SPECIFICS ON SURFACE AREA

Rebecca Lea Wolfrom

Surface area is an important property of solids with many industrial applications. Particle size is less influential on surface area than particle shape, texture, and porosity. Surface area calculated from particle size data should never be used independently. Isotherms are developed for materials to determine their behavior during gas adsorption under very cold temperatures. Characteristic isotherm shapes are defined by the International Union of Pure and Applied Chemistry (IUPAC) and used to describe classes of materials. The BET method is a way to use a subsection of a material isotherm to calculate surface area for that material. Regulatory bodies define the terms of acceptability for applying the BET calculation to gas adsorption results. Samples must be carefully prepared prior to gas adsorption experiments to remove contaminants. The two main gas adsorption techniques, dynamic flow and volumetric, are described in terms of detection method, advantages, and disadvantages. Considerations including changing absorptive gas and decreasing the number of isotherm points collected are discussed.

INTRODUCTION

Envision a perfectly smooth, solid, uniform cube of length, width, and height all 10 meters (see Figure 1).
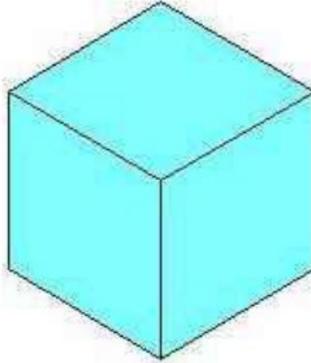

Figure 1: A perfectly smooth, solid, uniform cube with equal length, width, and height.

There are six surfaces: the top, the bottom, and four sides. The area (length × width) of each surface is 2 10m×10m = 100m . So, the total area of all surfaces exposed to the environment is 2 2 100m ×6 = 600m .This is the cube's surface area (SA). If the cube weighs 100 grams, then the surface area per unit weight, or specific surface area (SSA), is defined as Equitation 1:

Slice the cube in half once in each direction as in Figure 2.

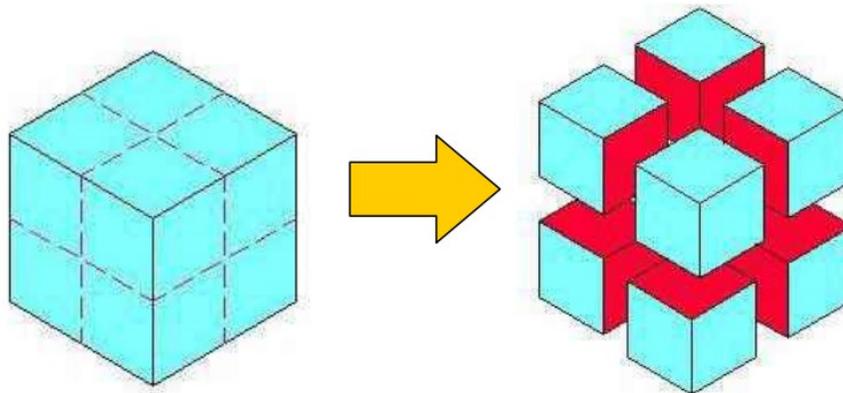$$\frac{600m^2}{100g} = 6\frac{m^2}{g}$$

[Equation 1]

Figure 2: Slicing the cube in half once in each direction exposes new surface area.

There are newly exposed surfaces to be considered in the overall surface area: 8 new cubes, 5m × 5m × 5m each. A single cube has a surface area of 150 m2 , multiplied by eight cubes gives 1200 m2 . Since the weight remains the same, the specific surface area of our material is now 12 m2 /g. Subdividing each of these eight cubes, the resulting specific surface area becomes 24 m2 /g. Nothing about the original material has changed except the size of its units. As the particle size gets smaller, more surface becomes exposed and the specific surface area increases.

Even more influential on overall surface area than particle size is the presence of pores. Imparting our smooth solid cube with a system of worm holes and texture will immediately create far more exposed surface than any simple slicing could. Therefore, a material having pore structure of some degree will have greater, possibly exponentially greater, specific surface area than that same material in solid nonporous form (Figure 3).
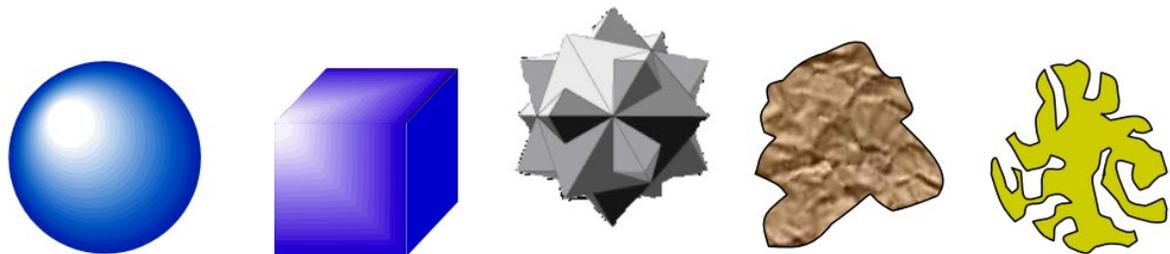
Figure 3: Particle shape (solid sphere, solid cube, solid polyhedron), particle surface texture (rough solid) and porosity (particle full of intruding pores) all affect surface area.

Surface area affects the dissolution rate of powders like pharmaceuticals. It also governs the adsorption capacity of filters like the charcoal in home water purifiers, and it controls the rate of water uptake like hydration in cement preparation, just to name a few. Each feature is critical to the behavior of the final product, and all depend upon the amount of surface available to a reactant. As a result, pharmaceutical, environmental, mining, catalysis, and many other industries have been evaluating the surface area of their materials for decades.

HOW IS SURFACE AREA DETERMINED?

Because particle size is relatable to surface area, simple geometry much like the aforementioned cube example can be applied to make estimates. A typical size distribution will show the relative amount of particles present in each of many narrow size ranges, so one may apply an assumption for equivalent shapes and thereby roughly sum up an overall surface quantity.

Some manufacturers include a particle size-derived surface area on their default instrument outputs. However, most common particle size techniques all report size in terms of equivalent spherical diameter (ESD) (1). While the ESD reporting style is generally known and accepted due to the complex calculations involved, it cannot be regarded as accurate because the

material under analysis is rarely made up of perfectly smooth solid spheres. Such data can only be used for relative comparisons between sample sets of the same material at best. Recall the earlier discussion of how significantly porosity can influence surface area: one source claims a possible underestimate of ≥ 1000 m2 /g by ESD calculations because pores, particle shape, and surface irregularities are disregarded (2). In short, surface area values derived from particle size data should never be used without understanding the assumptions behind the calculation.

How, then, can surface area be determined? The most effective way is by gas adsorption, in which individual molecules of an inert gas lay down on the test material surface and occupy a given amount of space. As more and more molecules lay down under a controlled temperature and pressure, eventually (theoretically) a monolayer forms. Gas molecules perfectly pack together with no open spaces between them in a layer one molecule thick. Using the size of each molecule and the quantity of molecules in place, the area is determined as in Equitation 2:

$$TotalSSA = \frac{Q \times A \times C}{W}$$

[Equation 2]

where

- Q = the quantity of gas molecules covering the surface
- A = the cross-sectional area of one gas molecule at the designated temperature and pressure
- C = mole and volume-to-weight conversions (if needed)
- W = total weight of sample tested.

ISO 9277:1995(E) and ISO 15901-2:2006(E) (3, 4) among others define adsorption as enrichment of the gas molecules at external and accessible internal faces of the solid. Note the spelling: ADsorption means the gas molecules are indeed laying down with essentially no motion, but that they may get up at any time with no change to themselves or the surface. The only push needed to drive them off is some change in their environment like a temperature increase or a pressure decrease. Adsorption is not to be confused with ABsorption, where the gas would actually intrude into the surface causing a chemical change. If the gas being used for surface area determination is ABsorbed by the solid, the theoretical assumptions break down and a different gas should be employed.

As shown in Figure 4, the gas being used for measurement is typically referred to as the adsorptive; it changes name to adsorbate and becomes fluid once it has laid still on the surface of the test material. That material is called the adsorbent. These definitions are established in the ISO documents (3, 4).
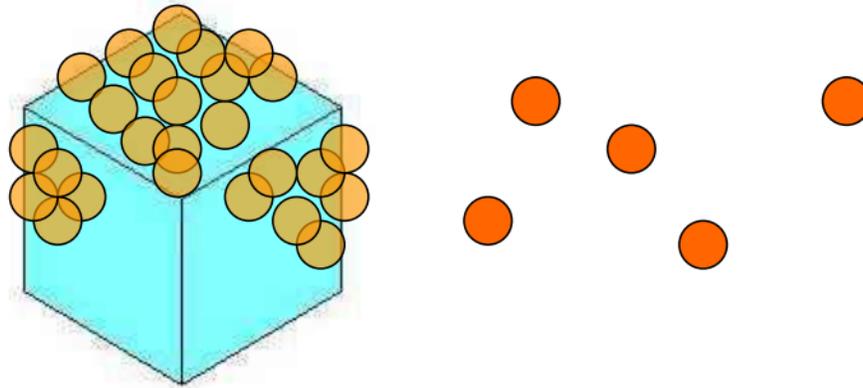
Figure 4: Freely moving adsorptive (gas molecules, dark orange spheres) condenses on the surface of the adsorbent (solid surface, blue) to become adsorbate (light orange spheres.)

HOW IS ADSORPTION DONE?

How does gas adsorption work in the laboratory on a practical level? Understanding the behavior and treatment of gases is critical. Important properties of a pure gas to be considered are as follows:

• Reactivity. The tendency of the gas to react with other materials. Inert gases are chosen for surface area determinations.
• Saturation Pressure. The saturation pressure P0 (or vapor pressure) of the gas, where liquid and gaseous states coexist in equilibrium, where the gas condenses/liquefies at varying temperatures.
• Molecular attributes. Molecular weight and molecular cross-sectional area of the gas at a range of temperatures.

Because the goal of the technique is to encourage fast-moving gas molecules to slow down and physically attach to a surface due to thermodynamics (i.e., condense) at pressures lower than their saturation pressure, the analysis is done at extremely low temperatures. In this way, one can achieve some measurable condensation for a series of pressures leading up to P0 for the gas. Any pure gas may be used as long as it adsorbs weakly to materials by van der Waals forces—a combination of London dispersion forces and polar or polarizable molecular interactions—and it may be used as long as it will readily desorb by either a small decrease in pressure (under constant temperature) or an increase in temperature (at steady pressure.) Nitrogen is the most popular gas to use, mainly because it is readily available in a very pure state; it is generally nonreactive with other substances; has a strong tendency to condense onto surfaces at the temperature of liquid nitrogen, which is also readily available; and it has a generally accepted value for its molecular cross-sectional area at liquid nitrogen temperature (5).

A clean sample in an enclosed nonporous, nonreactive (usually glass) cell, having openings for gas admittance only, is cooled in a liquid nitrogen bath, or other extremely cold liquid such as

liquid argon or solid carbon dioxide in acetone. A small known amount of adsorptive gas is admitted to the analytical cell to achieve a predetermined pressure at a fraction of its saturation pressure P0. The quantity of gas adsorbed at that pressure is determined by detecting changes in the environment. More increments of gas are then admitted at steadily increasing pressures up toward saturation. Each pressure point in this routine is termed a Relative Pressure P/P0. These adsorbed quantities plotted against each P/P0 point form a plot called an isotherm, so termed because the experiment was done all at the same (iso) temperature (therm).

Classes of materials like silicas or metal oxides can have similar-looking isotherms if the materials have comparable adsorption tendencies. If a researcher is investigating a brand new material, the literature recommends developing an isotherm using non-porous samples of the material, to avoid complicating variables of porosity (6). ISO (3) refers to IUPAC, which has compiled and named the six typical isotherm shapes found to date (7). The ones relevant to this discussion are addressed in the next section.

MODELING THE ISOTHERMS

Scientists began to develop theories on how to mathematically describe gas adsorption for the purpose of surface area determination around the time of World War I. At that time, the primary objective was to maximize the adsorptive capacity of activated carbon, the active ingredient in gas masks (6). In its characteristic isotherm plot, charcoal shows a constant uptake of gas that slows gradually as pressure increases toward the saturation point, see Figure 5.
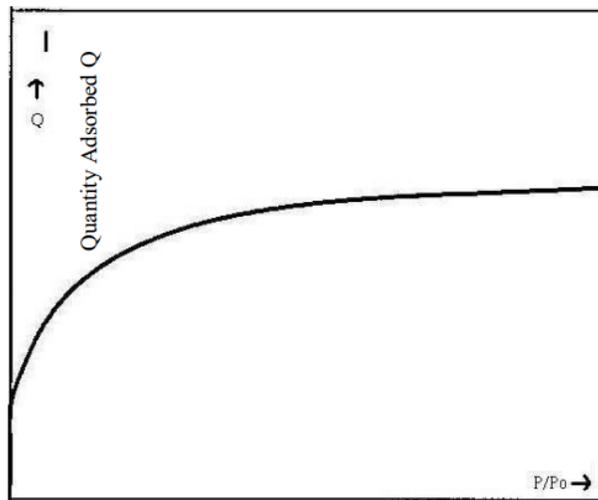

Figure 5: The characteristic isotherm of charcoal.

Dr. Langmuir is the first well-known, widely-cited researcher in the gas adsorption theorizing field. He envisioned a number of adsorptive molecules bombarding the test surface within a given time. At any moment, there is a certain amount of unoccupied surface space, and a certain probability for gas molecules to either stick to the surface or to bounce off. The rate of adherence (condensation to the surface) versus the rate of departure (evaporation from the surface) will eventually equilibrate. Langmuir (7) wrote an equation describing convergence to a

monolayer, which would occur in cases of his activated carbon test material, charcoal, or any other similar material having exceedingly small narrow pores (i.e., microporous solids, pore diameter < 2nm (3)). The IUPAC document on gas adsorption designates the gradually decreasing uptake of adsorptive as a Type I isotherm (8).

Twenty years after Langmuir's seminal publication, three others collaborated to extend the theory into broader use. Applying a host of gaseous adsorptives (e.g., N2, O2, Ar, CO, CO2, SO2, C4H10) to 30 different solids, they recorded many isotherms (9). All of the isotherms were S-shaped (with and without hysteresis): concave at low pressures, convex at high pressures, with a straight connector between the two regions (see Figure 6).
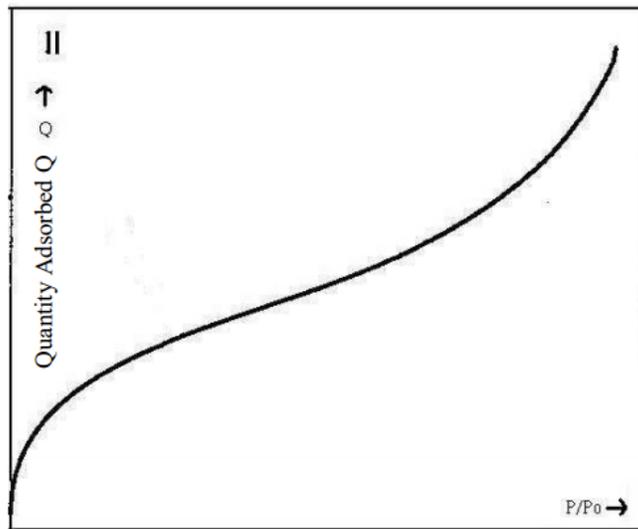

Figure 6: The typical profile of an isotherm produced by gas adsorption on macroporous solids.

The only exception was for the charcoal, which came out confirming Langmuir's results. The straight portion tended to always occur at the range 5 – 35% of saturation pressure (0.05 – 0.35 P/P0) for the gas in use. Their belief was that multilayers are more realistic than Langmuir's perfect monolayer. The researcher theorized that adsorptive molecules tend to condense first where there is highest potential to do so—inside a step or groove as in Figure 7 where two or three sites are attracting the molecule instead of just one site on a flat plane or in a narrow groove where both walls are attractive, as in Figure 8.
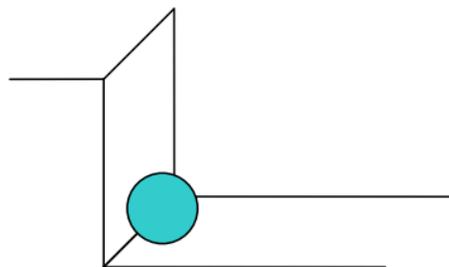

Figure 7: A gas molecule preferentially adsorbs in a "step" on a material surface because two faces are providing the attractive force.
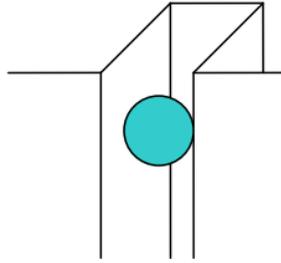
Figure 8: A gas molecule preferentially absorbs in a "groove" in the material surface because attractive forces are overlapping from either side.

As more molecules condense with increasing pressure, the open sites become occupied, so the probability increases that a gas molecule will land on another of its kind rather than on an empty site. For this reason, it's probable that multilayers build up before a perfect monolayer would form. The researchers, therefore, abandoned the concept requiring a monolayer to find surface area and instead developed an equation to calculate surface area understanding the multilayer possibility. Their self-claimed features of the derivation for the condition of multimolecular layers are the following:

- The equitation shows the shape of the isotherm
- The heat of adsorption for the first molecular layer is included in the equation
- The volume of gas needed for a monolayer is included (9).

The equation for this is shown in Equation 3:

$$\frac{P}{V(P - P_0)} = \frac{P}{P_0}\left(\frac{c-1}{V_m c}\right) + \frac{1}{V_m c}$$

[Equation 3]

where

- P/P_0 is the pressure of the adsorbate relative to its saturation pressure, known as the relative pressure
- P_0 is the gas saturation pressure
- V is the volume of gas admitted into the sample chamber
- c is the so-called BET constant
- P is the partial saturation pressure of the adsorptive gas in equilibrium with the surface
- V_m is the volume of gas needed to create a monolayer on the sample.

An astute eye may notice the same format above as in the equation of a straight line (Equitation 4, Figure 9)

$$y = mx + b$$

[Equation 4]

where

- m is the slope of the line $\left(\dfrac{c-1}{V_m c}\right)$
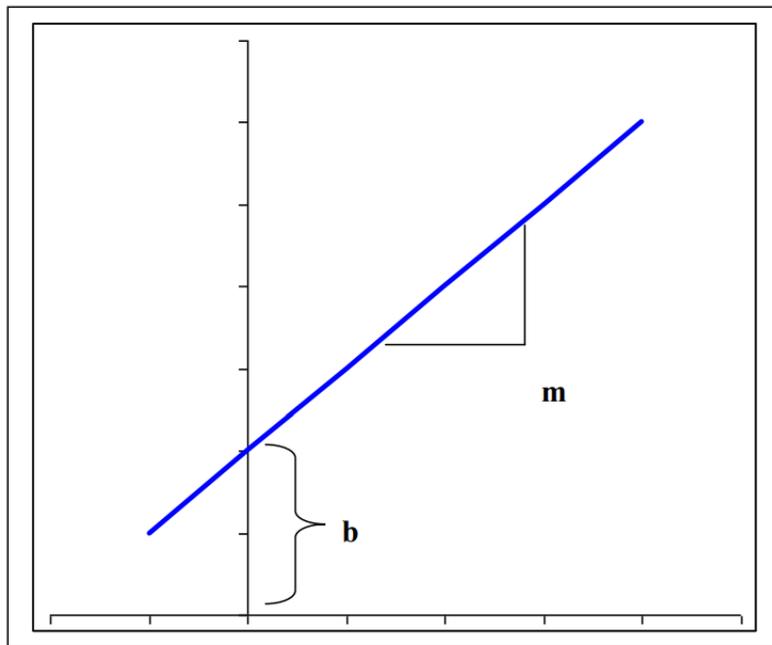
- b is the y-intercept $\left(\dfrac{1}{V_m c}\right)$.

Figure 9: Typical schematic of a straight line following the equation y = mx + b.

Aligning the two equations, the slope is $(c-1)/V_m c$ and the y-intercept is $1/V_m c$ A plot of P/V(P-P0) as the y-axis versus P/P0 on the x-axis gives the line illustrated in Figure 10.
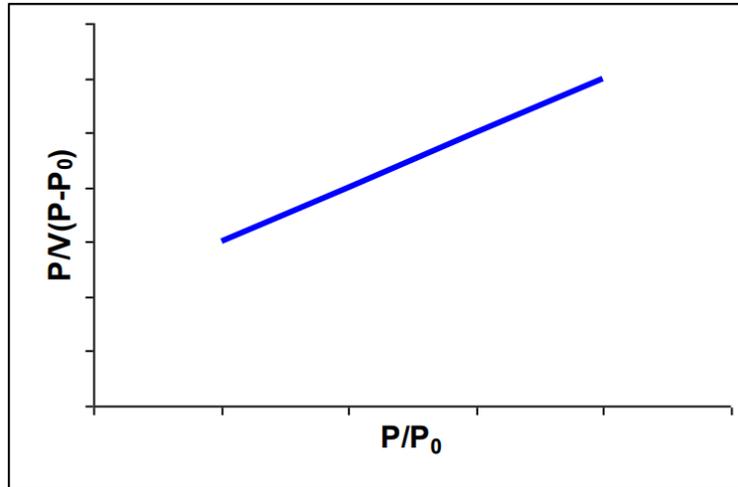
Figure 10: The typical BET plot with labeled axes.

This applies in that straight connector region of the S-shaped isotherms between the shoulder point where the monolayer exists and the next inflection point where multilayers have been established and the pressure begins to grow enough to cause the onset of bulk condensation.

The researchers who came up with this model? Drs. Brunauer, Emmett, and Teller, commonly known as BET. The so-called BET method is by far the most popular theoretical model used to depict gas adsorption and resolve specific surface area at this time. However, the theories of Langmuir and others are still viable and applicable in certain cases. It is important to remember that different materials will adsorb different gases in different ways. For specific industries and/or applications, other theories may be optimal.

The situations in which BET applies are for materials producing IUPAC's designated Type II and Type IV isotherms (Figure 11).
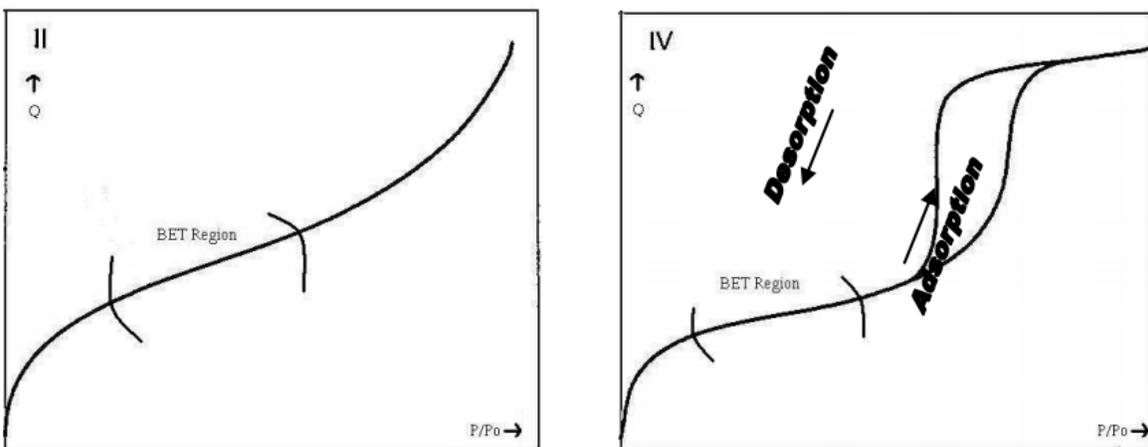

Figure 11: Type II isotherm (left) and Type IV isotherm (right) both showing the BET region.

Type II is the output of a typically nonporous or at most macroporous (>50 nm diameter (3)) solid, in which adsorption is free to occur without restriction since the surfaces are so large and

flat relative to the gas molecule size. Type IV isotherms differ from Type II in the occurrence of hysteresis, where adsorption is still reversible but not at the same rate. This occurs for mesoporous solids (2-50 nm diameters (3)) because the gas condenses in the pores earlier than on the bulk surface. By applying nuances of experimental setups, the gas adsorption technique can detect pore sizes from a fraction of a nanometer to over 100 nm.

The constant c in the BET equation has a physical meaning alluded to in the researchers' claims regarding their derivation. It relates to the strength of the interaction between the adsorbate gas and the adsorbent solid; the greater the c value, the stronger the attraction between the two. Typical values for c are 5-300; an extremely high value could begin to indicate unusually high attraction as in a microporous sample. As c increases, the inflection point of the isotherm curve at the onset of the BET region sharpens and moves to lower pressures.

Quantachrome, a well-known surface area instrument manufacturer, distributed a paper explaining concisely how to tell whether BET theory applies to collected data (10). A key theme is to be sure the straight portion of the isotherm is used for data reduction. This can be evaluated through the use of a correlation coefficient, an indicator of fit to a straight-line equation. When the correlation coefficient, usually a fraction, hits its maximum of 1, the line is perfectly straight, thus the points are a perfect fit to a straight line. Whether the correlation coefficient is low because the slope is still equilibrating to monolayer formation, or because the slope is increasing toward saturation and all multilayer equilibrium has passed, these conditions are not part of BET's region of interest or applicability. Many other caveats are also shared in the paper. This paper is highly recommended for those exploring the surface area of newly analyzed materials.

It must be remembered that focusing on a straight line can be misleading on occasion. In a Type I isotherm situation (where Langmuir—not BET—is appropriate), a correlation coefficient indicating a straight line fit may occur. This does not mean success for Langmuir! It only means the Langmuir equation fits the isotherm, nothing further (2).

HOW DO THE PROCEDURE AND INSTRUMENTATION WORK?

Key to the success of gas adsorption analysis is representative sampling and preparation of the material to be analyzed. At the risk of stating the obvious, gas adsorption only works with powders or dry solids, no liquids. The most statistically sound sampling technique is riffling. Riffling and other methods are described in ISO 8213:1986 (11); they should be used for all powder subdivision endeavors where practical.

The representative sample is loaded into a glass 'cell' that either resembles a test tube or something to that effect. As seen in Figure 12, their bulb and stems can vary greatly in size and shape depending on analytical needs.

Figure 12: Examples of surface area cells.

Powders can be loaded relatively easily, but rigid bodies would require a special design to get them in and out of the bulb while avoiding destruction. The sample weight must be known to complete the specific surface area determination. The weight must also be optimal—too low and there is insufficient detection signal, too high and preparation and analysis would take an impractically long time. In addition, a temperature gradient throughout an overly large powder bed or solid substrate could cause errors when the assumption is an isothermal condition.

During handling between production and analysis, solids are likely to acquire uncontrollable, inconsistent amounts of physically adsorbed vapors/gases/moisture. These would alter the intended adsorption properties of the material if they weren't removed, rendering the surface area results variable at best. Standard procedure, therefore, is to condition every sample before analysis to remove contaminants from the surface. The two most common techniques are either to flow inert gas over the sample or to hold it under vacuum, both often at elevated temperatures. A thorough study will demonstrate the maximum temperature at which, after a reasonable period of time, either the weight of the sample is steady (adsorbates are removed and decomposition is not occurring) or a vacuum reading is minimized and steady. The temperature, time, pressure, and technique must be defined in the analysis report (12) and should be used consistently for all subsequent preparations of the same material when data comparisons will be of use. These parameters are critical factors in establishing surface area test methods.

A thermogravimetric analysis (TGA) can show the decomposition of the solid so that a logical temperature may be chosen below that critical point. Melting points given by material safety data sheets (MSDSs) are also good starting points, although they are sometimes risky if changes happen cooler than the melting point. Differential scanning calorimetry (DSC) is another useful resource when attempting to identify a melting point. While it is tempting to increase the temperature to speed the process up (it can sometimes take tens of hours to fully clean a sample), be careful. At an inappropriate temperature, the sample can be ruined by melting, sintering, dehydration, or the like, none of which would produce a true clean surface of the originally intended material. In addition, chemisorbed water as in hydrated materials must be kept intact in most cases. Overall, successful outgassing conditions will show reproducible gas adsorption plots, constant weight (no decomposition), and no detectable chemical or physical changes in the test material (12).

CONDITIONING TECHNIQUES

A vacuum system, although expensive, is a convenient conditioning system because a simple gauge makes it easy to see when outgassing is complete. The calibration of the gauge means an absolute number representing completion is difficult to define, but 7.5 millitorr is claimed by Quantachrome and single digits of Pascals by ISO (2, 3). Typically, it is more important to reach a consistently low vacuum than it is to achieve a specific minimum value. Since some instruments need to pull a vacuum to start the analysis, conditioning by vacuum is a jumpstart. Because light powders (i.e., those of low bulk density) may elutriate and get drawn up the stem when the vacuum is initially applied, the valves must be carefully manipulated or the analyst should use cells designed with broader stems for gentle flow rates.

The flowing gas technique, while simple and basic to set up, is harder to read to determine whether it is completed. It also typically needs higher heat to drive off contaminants than does vacuum due to the basic thermodynamics involved.

Sensitive materials can benefit from other techniques like cryogenic conditioning or careful heating schedules. The cryogenic technique involves cycling between adsorption and desorption by super-cooling and then warming the sample while adsorptive gas is flowing over it and carrying contaminants away. Researchers have experimentally proven the technique (2). Samples having water in very small pores benefit from stepwise heating. Instead of setting a high temperature where the water in the smallest pores boil and cause a chemical change, stepwise heating is recommended so that surface moisture is pulled off first, then the higher temperature cleans the smaller pores.

INSTRUMENTATION

Once the sample is completely cleaned and returned to ambient conditions, it is ready for analysis. Since the surface area is the property of the solid, the technique by which it is determined generally shouldn't matter, and similar results will always be produced for similar materials of comparable physical and chemical makeup. However, once an adsorbent/adsorbate system is established, it should always be used so that true comparisons

can be made. Being an old concept, the interest in measuring surface area of a vast array of materials having their own huge varieties of physical properties has necessitated many analyzer inventions over the years. While the dated concepts still apply, modern technology has minimized human input and increased sensitivity of the detectors for our convenience. The detection method can be volumetric, gravimetric, calorimetric, or spectroscopic (3). Allen comprehensively describes all in his book on gas adsorption (13). The two major currently used techniques in the pharmaceutical industry detailed in the United States Pharmacopoeia (USP) Chapter are described as follows (12).

Method I. Dynamic Flow

In the dynamic flow method, a mixture of adsorptive gas with helium (which generally will not adsorb to anything at the analysis conditions) at a known relative pressure of the adsorptive at liquid nitrogen temperature (P/P0 < 1) is flowed at a known rate through an initial thermal conductivity cell, then through the sample under liquid nitrogen, then through a second thermal conductivity cell. Because the sample is super-cooled, the adsorptive (usually nitrogen) adsorbs to some degree on its surface, so an imbalance in adsorptive content is detected (before versus after). The conductivity detectors commonly feed an electronic integrator that registers a series of pulses proportionate to the imbalance. A schematic is detailed in USP (12). These pulses are counted and integrated by creating a curve rising from baseline through a maximum peak back down to baseline on a stripchart recorder connected to the device. The rise occurs as the increase in imbalance grows; as the detectors return to their equivalent state, the deviation from baseline falls back down to zero.

When the cold liquid nitrogen is removed from the sample cell, the driving force of gas condensation (low temperature) is no longer present, so the gas desorbs. This desorption is often "encouraged" by quickly immersing the sample cell in some room-temperature water. By the same mechanism as described above, another deviation from baseline is produced, this one falling below the baseline at or near the same peak magnitude.

The steps are repeated for a series of adsorptive/helium mixtures of increasing relative pressure P/P0 for a total of three mixtures between P/P0 = 0.05 – 0.30. The area under each curve is proportionate to the surface area of the sample. Because the desorption peak usually has sharper definition at the edges, it is used for data reduction. To define the proportion, a calibration is conducted by admitting a known volume of pure adsorptive into an empty system. Because the amounts adsorbed and desorbed are known and identical (no sample is present to take up molecules), the instrument is dialed in to the known volume. ISO advises that the peaks for both the calibration and the sample should be at approximately equal sizes for detection and equivalency (3, 4). Nitrogen is the most common of the used adsorbates, but Krypton may be used as well. The BET calculations apply to this technique.

Dynamic flow is an advantageous method because it reports on a direct measurement basis (not by differences) and is relatively simple to set up. No complex costly vacuum system is needed and no corrections for dead space complicate the calculations (14). However, the claimed advantage of speed is becoming a characteristic dependent upon perspective. Dynamic flow is human dependent, while more modern techniques tend to allow a "set it and walk away"

approach, allowing the analyst to multitask instead of continually monitoring the apparatus. The minimum detection limit for dynamic flow is about 0.1 m2 or so (other instrumentation designs can go lower at greater confidence), and it requires cumbersome numbers of compressed gas tanks filling up the lab or equipment on site for mixing known concentrations of gas with the associated control procedures in place for regulated environments. Gas mixtures like these are prone to thermal diffusion, so employing a perfect mixture at the varying temperatures can be difficult.

Method II. Volumetric (Static Pressure)

More recent instrumentation employing sensitive pressure transducers makes the volumetric method possible. The volume of empty space in the sample cell (i.e., the volume not occupied by the sample, or "dead space") must be detected first; this technique produces data by difference. Filler rods are typically placed in the sample cell stem to minimize unnecessary empty space and thereby increase resolution. First a vacuum is drawn on the cell to evacuate all gases. Then non-adsorbing helium fills the calibrated manifold of the instrument. Next a valve opens to admit it to the equilibrated cold sample cell (again) immersed in liquid nitrogen or some other very cold liquid medium of known temperature. The Combined Gas Law is shown in Equitation 5:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

[Equation 5]

Where
- P = pressure
- V = volume
- T = temperature

of (1) the gas at the initial condition and (2) the gas at its final condition determines the volume by difference. Alternatively, an empty but otherwise identical cell is analyzed concurrently with the occupied cell, and all determinations are made by difference. After pinpointing the empty volume, the helium is evacuated; at this point, no gas is present in the cell. Pure adsorptive (e.g., nitrogen) is admitted to the manifold of a known volume. The volume of nitrogen admitted is calculated to produce a goal P/P0, requested by the computer. For a short time, the valve between the manifold and the sample cell opens, so the nitrogen expands into the cell. The change in pressure inside the manifold (which has a fixed and known volume and temperature) gives a calculation by difference toward the amount of gas that moved into the cell.

Since the gas in the cell is now super-cooled, it condenses on the surface of the sample. The system remains static until the pressure in the cell stops falling and stabilizes, indicating the gas molecules are at equilibrium and no further molecules will adsorb. Knowing the volume of the space in the cell, its temperature (that of liquid nitrogen), and the pressure, the electronics calculate the amount of gas not adsorbed. Knowing the total amount of gas dosed into the cell as well as the amount not adsorbed, by difference the amount adsorbed is calculated (15).

Manufacturers may differ as to whether weight or volume of adsorbate is used in calculations. One quantity adsorbed vs. P/P0 point on the isotherm is now known. The instrument now increases pressure to reach the next requested P/P0 point. In this way, the dataset is built.

Advantages of the volumetric method are that pure adsorptive gas is used, so mixtures subject to thermal diffusion are not a concern. Very pure gas is preferred. ISO requires dry, clean, 99.99% purity for both the adsorptive and helium, but 99.999% purity is readily available and is generally recommended to increase precision (3). The maintenance of a known temperature is critical for a successful measurement. Scientifically, to guarantee a minimal temperature gradient in the sample cell, the sample should reside 18- 22 mm below the surface of the coolant throughout the analysis (2). ISO requires immersion at 49-51 mm (3) or 14-16 mm (4) throughout; USP does not define the requirement. Because these cold condensed gases tend to evaporate quickly at atmospheric pressure in the lab, either the bath has to elevate during prolonged analyses to maintain its level relative to the sample, or the sample has to move down (not preferable given the complicated fixed volume system), or the coolant must be drawn up by accessories like a porous jacket. The patent holders on the Isothermal Jacket (Micromeritics) designed porous insulator sleeves to draw liquid nitrogen up around the cell stem by capillary action throughout the analysis.

A clear disadvantage to the volumetric method is that all the moving parts can wear and create potential for leaks, rendering the vacuum system useless. Periodic testing for leaks is easily done to thwart these issues.

The most influential regulatory bodies (i.e., ISO, ASTM, and USP) all approve using gas adsorption in conjunction with the BET method to determine surface area. Two of them also require recording data at not less than three values of P/P0 (USP, 12) or four values (ISO, 3) in the range P/P0 = 0.05 – 0.3. Both bodies also require a straight line to be produced in order to apply the BET theory; USP actually requires a correlation coefficient > 0.9975 (r^2 > 0.995). ISO requires the y-intercept (and therefore, mathematically, the c value) to be positive. Combining both conditions would give the most robust output.

The Gravimetric Method

The gravimetric method of data collection is cited but antiquated and not so popular, having been eclipsed for efficient quality control purposes by the methods described above. ISO mentions it in passing and Allen goes into depth (3, 13). Here, not volume but weight of the adsorptive gas is monitored. A sample is suspended from a delicate quartz spring or electrobalance in an evacuated chamber. The adsorptive gas is added at constant pressure stepwise until a constant weight is detected. This endpoint indicates no more adsorption sites are available. The weight of adsorptive is pinpointed from calibrations (14).

SIMPLIFYING SUBSEQUENT MEASUREMENTS

Once a sample/adsorbate system is evaluated and proven for precision and accuracy by repeating measurements with several fresh samples of the same material (through method validation, for example), the c value is established. If c is much greater than 1 and consistent

over the measurement set, it is then acceptable to simplify the analysis down to a single P/P0 point. The sheer time savings is the main benefit sought here. One option offered by ISO (3) is to record data for one P/P0 point, then to fill in c and yintercept values generated during the multipoint testing. Academically, as long as c is relatively large (so that 1/c approaches 0), a multipoint BET plot is essentially the same as a single point plot (from the BET equitation, Equitation 6).

$$c = 1 + \frac{slope}{y - \mathrm{int}\, ercept}$$

[Equation 6]

From this equation, it can be seen that bringing the y-intercept very close to 0 supports the large c statement. Thomas et al. explore the error incurred by running one point versus three: increasing the value input for P/P0 decreases error, especially as c increases, so it is advised to use the maximum P/P0 within the BET region (2). This is conventionally taken as P/P0 = 0.3.

WHAT IF NITROGEN DOESN'T WORK?

At very low surface areas (< 0.5 – 1 m2 /g) it becomes difficult to adsorb enough nitrogen gas to be detectable. To overcome this drawback, a straightforward solution is to increase the sample weight. Unfortunately, the range here is limited—only so much sample weight is practical. A preferred method that makes a more significant difference is to change the adsorptive gas. Nitrogen's saturation pressure P0 at liquid nitrogen temperature is 760 torr, whereas krypton's P0 is only 2.5 torr at the same temperature. Therefore, at any given time, for every 2.5 Kr molecules in a volume of free space there would exist 760 N2 molecules. With far less unadsorbed krypton obscuring detection, the sensitivity of the instrument increases (6).

In any case, the USP advises that samples ≤ 0.2m2 /g be analyzed by krypton, and that at least 1 m2 of nitrogen (0.5 m2 of krypton) be adsorbed to keep detection levels robust. These minimum adsorbed quantities may be decreased after a method is validated.

Changing the adsorptive gas can change the surface area result. While surface area of a material shouldn't be variable (it's the property of the solid), a change in its detector can mean varying reports. This is mainly due to possible differences in reactivity between the gas and the solid, but is more likely due to differences in the ability of the gas molecules to access adsorbing sites on the solid. Although nitrogen might be smaller than krypton by its location on the periodic table, scientifically it exists as a diatom and is, therefore, long and narrow. Argon is close to nitrogen in cross-sectional area but is more rounded, allowing it greater access to the thinnest pores.

No matter what technique is used, both ISO and USP require periodic verification of instrument performance using certified reference materials. USP advises that the references be of a specific surface area at or near that of the test material.

CONCLUSION

Surface area is an important property of a solid governing its capacity for reaction with many environmental stimuli. Often, such materials have surface area specifications in order to monitor their quality of production. The specific surface area of any solid may be determined by first developing a gas adsorption isotherm, then by using the well-established BET method of calculating the area occupied by the adsorbed gas within a specific region shown by the isotherm. Automated instrumentation is available to do so, but the quality of its output depends significantly on the controls employed during sample preparation and instrument setup. Using the guidelines established by regulatory bodies, consistent results for surface area may be generated over many years to monitor quality control.

ARTICLE ACRONYM LISTING

BET Brunauer, Emmett, and Teller Model
DSC Differential Scanning Calorimetry
ESD Equivalent Spherical Diameter
ISO International Organization for Standardization
IUPAC International Union of Pure and Applied Chemistry
MSDSs Material Safety Data Sheets
SA Surface Area
SSA Specific Surface Area
TGA Thermogravimetric Analysis
USP United States Pharmacopeia

ABOUT THE AUTHOR

Rebecca Lea Wolfrom is Projects Manager at Particle Technology Labs in the Chicago area. She earned a B.S. in GeoEnvironmental Engineering and an M.S. in Mineral Processing from The Pennsylvania State University under the advisorship of Dr. Richard Hogg and Dr. Subhash Chander in the College of Earth and Mineral Sciences. Prior to her employment at PTL, Rebecca was a Scientist in the formulations development department of a multinational personal care company. In her spare time, Rebecca enjoys traveling, creating with textiles, and spending time with her new puppy.

REFERENCES

1. Wolfrom, R.L., "The Language of Particle Size," GXP Compliance Vol. 15, No. 2, Spring 2011.

2. Lowell, S., Shields, S.E., Thomas, M.A., and Thommes, M., Characterization of Porous Solids and Powders: Surface Area, Pore Size, and Density, 2004.

3. ISO 9277:1995(E), Definition of the Specific Surface Area of Solids by Gas Adsorption using the BET Method, 1995.

4. ISO 15901-2:2006(E), Pore Size Distribution and Porosity of Solid Materials by Mercury Porosimetry and Gas Adsorption – Part 2: Analysis of Mesopores and Macropores by Gas Adsorption, 2006.

5. Quantachrome Instruments Primer Series, Surface Area Determination, www.quantachrome.com.

6. Webb, P.A., and Orr, C., Analytical Methods in Fine Particle Technology, 1997.

7. Langmuir, I. Journal of the American Chemical Society, Vol. 40, p. 1368, 1918.

8. IUPAC: Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscov, L., Pierotti, R.A., Rouquerol, J., and Siemieniewska, T., Pure and Applied Chemistry, Vol. 57, No. 603, 1985.

9. Brunauer, S., Emmett, P.H., and Teller, E., "Adsorption of Gases in Multimolecular Layers", Journal of the American Chemical Society, Vol. 60, p. 309, 1938.

10. Quantachrome Corporation, "Interpretation of the Multi-point BET Plot", 2003.

11. ISO 8213:1986, Chemical Products for Industrial Use – Sampling Techniques – Solid Chemical Products in the Form of Particles Varying from Powders to Coarse Lumps, 1986.

12. USP 34 / NF 29 Specific Surface Area / Physical Tests.

13. Allen, T.A., Particle Size Measurement Volume 2: Surface Area and Pore Size Determination, Fifth Edition, 1997.

14. Hogg, R., Particle Technology Laboratory, Notes on Particle Characterization, Penn State Department of Energy and GeoEnvironmental Engineering, Mineral Processing Program, MnPr 421, 2000.

15. Thomas, M., Personal communication, 2010.