

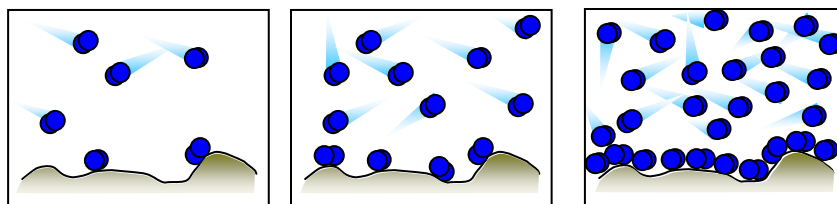
SURFACE AREA DETERMINATION

Introduction

The surface of a material is the dividing line between a solid and its surroundings, liquid, gas or another solid. We can anticipate therefore, that the amount of surface, or surface area, is an important factor in the behavior of a solid. Surface area affects, for example, dissolution rates of pharmaceuticals, the activity of an industrial catalyst, how fast cement hydrates, adsorption capacity of air and water purifiers, and the processing of most powders and porous materials. Whenever solid matter is divided into smaller particles new surfaces are created thereby increasing the surface area. Similarly, when pores are created within the particle interior (by dissolution, decomposition or some other physical or chemical means) the surface area is also increased. *There may be more than 2000 m² of surface area in a single gram of activated carbon, for example!*

Gas Sorption

The true surface area, including surface irregularities and pore interiors, cannot be calculated from particle size information, but is rather determined at the atomic level by the adsorption of an unreactive, or inert gas. The amount adsorbed, let's call it X , is a function not only of the total amount of exposed surface, but also (i) temperature, (ii) gas pressure and (iii) the strength of interaction between gas and solid. Because most gases and solids interact weakly, the surface must be cooled substantially in order to cause measurable amounts of adsorption – enough to cover the entire surface. As the gas pressure is increased, more is adsorbed on the surface (in a non-linear way). But, adsorption of a cold gas does not stop when it has covered the surface in a complete layer one molecule thick (let's call the theoretical monolayer amount of gas X_m)! As the relative pressure is increased, excess gas is adsorbed to form “multilayers”.



So, gas adsorption - as a function of pressure - does not follow a simple relationship, and we must use an appropriate mathematical model to calculate the surface area. We use the BET equation,

$$\frac{1}{X[(P_0/P)-1]} = \frac{1}{X_m C} + \frac{C-1}{X_m C} \left(\frac{P}{P_0} \right)$$

where P/P_0 is the gas's *relative pressure* and constant C is related to the strength of interaction between gas and solid. It's nice to be able to remember this equation, but not essential... just

refer back to it here when you need to. What is important is that X and P/P_0 are the data the surface area analyzer measures, and that X_m relates directly to surface area. All that remains is to convert this theoretical (we prefer to say statistical) amount of gas, X_m , to an area.

The Principles of Measurement

The gas most commonly used is nitrogen, for a number of reasons. Firstly, it is readily available in high purity. Secondly, the most appropriate coolant, liquid nitrogen, is also readily available. Thirdly, the interaction of nitrogen with most solid surfaces is relatively strong. Lastly, there is wide acceptance of the *cross-sectional area*.

In the classical *manometric* technique, relative pressures less than unity are achieved by creating conditions of partial vacuum (absolute pressures of pure nitrogen below atmospheric pressure). High-precision and accurate pressure transducers monitor those pressure changes (in a fixed and known volume) due to the adsorption process. Details of such an analyzer and the exact measurement process are described in a separate primer. This method is easily automated and the amount of gas adsorbed is made at a number different relative pressures. Usually, the analyzer obtains at least three data points in the relative pressure range between 0.025 and 0.30. Experimentally measured data are recorded as pairs of values: the amount of gas adsorbed expressed as STP volume (V_{STP}) and the corresponding relative pressure (P/P_0). A plot of these data is called an *isotherm*.



The NOVAe (*right*) is an example of a manometric surface area analyzer.

The Principles of Calculation

The computer program takes over and a least-squares linear regression is used to fit the best straight line through a *transformed* data set consisting of the following pairs of values: $1/V_{STP}(P_0/P)-1$ and P/P_0 . If you want the details, the monolayer capacity, V_m , is calculated from the slope, s ,

$$s = \frac{C - 1}{V_m C}$$

and the intercept, i , of the straight line

$$i = \frac{1}{V_m C}$$

Solving for V_m

$$V_m = \frac{1}{s + i}$$

Now we need the number of molecules in the monolayer, and we get that from the number of moles. Just divide V_m by the molar volume (M_V) for the number of moles. Multiply moles by

Avogadro's number to arrive at the number of molecules covering the surface in a layer one molecule thick. If we know how much area one molecule occupies, the total area is one simple multiplication away. Different gas molecules have different sizes and occupy different areas. We call that area the "cross-sectional area" (please see later for how we handle this). Therefore, the total surface area, S_t , is then calculated from

$$S_t = \frac{V_m L_{Av} A_m}{M_V}$$

where L_{Av} is Avogadro's number and A_m is the cross-sectional area. So what is the cross sectional area of an adsorbed nitrogen molecule? We (the surface area community) take a pragmatic approach, and assume it to be 16.2 square angstroms (0.162 nm²) on all surfaces. All surface area results are finally reported normalized by sample weight, or mass, as square meters per gram, written m²/g or m²g⁻¹.

Some important terms you should know:

Avogadro's Number: 6.022 x 10²³

BET: acronym after the developers of the surface area calculation, S. Brunauer, P. Emmet and E. Teller.

Cross-sectional area: the area occupied by a single adsorbed gas molecule

Manometric: based on changes in gas pressure

Molar Volume: the volume occupied by one mole of any gas. Equal to 22414cc (22.414 liters) at STP.

Mole (dimensionless): an amount of a substance that contains an *Avogadro's number* of atoms or molecules.

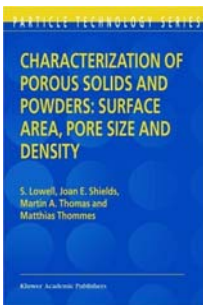
Monolayer: denoted by the subscript m, means the gas adsorbed in a layer just one molecule thick.

Relative pressure, P/Po: the ratio of absolute pressure, P, to the *saturated vapor pressure*. It has a value between 0 and 1.

Saturated Vapor pressure, Po: the pressure at which a gas liquefies at a given temperature.

STP volume: the volume occupied by an amount of gas it were at a Standard Temperature of 0degC (273.15K) and a Standard Pressure of 1 standard atmosphere. See *molar volume*.

Next Step



Further reading is recommended, and the book entitled "Characterization of Porous Materials and Powders: Surface Area, Pore Size and Density" by Lowell, Shields, Thomas and Thommes (Springer, 2004) ISBN 1402023022 gives a complete description of the gas sorption process, measurement and calculation of surface area.