1.06

Determination of the Surface Area of Alumina by Nitrogen Adsorption at 77K

(4 points)

What you will do

In this experiment you will study the physisorption of nitrogen on alumina at 77K, in order to determine the total surface area per gram of powdered alumina. By recording the pressure when known volumes of gas are added to the apparatus, you will check the validity of one of the simplest mathematical descriptions of adsorption, the BET isotherm.

How you will do it

The experiment has two parts. In the first, known volumes of gas are allowed to expand into the apparatus and the resulting pressure is recorded. From these measurements the total volume of the apparatus can be determined.

Subsequently, any gas adsorbed on the surface of alumina is removed by heating a sample of the solid in a vacuum. Once the surface has been stripped of adsorbed gas, known volumes of nitrogen are fed in and allowed to reach equilibrium with the alumina. By measuring the resulting pressure in the apparatus, the amount of gas that remains unadsorbed can be found and, therefore, the amount adsorbed on the solid can also be determined.

BACKGROUND INFORMATION

You should be able to understand and carry out this experiment using your knowledge from 1st year courses only. However, if you have not yet completed the Solids and Surfaces course (3rd year) you should start with some background reading. "Processes at solid surfaces" (Chapter 25 in Atkins Physical Chemistry, 8th edn.) provides a suitable introduction.

Relevant lecture courses

Introduction to Thermodynamics (1st year)
Solids and surfaces (3rd year)

Web page for the experiment

http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/106.html

Recent finals questions related to this experiment

Part IB 2007, question 4.
Part IB 2006, question 4.
Part IB, 2005, question 4.
Physical option 1 paper 2007, question 2.
Physical option 1 paper 2006, questions 2,3.

SAFETY

The apparatus you will use contains a considerable quantity of mercury. Handle the gas burette with care, always supporting its weight while you move it. Wear safety glasses, since you will be using apparatus under vacuum, pressurized gas lines and liquid Nitrogen.

THEORY

Adsorption is the process by which atoms or molecules become attached to a surface. In principle adsorption can occur at any surface, but it has particular significance when a gas or liquid is in contact with a porous solid such as charcoal or alumina. Gas chromatography, liquid chromatography and most examples of heterogeneous catalysis depend directly upon adsorption processes, so the phenomenon is of considerable practical importance.

The forces that bind an adsorbed molecule (*adsorbate*) to the surface may be physical or chemical in nature (though the dividing line between the two is not sharp), giving rise to the phenomena of *physisorption* and *chemisorption* respectively. In practical terms, the two types of adsorption are normally distinguished on the basis of the strength of the bond formed between adsorbate and surface - weak van der Waals bonds are deemed to give rise to physisorption, while shared electron bonds are responsible for chemisorption.

Adsorption is described using an *adsorption isotherm*; this shows the amount of gas adsorbed as a function of pressure, at constant temperature. The simplest isotherm is due to Langmuir, and can readily be derived with the following assumptions:

1. In the gas phase, the adsorbate behaves ideally;
2. Adsorbed molecules are confined to a monolayer and never form multilayers;
3. Every part of the surface has the same energy of adsorption (the energy that is released as the adsorbate bonds to the surface);
4. No adsorbate-adsorbate interaction takes place;
5. Every site is equivalent;
6. The adsorbed molecules are immobile.

Let us consider each of these assumptions: The first is often reasonable, but the second is unreasonable for physisorption, since multiple layers are common. The next three assumptions are never correct - no surface is ever uniform, and even for a noble gas, the interaction between adsorbed molecules may account for as much as 25% of the measured heat of adsorption at half coverage of the surface. The final assumption is usually true at low temperature, but not at room temperature for physisorption, since, although the bonds joining each molecule to the surface have an energy usually greater than kT, it is not true that $e^{-E/RT} \ll 1$. Quite recent work has shown that many molecules are in fact highly mobile when "stuck" onto the surfaces of solids.

With such an awful set of assumptions, it might seem the Langmuir isotherm would be doomed. Happily though, the effect of surface non-uniformity is to decrease the average enthalpy of adsorption, while adsorbate-adsorbate interactions tend to increase it. The two effects largely cancel, and the Langmuir isotherm generally gives results that are better than would be expected. However, especially at low temperatures such as we use in this experiment, multilayer adsorption is common, and the BET (Brunauer, Emmett and Teller) isotherm is more useful under these conditions.

The BET isotherm makes the same assumptions as the Langmuir isotherm, except that multilayer adsorption is permitted. The derivation of the Langmuir and BET isotherms is given in standard physical chemistry texts (derivation of the Langmuir isotherm frequently appears in physical chemistry exam papers); we shall quote only the final BET result here:

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{(C-1)x}{V_m C} \qquad (1)$$

In equation (1), x is the relative pressure (p/p_0) at which a volume of gas V, measured at room temperature and pressure, is adsorbed. p is the pressure of the gas, and p_0 its saturation vapour pressure at the temperature of the vessel containing the adsorbent. In this experiment nitrogen is the gas, and the adsorbent alumina is held at 77K, the normal boiling point of liquid nitrogen where, by definition, its vapour pressure p_0 equals atmospheric pressure.

V_m is the volume of adsorbed gas required to form a monolayer on the adsorbent, and is a constant for a given temperature. Equation (1) demonstrates that a plot of $x/[V(1\text{-}x)]$ against x should give a straight line, whose intercept is $1/V_mC$ and slope is $(C\text{-}1)/V_mC$. Thus from the slope and intercept, C and V_m can be found.

The constant C is given by:

$$C = \frac{a_1 b_2}{a_2 b_1} \times e^{-(E_1 - E_L)/RT} \tag{2}$$

where (E_1-E_L) is the difference between the average enthalpy of adsorption in the first layer and the enthalpy of liquefaction of the adsorbate. a_1, a_2, b_1 and b_2 are constants connected with the formation and evaporation of the first and higher layers of adsorbed molecules.

Brunauer and his co-workers have suggested that in certain circumstances a_1b_2/a_2b_1 should be close to unity. If this is so, it would be possible to determine E_1 from a measurement of C from the isotherm.

The BET method yields a value for V_m, the volume of gas required to form a monolayer. Brunauer and Emmett suggested that the area of each adsorbed molecule could be found from the density of the liquid adsorbate according to the equation:

$$Molecular\ \ area = 4(0.866)\left\{\frac{M}{4(2)^{\frac{1}{2}} Nd}\right\}^{\frac{2}{3}} \tag{3}$$

where M is the molecular weight of the adsorbate, N is Avogadro's number and d the density of the liquefied adsorbent, which equals 0.808 g cm^{-3} for liquid nitrogen. Knowing V_m, the surface area can then be found.

Procedure

When using any piece of apparatus for the first time, it is important to make yourself familiar with it before starting work; *this is especially important with vacuum lines*, which may easily be damaged or contaminated by incorrect handling.

Therefore, start by checking the apparatus (a diagram is given below) and working out what each part of it accomplishes. It is helpful to start at one "end" of the apparatus; in this instance the sample tube on the left hand side provides a suitable point.

Refer to Figure 1 and check that you fully understand how the apparatus works. The sample tube holder on the left is where the sample will be placed. This is connected to a mercury manometer, which is used to measure the pressure in the sample tube.

Tap A is a three-way tap that connects the apparatus, via a strong conical flask, to a vacuum pump situated under the bench. Tap B is a second three-way tap that connects the sample tube to the gas burette.

The gas burette is a simple means to introduce a known volume of gas at a known pressure into the apparatus. Nitrogen from a cylinder can be fed into the left hand side of the burette. Once a volume of gas has been fed in, Tap B is turned to isolate it from the nitrogen supply. By raising or lowering the mercury reservoir the pressure inside the burette can be adjusted so that it is equal to atmospheric (when the two mercury levels match).

A nitrogen blow-off is also provided to prevent the pressure becoming too high. The nitrogen line should be turned OFF at the cylinder throughout the experiment except when you fill the burette.

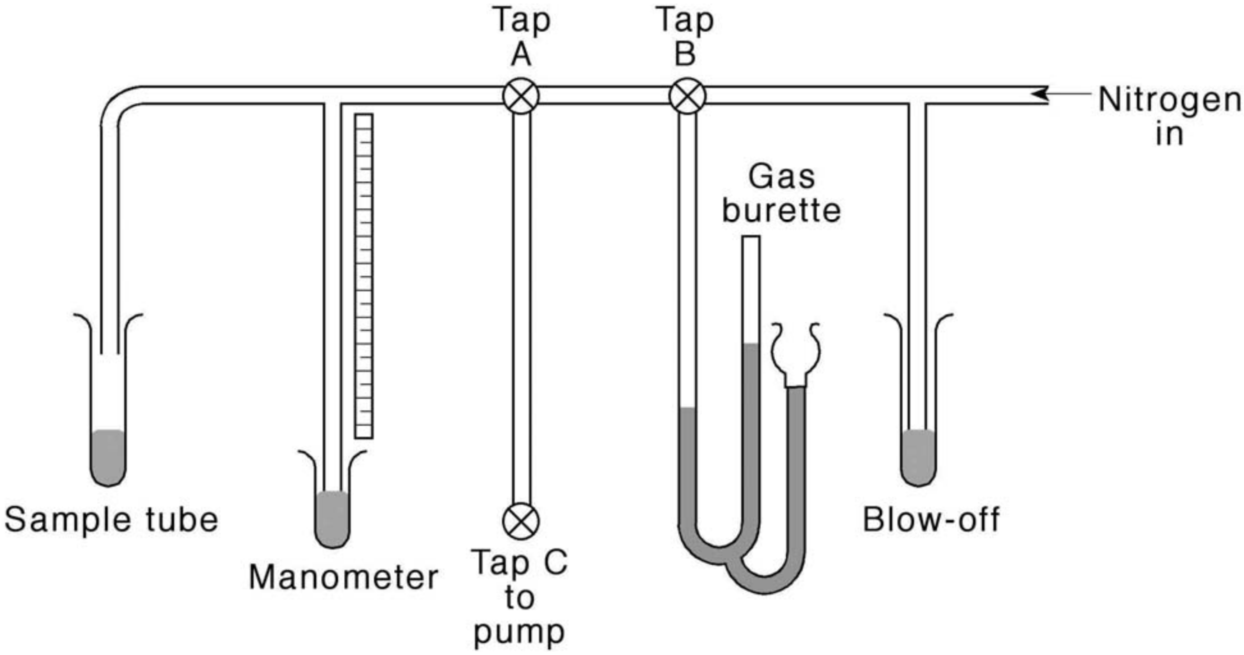

Figure 1. The vacuum manifold

The steps you need to take in the experiment are as follows:

1. Remove air from the apparatus by purging the burette with nitrogen.
2. Determine the "dead volume" by feeding known amounts of nitrogen into the left hand side of the apparatus and measuring the pressure after each addition.
3. Bake the sample under vacuum, to remove adsorbed gases
4. Conduct adsorption measurements

1. Removal of air from the apparatus

<u>Wear safety glasses throughout the experiment.</u>

Flush air from the gas burette as follows:

1. Check that the sample tube has been taken off the line. If it is still in place, remove it by holding the glass above the sample tube and gently pulling and twisting the tube.

2. Cautiously turn on the nitrogen cylinder and adjust the outlet pressure so that it is only slightly above zero. If in doubt, ask a demonstrator for guidance. Turn the three-way tap B

so that the nitrogen line is connected to the gas burette. Gas should be bubbling slowly and gently through the blow-off.

3. Lower the mercury reservoir to almost fill the burette with nitrogen (move the reservoir by holding the sliding clamp, **not** just the reservoir); turn off the nitrogen supply.

4. Turn taps A and B to connect the gas burette with the sample side of the vacuum line (check that tap B is turned so that the gas burette connects only with the left hand side of the apparatus, not both that and the nitrogen supply).

5. Raise the mercury reservoir carefully until the mercury level reaches roughly the top of the graduated portion of the burette to flush the nitrogen to the atmosphere; take care that mercury does not enter the vacuum line.

6. Close the two-way tap and repeat this procedure twice more to remove all air from the burette.

2. Determination of the dead volume

When gas is allowed into the apparatus to adsorb on the alumina, some gas will remain unadsorbed in the left-hand section of the vacuum line. In order to determine what quantity of gas has not been adsorbed, you need to know the volume of this part of the apparatus; once that is know, you can use the measured pressure of the gas in this section to determine the amount of gas. We must, therefore, determine the volume available to gas in this part of the line - the so-called "dead volume".

Fill the gas burette with nitrogen as before. Turn the three-way tap so that the burette is no longer connected to the nitrogen supply. Turn off the gas supply.

Clean the grease from the empty sample tube and from the socket on the gas line using a tissue and Volasil. If the sample tube appears dirty, wash it out with a little acetone and dry it using compressed air (gently!). Apply a thin ring of Apiezon T high temperature grease around the wide end of the tube and push it gently into position.

Switch on the pump and evacuate the manometer and sample tube until the pressure is constant. Close the connection to the vacuum pump (tap A) and monitor the pressure to check for leaks. Once you are sure the apparatus is gas-tight, adjust the mercury reservoir until the mercury levels in burette and leveling tube are equal. Record the manometer reading p_i and read the initial volume of nitrogen V_i.

Open Tap A carefully to admit a *little* nitrogen from the burette into the sample space. Be aware that there is a vacuum in the left hand side of the apparatus, while on the right hand side the gas is at atmospheric pressure, so you must be cautious in opening tap A, otherwise most of the gas from the burette will flow into the left hand side very quickly. The simplest way to ensure that only a small amount of gas is admitted is to close tap A, then open and close tap B. This will trap a small volume of gas in the space between the two taps, and this can then be allowed to expand into the rest of the apparatus by opening tap A. Repeat if necessary to give a fall in the level of the manometer of about 4 cm. Equalize the mercury levels in the burette and read the volume of nitrogen left in the burette (V_n); measure the pressure in the sample volume (p_n).

In this procedure you have allowed a known volume of gas (V_n-V_i) measured at atmospheric pressure (mercury levels equal on both sides of the burette when both measurements were taken) to expand into the rest of the apparatus and have measured the pressure that resulted (related to, but not equal to, p_n – see below).

Admit further small amounts of nitrogen to the apparatus and repeat the measurements to give a total of about 12 readings.

3. Baking of the sample under vacuum

Remove the sample tube. Weigh accurately into it about 0.5 g alumina. Grease the joint if necessary (Apiezon T) and replace the tube.

Turn tap A to connect the apparatus to the vacuum pump and pump out the apparatus. Place the furnace around the sample tube. (CARE! It is easy to place a sideways strain on the sample tube when doing this and thus break the vacuum line.) Place ceramic fibre around the top of the furnace, then turn it on and heat the sample for 40 minutes with the pump running, to drive off adsorbed gases from the alumina.

Allow the alumina to cool with the pump running. This period can be a convenient time to go off and have lunch, or start on the analysis of the dead volume data.

4. Adsorption measurements

Close tap A so that the apparatus is no longer being pumped out, reverse the air leak on the conical flask to admit air to the rotary pump, then turn off the pump.

Once the sample tube is cool enough to touch, but not before, place a small Dewar around it, and fill the Dewar completely with liquid nitrogen (available from the technician).

You need now to admit small quantities of nitrogen (2 - 4 cm^3 as measured at the gas burette) to the vacuum line. Read this entire section before continuing, and if in any doubt, consult a demonstrator, since a mistake now will set you back about an hour.

Using the same method as earlier, fill the burette with nitrogen. Very cautiously admit a little gas, between 2 and 4 cm^3, to the sample region. (Don't forget that a movement of 4 cm by the mercury up the gas burette will amount to a volume of more than 4 cm^3 once you equalize the mercury levels.)

Note: If you turn tap A too far, you will admit too much nitrogen and you will need to start the adsorption section of the experiment again from scratch, so be cautious.

When between 2 and 4 cm^3 nitrogen has been admitted, close tap A, equalize the mercury levels and determine the volume of gas admitted, measured at room pressure. Tap the manometer gently to prevent the mercury from sticking. Read and record the pressure above the sample every 30 seconds until the readings stabilize (stabilization should require between 3 and 6 minutes, with the longer times required later in the experiment). (Question: why does the pressure change?)

Record the equilibrium pressure p. Now continue adding nitrogen in smaller steps, (about 2 to 3 cm^3 each time) until a pressure of about 2/3 atmosphere has been reached inside the apparatus. You will need to refill the burette at least once during these measurements.

On completion of the experiment remove the Dewar, **RELEASE THE PRESSURE IN THE LINE AND REMOVE THE SAMPLE TUBE. IF YOU DO NOT DO THIS, PRESSURE WILL RISE IN THE APPARATUS AND MAY CAUSE IT TO BURST**. Turn off the nitrogen cylinder. Measure and record room temperature and pressure.

Calculations

Tabulate the raw pressure and volume readings. The readings of the manometer do not give the pressure inside the apparatus directly, since when there is a vacuum inside the reading will be roughly 76 cm. To determine the pressure in the apparatus you therefore need to subtract the measured pressure p from the pressure recorded when the apparatus was evacuated; it is the difference in these readings that gives the actual pressure.

Dead Volume

Calculate the dead volume of the apparatus, as follows:

Let the volume of sample tube and manometer combined be V'. The volume of gas admitted to this part of the apparatus is (V_i - V_n) at the ambient pressure, p_{atm}. When the gas enters the volume V', it creates a pressure p_n, and therefore:

$$p_n V' = p_{atm}(V_i - V_n) \tag{4}$$

Plot a graph of pressure against the volume of gas admitted and thus determine the dead volume (the volume of gas which would need to be admitted to give a pressure of one atmosphere within the apparatus).

Surface Area

For the second part of the experiment, tabulate for each addition of gas: the manometer reading, the actual pressure in the gas line, the burette reading, and the volume of gas, at room T and P, admitted to the line (remember your readings are cumulative).

Use the graph you constructed above to determine the volume of gas not adsorbed. (You should be able to do this very simply, since your graph relates the pressure of unadsorbed gas in the apparatus to the volume of gas needed to create such a pressure). Hence, for each reading determine the volume of gas adsorbed, measured at room T and P.

Plot the volume of gas adsorbed as a function of pressure of gas above the sample.

Test the validity of the BET isotherm for this system by using equation (1) to make a suitable plot. Fit a straight line through your points, determine V_m and thus find the surface area of 1g alumina.

Estimate E_1, the enthalpy of adsorption of nitrogen on alumina, given that the molar value of E_L is 5.6 kJ.

An expression for the time an adsorbed molecule stays on the surface before evaporating is

$$\tau = \tau_o \times e^{-E_1/RT} \tag{5}$$

where t_o is the time for a single vibration of the molecule in the absorbed state (which you can assume to be 10^{-13} s.)

Question: How could you estimate this time if it were not given?

Calculate the time an average nitrogen molecule spends on the surface.

Comment on your results. Compare your value for E_l with that for hydrogen adsorbed on nickel (125 kJ mol^{-1})

Discuss the source and magnitude of errors in your results.

Chemical properties, hazards and emergency treatment

Alumina presents few hazards, but the powder may irritate the eyes. Wear safety glasses throughout the experiment, since the vacuum line will normally be under reduced pressure. A spill of liquid nitrogen onto the skin should neither damage the skin nor hurt you, but a spill large enough to soak clothing may lead to burns, so handle liquid Nitrogen with care. If in doubt about any aspect of the procedure, ask a demonstrator.

Appendix A Problems and Solutions

Observation	Indicates	Solution
Calculation gives meaningless results	Probably a mistake in the calculation!	(i) Incorrect pressures used. The values that you read from the manometer are not the pressure of the gas in the apparatus, but values which must be subtracted from the manometer reading when the apparatus is evacuated, to give the actual pressure. e.g. if the manometer reading was 762 mm Hg when the apparatus was evacuated, and 609 mm Hg at some later stage, the pressure of gas inside would then be 153 mm Hg.
Minimal amounts of gas adsorbed	Adsorbent is already covered with a monolayer	(i) Solid not degassed. (ii) Leak in the apparatus has allowed air to seep in - ask technician to check (iii) You forgot to place any solid in the apparatus! (iv) Too large a volume of gas was added at the start of the absorption process - restart from the degassing stage.
Manometer falls slowly and continuously	Leak in apparatus	(i) Ask technician or demonstrator to check.