

## Surface Adsorption

In this lab, you will be adsorbing N<sub>2</sub> on alumina at 77.4 K while monitoring the pressure at a given volume, to calculate the amount of adsorbed gas. Using a BET isotherm analysis, the volume of adsorbed molecules required to form one monolayer can be found which then can be used to determine the surface area of alumina.

Adsorption is the process by which molecules attach to a surface. The molecule that adsorbs is the adsorbate and the surface is the adsorbent. There are two types of adsorption, chemisorption and physisorption. Physisorption occurs when molecules physically interact with a surface through van der Waals forces, which are long-range, weak attractive forces. The energy of adsorption is approximately 20 kJ/mol, insufficient to break bonds; therefore the adsorbed molecules retain their identities. Chemisorption occurs when a molecule chemically bonds to a surface, usually through a covalent bond. The energy of this adsorption is approximately 200 kJ/mol.

The extent of surface coverage is expressed as a fraction:

$$\theta = (\# \text{ sites occupied})/(\# \text{ sites available}) = V_a/V_m = n_a/n_m \quad (1)$$

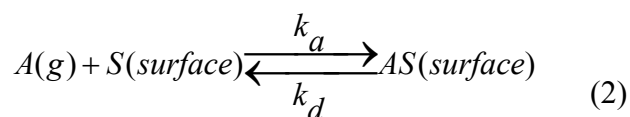
where  $V_a$  is the adsorbed volume,  $V_m$  is the volume of molecules in one monolayer,  $n_a$  is the number of adsorbed moles and  $n_m$  is the number of moles in one monolayer.

Conventionally the amount of adsorbed gas is referred to as a volume at standard state; however the volume of adsorbed gas is proportional to the number of moles of adsorbed gas. The rate of adsorption,  $d\theta/dt$ , is the change in fractional coverage with time. The adsorption of a gas to a surface can most easily be characterized by the Langmuir adsorption isotherm. And adsorption isotherm relates the number of molecules adsorbed to the equilibrium pressure and temperature. The adsorption of N<sub>2</sub> will be studied at 77.4 K, near the boiling point of the adsorbate, to assure appreciable amounts of adsorption occurs. The Langmuir isotherm is characterized by the following assumptions:

1. Gaseous molecules behave ideally.
2. Only one monolayer forms.
3. All sites on the surface are equivalent.

4. There are no adsorbate-adsorbate interactions.
5. An adsorbed molecule is immobile.

The gaseous molecules and the adsorbed molecules are in dynamic equilibrium.



The rate of adsorption depends on the pressure of gas above the surface,  $P$ , and the number of empty sites,  $N(1-\theta)$  while the rate of desorption depends on the number of occupied sites,  $N\theta$ . The rate of change of the surface coverage is

$$\frac{d\theta}{dt} = k_a P N (1 - \theta) - k_d N \theta \quad (3)$$

At equilibrium,  $d\theta/dt = 0$ . Solving for the surface coverage,  $\theta$ , gives the Langmuir isotherm.

$$\theta = \frac{KP}{(1 + KP)} \quad (4)$$

where  $K$  is the equilibrium constant,  $K = k_a/k_d$ .

The assumption that only a monolayer is formed typically does not hold. Brunauer, Emmett, and Teller modified Langmuir's theory to allow for multilayer adsorption. The BET isotherm, as it is known, allows for multilayer adsorption, but retains the other original assumptions. The assumption that gases behave ideally generally holds. However, the other assumptions are problematic: Not every site on the surface is equivalent, molecular interactions on the surface do occur, and molecules can move on the surface, especially if they are physisorbed. Fortunately the shortcomings in Langmuir's assumptions result in deviations that occur in opposite directions and mostly

cancel. The BET isotherm works best at low pressures where only a few complete monolayers of adsorbate may have formed since highly porous or irregular solids, such as alumina, cannot form regular layers.

The derivation of the BET isotherm requires a statistical derivation based on equilibrium considerations:

$$\theta = \frac{n_a}{n_m} = \frac{cx}{(1-x)[1+(c-1)x]} \quad (5)$$

where  $n_a$  is the adsorbed amount,  $n_m$  is the amount of gas required to form a monolayer of the adsorbate on the surface, and  $c$  is a dimensionless constant greater than one and dependent on temperature.  $x$  is the relative pressure,  $P/P_0$ . Here  $P_0$  is the vapor pressure of the adsorbate, which resembles a pure bulk liquid.

$$c \approx \exp\left[\frac{(\Delta_{des}H^\circ - \Delta_{vap}H^\circ)}{RT}\right] \quad (6)$$

The BET isotherm can be rearranged to give

$$\frac{x}{n_a(1-x)} = \frac{1}{n_m c} + \frac{(c-1)x}{n_m c} \quad (7)$$

A plot of  $x/n_a(1-x)$  vs.  $x$  should give a straight line. In practice, when  $x < 0.05$  or  $x > 0.3$  the fit will deviate from linearity, underestimating adsorption at high pressures. From the slope and intercept,  $c$  and  $n_m$  can be determined.

$$A = N_o n_m \sigma \quad (8)$$

Here  $N_o$  is Avogadro's number and  $\sigma$  is the cross sectional area of the adsorbate. For  $N_2$ ,  $\sigma = 15.8 \text{ \AA}^2$ .

## EXPERIMENTAL PROCEDURE

Since this experiment requires the use of a vacuum line to prepare the sample and transfer gasses, the procedure is divided into two parts. The first part is an introduction to high vacuum systems. The second part is the measurement of a surface area.

**Part I. HIGH VACUUM SYSTEM FAMILIARIZATION** (see figure at the end of this document)

You will need to determine the volume of the manifold and stem using the ideal gas relationship. Here you will be given a glass bulb with a known volume. Determine these volumes by the end of the end of the lab period.

(NOTE: The diffusion pump may already be turned on when you start the experiment. Look at the switch mounted under the diffusion pump. If it is on, then the pump has been warmed up by the lab staff.)

### **PRIMARY RULE !!!**

**NEVER open a valve or disconnect a joint, coupling, tube, etc. until you have considered carefully what is going to happen when you do!**

First examine the valves on the manifold. Operate one so that you can tell visually when the valve is open and when it is closed.

Make sure that the five attachment valves are closed. The three gauge valves should be open for all work done on the system. Make sure that the inlet, outlet, and bypass valves on the diffusion pump are closed.

Turn on the mechanical pump (if it is not already on) and leave it on throughout all the following work. Turn on the capacitance manometer and thermocouple gauges if they are not already on.

### A. MECHANICAL PUMP

Open the bypass valve over the diffusion pump.

Open the vacuum line valve.

Observe readings on capacitance manometer and thermocouple gauge.

Capacitance manometers are quite linear but tend to have a zero offset. One can determine this offset by observing the thermocouple gauge. When the pressure on the thermocouple gauge is  $< 50$  mtorr, the reading on the capacitance manometer should be stable and taken as the zero offset.

If the pressure as shown on the thermocouple gauge is below 50 mtorr, then turn on the Penning gauge. The Penning gauge **MUST BE TURNED OFF** if the pressure in the manifold is expected to be above 50 mtorr.

How low a pressure can you get with the mechanical pump after pumping for fifteen minutes? Record the readings on the capacitance manometer, thermocouple gauge, and Penning gauge.

### B. COLD TRAP

Place a dewar around the trap and fill the dewar with liquid nitrogen. Does the pressure change? Why? (The best way to do this step is for one person to fill the dewar while the other watches the thermocouple and Penning gauges.)

### C. DIFFUSION PUMP

With pressure less than one torr the diffusion pump can be used. Since this pump is heat driven and takes time to warm up, the lab staff will try to have it pumped out and warmed up before lab starts. Close the bypass valve. Open the outlet valve first, and then open the inlet valve.

[If the diffusion pump is off check that the pressure is still less than one torr (there may have been air in the diffusion pump that needs to be pumped out) then turn pump on. You will need to wait about 30 minutes for it to warm up.]

How low a pressure can you reach with this pump, again after fifteen minutes of pumping (with a warmed up pump)? Record pressure readings from the gauges.

#### D. VOLUME DETERMINATIONS

Connect a bulb to the system and pump the air out of it. Remember that the diffusion pump and Penning gauge should not be exposed to pressures greater than 1 torr.

Turn off the Penning gauge. Isolate the diffusion pump by closing first the inlet valve then the outlet valve, and then open the bypass valve. (Leave the diffusion pump turned on.)

A chart is attached to the vacuum system delineating various parts of the system and giving their volumes. Assuming that you know only the volume of the bulb,  $V_b$ , how can you determine the volume of the manifold ( $V_m$ ) and the stem volume ( $V_{xb}$ )? (Hint: you can use the ideal gas law for air at room temperature and pressures under 300 torr.) Using the method you've just worked out, determine experimentally  $V_m$  and  $V_{xb}$ . Compare your values with those on the chart. If you got a value within a few percent of the listed value, you probably got the method right. You need to know the manifold volume for the measurements in part II.

#### Part II. SURFACE ADSORPTION MEASUREMENT

In this section you will need to determine the number of moles of  $N_2$  that are adsorbed onto a sample of alumina powder at several equilibrium points. You will use this data to determine the surface area of the alumina sample.

To study surface adsorption we need to work out a method to measure the quantity of gas adsorbed by the sample as a function of the pressure of the gas. With the setup in our lab, a known volume (i.e. the manifold) is filled with a known amount of gas, then the valve to the sample chamber is opened and the gas is adsorbed on the sample until an equilibrium is reached. The amount remaining in the gas phase is determined and subtracted from the total amount known to be in the system to obtain the amount adsorbed. (If the initial conditions are that the sample chamber is evacuated and no

nitrogen has been adsorbed by the sample, then the calculations for the first addition of gas are straightforward. For subsequent additions of gas, the amount remaining as gas in the sample chamber and the amount so far adsorbed on the sample must be taken into account.)

### Calculations

- Use the ideal gas relationship (Boyle's Law) to determine the volume of the manifold (you did this in Part 1.) The volume of the stem and sample holder are given on the data card on the apparatus..
- Using the ideal gas relationship, determine the amount of adsorbed gas at each equilibrium pressure.

$$N_m + N_{sv} + N_s = N_m' + N_{sv}' + N_s'$$

Here  $N_m$  is the moles of  $N_2$  in the manifold,  $N_{sv}$  is the number of moles of  $N_2$  in sample volume, and  $N_s$  is the number of moles of  $N_2$  adsorbed on sample before the valve to the sample holder is opened. The primes indicate the number of moles of  $N_2$  after the valve to the alumina sample has been opened and system has been allowed to come to equilibrium. Make sure that you record the volume of the sample chamber.

- Plot the BET isotherm,  $x/[n(1-x)]$  vs.  $x$ , Fit a linear trend line between  $x = 0.05$  and  $x = 0.3$ . Use slope and intercept to find  $c$  and  $n_m$ .
- Given the effective cross-sectional area of the nitrogen molecule the surface area can be determined. Find the surface area of the alumina sample.

In your discussion section make sure to address the relevance of assumptions made to arrive at the BET isotherm. Why is the BET analysis less relevant when  $\theta > 0.3$  and  $\theta < 0.05$ ?

**References**

Atkins, P. Physical Chemistry, 5<sup>th</sup> edition. New York: W.H Freeman and Company, 1994.

Houston, P.L. Chemical Kinetics and Reaction Dynamics. New York: McGraw-Hill, 2001.

Levine, I. N. Physical Chemistry, 5<sup>th</sup> edition. New York: McGraw-Hill, 2002.

Pilling, M.J., Seakins, P.W. Reaction Kinetics. New York: Oxford Science Publications, 2003.

Shoemaker, D.P, Garland C.W., Nibler, J.W., Experiments in Physical Chemistry 7<sup>th</sup> edition. New York: McGraw-Hill, 2003.

