liquid N\textsubscript{2} or a VIOLENT EXPLOSION may result.

**Procedure**

| SAFETY GLASSES MUST BE WORN AT ALL TIMES WHEN WORKING WITH A HIGH VACUUM GLASS SYSTEM. |

**B. Pumping Down and Filling the Storage Bulbs**

When you enter the laboratory, the secondary manifold will be evacuated, the two storage bulbs will be empty, and the vacuum pumps should be running. If the vacuum pumps are not running, they should be turned on immediately.\(^5\) You can familiarize yourself with the actual experimental layout while the pumps are warming up!

The entire system (excluding the silica compartment) should now be evacuated. Ask the instructor to demonstrate the use of the Baratron gauge, then use it to measure the system pressure. When it is less than \(\approx 0.1\) torr, close off the storage bulbs and evacuate the silica gel compartment. (Close valves 2, 4, 5 and 8. Then open valve 9.) Pump on the silica gel until the pressure (as read on the Baratron gauge) is again less than \(0.1\) torr. Then close off the silica gel compartment and the calibrated bulb. (Close valves 8 and 9.)

Fill the N\textsubscript{2} storage bulb by connecting the rubber tubing at valve 2 to the N\textsubscript{2} cylinder. Briefly pump air out of the rubber tubing by opening valve 2 for approximately 30 seconds. Then, close valves 1 & 2. Ask the instructor to show you how to operate the regulator on the N\textsubscript{2} cylinder. Then set the regulator to \(\approx 5\) psi and charge the rubber tubing with this pressure of N\textsubscript{2}. With valves 3 and 6 open to the Baratron (to measure the pressure), open valve 2 S L O W L Y and fill the vacuum system to a pressure of \(\approx 0.9\) atm (680 torr) as measured on the Baratron. Evacuate the manifold. (Close valve 2, open 1.) Close off the pump (valve 1) and repeat the flushing procedure by opening valve 2. The rubber tubing should now contain pure N\textsubscript{2}. Finally close off the pump, open the N\textsubscript{2} reservoir (close valve 1, open 5) and then open the valve to the nitrogen tank (valve 2) to fill the bulb to 0.9 atm N\textsubscript{2}. When the bulb contains this amount of N\textsubscript{2}, close off the nitrogen fill line and the N\textsubscript{2} reservoir (valves 2 and 5), and evacuate the main manifold (valve 1).

---

\(^5\) Before turning on the pumps, make sure that all valves are closed. Turn on the mechanical pump. After approximately 1 minute the gurgling noises should cease, indicating that air has been pumped out of the system.) Now turn on the cooling water supply to the diffusion pump. Then turn on the diffusion pump itself. Finally, fill the Dewar (“thermos”) flask placed on the trap at valve 1 with liquid N\textsubscript{2} (if it is not available, see the instructor), and wait 15 - 20 minutes for the pumps to warm up.

After the pump has warmed up, evacuate the system, and measure the vacuum. First check to see that valves 2, 4, 5 and 9 are closed. Then evacuate the manifolds by S L O W L Y opening valve 1 (with valve 3 open).
Now connect the rubber hose to the helium cylinder, and repeat the above procedure (substituting valve 4 for valve 5) in order to fill the helium storage bulb. At this point close valve 2.

C. Volume Determinations

At this point only valves 1, 3, 6 & 7 should be open. Pump on the primary and secondary manifolds for about 3 minutes or until the pressure reads less than ≈ 0.1torr. Then, close off the pump (close valve 1), and open the calibrated bulb to the secondary manifold (open valve 8). Introduce Helium into the secondary manifold and fill the calibrated volume (slowly open valve 4) with a pressure of 400 - 500 mm of He as indicated on the Baratron. Then close the He reservoir (valve 4) and read the pressure, $P_0$, of the gas in the calibrated bulb. Isolate the gas in the calibrated volume (close valve 8), and open 1 to evacuate the manifolds to ≈ 0.1torr. Isolate the secondary manifold (close 3). Then SLOWLY open valve 8 to allow the gas stored in the calibrated volume to be shared between it and the secondary manifold.

The gas is now contained in the space shown in Fig 2a. Carefully record the new pressure, $P_1$. Open the silica compartment (valve 9), and record the new pressure, $P_2$. The gas has expanded to the space shown in Fig 2b. Now place a Dewar flask around the silica tube, and fill with liquid $N_2$ to the bottom of the piece of tape wrapped around the capillary tube above the sample bulb which is a fiduciary mark for the liquid nitrogen. Cover the Dewar with the Styrofoam stopper to minimize condensation of water and oxygen. Allow the system to come to equilibrium. Record the final pressure, $P_f$.

The measurements for the volume determinations are now complete. Evacuate the secondary manifold, the silica tube and the calibrated volume by SLOWLY opening valve 3, leaving the Dewar flask in place around the silica gel. Monitor the pressure using the Baratron gauge. When it is below ≈ 0.1torr, close valves 1, 8 and 9.

Record the atmospheric pressure and temperature using the barometer and thermometer situated on the outside wall of the darkroom.
Fig 2a. Gas contained in vacuum line

Fig 2b. Expansion of gas into sample tube, showing the various volumes to be determined
D. Isotherm Measurement

At this point only valves 6 and 3 should be open.

Admit $\approx 100$ mm Hg of $N_2$ from the $N_2$ reservoir into the secondary manifold (valve 5). Close off the $N_2$ reservoir and secondary manifold (close 5 and 3), and measure the initial pressure, $P_{1i}$, of the nitrogen in the secondary manifold using the Baratron. Keep the level of liquid $N_2$ in the Dewar flask around the silica bulb at the predetermined mark on the silica capillary chosen during the volume measurements (i.e., the bottom of the tape). Open the silica compartment (valve 9) and allow the system to equilibrate for 5 - 10 minutes. (Make sure the liquid $N_2$ level remains just under the tape.) Monitor the pressure with the Baratron, and when equilibrium has been reached, record the final pressure, $P_{1f}$, and close off the silica compartment (valve 9).

Now carefully connect the manifolds (valve 3), and introduce an extra 50 mm Hg of $N_2$ into the secondary manifold by gently opening the $N_2$ storage bulb (valve 5). Close off the storage bulb and secondary manifold (valves 5 and 3), and record the second initial pressure, $P_{2i}$. Open the silica gel compartment (valve 9), and wait until equilibrium over the silica is reestablished, again checking the liquid $N_2$ level in the Dewar flask. Then record the second final pressure, $P_{2f}$.

Repeat this procedure of adding extra $N_2$, measuring the initial pressure and final pressure until the final equilibrium pressure above the powdered silica reaches approximately 350 mm Hg.

Note that while you are making the isotherm measurements, valves 3 and 9 should never be open simultaneously.

E. Shutdown

WITH THE LIQUID $N_2$ STILL IN PLACE AROUND THE SILICA COMPARTMENT, evacuate the silica sample tube (open 1, 3 and 9). Pump on the silica for 5 - 10 minutes. Then remove the liquid $N_2$ Dewar, and continue pumping on the silica for an additional 5 - 10 minutes. Make SURE you remove any $N_2$ adsorbed on the silica, and then close off the silica gel compartment and secondary manifold (valves 9 and 3).

THE ABOVE PROCEDURE IS NECESSARY TO PREVENT PRESSURE BUILT UP IN THE SILICA TUBE FROM PRODUCING A VIOLENT EXPLOSION!

Now unplug the diffusion pump (leave cooling water running), and evacuate the storage bulbs by SLOWLY opening valves 4 and 5. The diffusion pump will continue operating for $\approx 15$ minutes while it is cooling down. Wait 5 minutes, and then close off the storage bulbs (valves 4 and 5).

Make sure the Baratron gauge is evacuated and that the main manifold (valve 1) is still open to the pump. Leave the Dewar at valve 1 in place, the diffusion pump cooling
water flowing, and the main mechanical pump on. The instructor will complete the shutdown of these components after the diffusion pump has fully cooled. This takes at least 30 - 40 minutes.

**Data Analysis**

<table>
<thead>
<tr>
<th>Volume calibrated bulb</th>
<th>56.83 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight silica gel</td>
<td>0.539 g</td>
</tr>
</tbody>
</table>

**A. Volumetric Determination**

It is necessary to determine \( V_{\text{man}} \) (volume in the adsorption manifold), \( V_{\text{ds}} \) (volume of "dead space" in the sample tube above the liquid Nitrogen level), and \( V_{\text{dc}} \) (the volume of the sample tube "dead space" below the liquid nitrogen level). Expanding He from the calibrated bulb, \( V_c \), at pressure \( P_0 \) into the evacuated manifold and applying the ideal gas law gives

\[
\frac{PV}{T} = \text{const} = (V_{\text{man}} + V_c) \left( \frac{P_{\text{man}}}{T_a} \right) = V_c \left( \frac{P_c}{T_a} \right)
\]

where the volume of the calibrated bulb, \( V_c = 56.67 \text{ ml} \), was determined before being sealed onto the vacuum line by filling it with mercury and weighing the mercury. Expanding gas contained in \((V_{\text{man}} + V_c)\) at pressure \( P_{\text{man}} \) into the sample tube without liquid nitrogen in the Dewar gives a pressure \( P_{\text{tot}} \) and the gas law gives

\[
\frac{P_{\text{tot}}V_{\text{tot}}}{T_a} = (V_{\text{man}} + V_c) \left( \frac{P_{\text{man}}}{T_a} \right)
\]

where \( P_{\text{tot}}, T_a \) are the final pressure and temperature. The complete volume of the sample tube, \( V_{\text{dstat}} \), is obtained by difference: \( V_{\text{tot}} = V_{\text{dstat}} + V_{\text{man}} + V_c \).

The sample tube, in a two temperature approximation, may be considered as having two volumes, \( V_{\text{dsa}}, \) and \( V_{\text{dsc}}, \) the first at ambient temperature, \( T_a, \) and the second at liquid nitrogen temperature, \( T_N. \) When liquid nitrogen is put into the Dewar surrounding the sample tube the amount of gas in volume \( V_{\text{tot}} - V_{\text{dsc}} \) is at ambient temperature, \( T_a, \) and the amount in volume \( V_{\text{dsc}} \) is at the boiling point of liquid nitrogen, \( T_N. \) Thus

\[
P_{\text{f}} \left( \frac{V_{\text{tot}} - V_{\text{dsc}}}{T_a} + \frac{V_{\text{dsc}}}{T_N} \right) = \frac{P_{\text{tot}}V_{\text{tot}}}{T_a}
\]

**B. Amounts of Adsorbed Gas**

The number of moles of gas entering the sample bulb for a particular dose is defined by

\[\text{...}\]

---

6 This closely follows the discussion in Davis, et al.
7 This closely follows the discussion in Davis, et al.
8 Allowance is made here for the possibility that the temperature has changed. It is anticipated that all temperatures (except liq N2) will be the ambient, \( T_a \).
where $n_i$ is the number of moles initially present in the adsorption manifold and $n_{ff}$ the final number of moles in the manifold after adsorption has taken place. After a series of doses, the total amount adsorbate in the sample bulb is just the sum of all doses. Not all of the gas in the sample tube is adsorbed on the sample, so it is necessary to correct for the amount of gas unadsorbed in the sample tube "dead space" which is

$$N_{ads_i} = \sum_{j=1}^{i} N_{sbj} - N_{dsj}$$

where $N_{ads_i} =$ number of moles adsorbed after $i$ doses, $N_{sbj} =$ amount of $N_2$ added to the sample bulb in the $j$th dose, and $N_{dsj} =$ amount of $N_2$ in the sample bulb “dead space” after the $i$th dose.

C. Report

The calculations here are simple, but somewhat repetitious. Write a simple Matlab program to perform the calculations, and turn in a documented copy of your program (i.e., what are the calculations doing?) Also email the program to your teaching assistant. Make your name part of the title!

You should turn in the following:
1. $V_{man}$, $V_{dstot}$, $V_{dsc}$, and $V_{dsa}$
2. an isotherm plot (i.e., total gas adsorbed vs. $P/Po$)
3. a BET plot
4. the specific surface area of the silica gel in square meters/gram
5. the heat of adsorption (with the correct sign!)

Error Analysis

Your error analysis must include a propagation-of-statistical-errors treatment as shown in SGN (Chapter II) for the following quantities:

$V_{man}$, $N_{adsi}$

$X$, $Y$ (as defined in eq 24(b))
surface area

Start with an estimate of your uncertainty in the quantities you actually measure, and propagate this to an uncertainty in each of the above quantities. Compare your uncertainty in a quantity to the quantity itself (i.e., calculate the relative uncertainty). Note SGN’s discussion of independent variables in the context of error propagation.

The uncertainty in $N_{ads}$, $X$, and $Y$ needs to be calculated for one point (i.e., one dose) only, but not for the first point. The uncertainty in the area may be calculated using the standard deviations in the coefficients of the BET plot. You may use a computer program to calculate the coefficients (i.e., the “fitting parameters”) and the standard deviations of these coefficients.
Show explicitly what values you use for p, T, etc. All fundamental constants, as well as values given you in this write-up may be assumed to be exact.

**Discussion**

The following are suggested topics for your consideration:

1. Evaluate the reliability of your results. What does your uncertainty propagation tell you about reliability? What are some of the sources of systematic errors in your results? Which of these are the most significant?

2. Do your results indicate that adsorption is an endothermic or exothermic process? Does this make sense? Why?/Why not? (Is adsorption endo- or exo-entropic?)
Appendix. Data Entry and Computer Exercise

Before leaving, enter your results on the computer situated in the lab using the program \texttt{N2DataEntry}. The format will be specified in the computer program.

\begin{verbatim}
\textbf{N}_2 \textbf{ Adsorption Exercise}

Using the following data (also on the web as \texttt{CMLData.html}), write a Matlab program to calculate the following quantities as defined in this Chapter:
\[ V_{\text{man}}, V_{\text{dstot}}, V_{\text{dsa}}, V_{\text{dsc}} \]

It is not necessary to consider error analysis for this exercise. This program, corrected if necessary, will be used for the data you take and writing it will help in understanding the operations you will actually perform in the lab.

Using these values and the isotherm pressures, calculate the number of moles of gas adsorbed after each exposure. Plot the number of moles vs. the nitrogen pressure (i.e., the isotherm). Then make a BET plot and determine values for:
\[ n_m \text{ (number of moles in a monolayer), and} \]
\[ c \text{ (the proportionality constant relating the equilibrium constant for adsorption to an already bound layer $K$ to the equilibrium constant for adsorption to the bare surface $K_0$. ($K_0 = cK$. Since the adsorbate is more strongly held by the bare surface, $c>1.$)} \]

\textbf{DATA}

\begin{verbatim}
T=24.0
P=760
% following are pressure readings in the format given at the
% end of Chapter 6 "Adsorption of Nitrogen"

% volume determination
P=[
  479.6000
  113.3000
  102.3000
  96.7000]

% isotherm determination
P=[
  98.2  27.7]
\end{verbatim}
\end{verbatim}
<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>78.0</td>
<td>52.5</td>
<td></td>
</tr>
<tr>
<td>107.0</td>
<td>85.7</td>
<td></td>
</tr>
<tr>
<td>137.5</td>
<td>128.1</td>
<td></td>
</tr>
<tr>
<td>174.6</td>
<td>155.8</td>
<td></td>
</tr>
<tr>
<td>208.7</td>
<td>188.0</td>
<td></td>
</tr>
<tr>
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