Quantachrome INSTRUMENTS

Porous Material Primers

AN INTRODUCTION TO CALCULATION METHODS FOR SURFACE AREA AND PORE SIZE FROM GAS SORPTION DATA

The variety of ways to calculate surface area and pore size can, at first, seem daunting to a beginner in the field of porous materials characterization and still somewhat confusing to those who do not dedicate their lives to this particular field of study. This guide aims to give you an overview of the most commonly encountered mathematical models. It is not a detailed treatise and you are encouraged to consult the recommended reading at the end of this guide.

P/Po range	Mechanism	Calculation model
$1x10^{-7}$ to 0.02	micropore filling	DFT, GCMC, HK, SF, DA, DR
0.01 to 0.1	sub-monolayer formation	DR
0.05 to 0.3	monolayer complete	BET, Langmuir
> 0.1	multilayer formation	t-plot, α_S
> 0.35	capillary condensation	BJH, DH
0.1 to 0.5	capillary filling in M41S-type materials	DFT, BJH

Legend

DFT = Density Functional Theory

GCMC = Grand Canonical Monte Carlo

HK = Horvath-Kawazoe

SF = Saito-Foley

DA = Dubinin-Astakhov

DR = Dubinin-Radushkevic

BET = Brunauer, Emmett & Teller

Langmuir = Langmuir

t-plot = statistical Thickness method

α_S = alpha-S (Sing) method

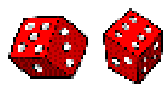
BJH = Barrett, Joyner & Halenda

DH = Dollimore-Heal

Look for the recommended methods  *scores!*

DFT 

Provides a microscopic treatment of sorption phenomena in micro-and mesopores on a molecular level, i.e. based on statistical mechanics. Complex mathematical modeling of gas-solid and gas-gas (gas-liquid) interactions plus geometrical considerations (pore geometry) leads to realistic density profiles for the confined fluid as a function of temperature and pressure. From these density profiles the amount adsorbed can be derived. Gas-solid interactions are “calibrated” against real isotherm data of non-porous material. Gas-gas-liquid interactions are “calibrated” against physical data e.g. boiling points. For pore size analysis a “kernel” is created which consists of up to 100 theoretical, individual pore isotherms. This “shopping list” is used by the software to match the experimental isotherm under test. Extensive list of kernels commercially available for a wide range of materials, pore geometry and analysis conditions. State of the art.



GCMC 

Provides a microscopic treatment of sorption phenomena in micro-and mesopores on a molecular level based on statistical mechanics. Monte-Carlo computer simulations are also considered as “computer experiments”. Similar to the DFT-theory detailed assumptions concerning details of gas-solid and gas-gas (gas-liquid) interactions and pore geometry are required to obtain realistic results. A “kernel” is created which consists of up to 100 theoretical, individual pore isotherms. This “shopping list” is used by the software to match the experimental isotherm under test. Limited availability of kernels.

HK

Direct mathematical relationship between relative pressure (P/Po) and pore size. Relationship calculated from modified Young-Laplace equation, and takes into account parameters such as magnetic susceptibility. Based on slit-shape pore geometry (e.g. activated carbons). Calculation restricted to micropore region (≤ 2nm width). Underestimates true pore size. Historical.

SF

Similar mathematics to HK method, but based on cylindrical pore geometry (e.g. zeolites). Calculation restricted to micropore region (≤ 2 nm diameter). Underestimates true pore size. Historical.

DA

Closely related to DR calculation based on pore filling mechanism. Equation fits calculated data to experimental isotherm by varying two parameters, E and n. E is average adsorption energy that is directly related to average pore diameter, and n is an exponent that controls the width of the resulting pore size distribution. The calculated pore size distribution *always* has a skewed, monomodal appearance (Weibull distribution). Historical.

DR

Simple log(V) vs $\log^2$(Po/P) relationship which linearizes the isotherm based on micropore filling principles. "Best fit" is extrapolated to $\log^2$(Po/P) (i.e. where P/Po = 1) to find micropore volume. Useful to find total micropore volume when chosen analysis conditions do not allow for complete filling during measurement.

BET

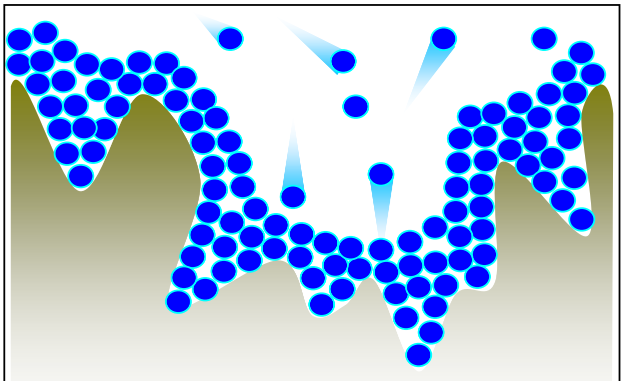
The most famous gas sorption model. Extends model of gas sorption to multi-layer. BET equation linearizes that part of the isotherm that contains the "knee", i.e. that which brackets the monolayer value. Normally solved by graphical means, by plotting 1/(V[(Po/P)]-1) versus P/Po. Monolayer volume (Vm) is equal to 1/(s+i) where s is the slope and *i* is the y-intercept. Often, BET theory is also applied to obtain the specific surface area of microporous materials, although from a scientific point of view the assumptions made in the BET theory do not take into account micropore filling. Please note, that for such samples the linear "BET" range is found usually at relative pressures< 0.1, in contrast to the classical BET range, which extends over relative pressures between 0.05 – 0.3. Despite its inability to accurately measure the true surface area of microporous materials it is easy to apply and is widely accepted.

Langmuir

Adsorption model limited to the formation of a monolayer that does not describe most real cases. Sometimes can be successfully applied to type I isotherms (pure micropore material) but the reason for limiting value (plateau) is not monolayer limit, but due to micropore filling. Therefore type I physisorption isotherm would be better called "pseudo-Langmuir" isotherm. Historical.

t-plot

Multi-layer formation is modeled mathematically to calculate a layer "thickness, t" as a function of increasing relative pressure (P/Po). The resulting t-curve is compared with the experimental isotherm in the form of a t-plot. That is, experimental volume adsorbed is plotted versus statistical thickness for each experimental P/Po value. The linear range lies between monolayer and capillary condensation. The slope of the t-plot (V/t) is equal to the "external area", i.e. the area of those pores that are NOT micropores. Mesopores, macropores and the outside surface are able to form a multilayer, whereas micropores, which have already been filled, cannot contribute further to the adsorption process. Three standard t-curves are offered (deBoer, Halsey and carbon-black, plus a fourth customizable curve called the “generalized Halsey). It is recommended to initially select P/Po range 0.2 – 0.5, and subsequently adjust it to find the best linear plot.



Multi-layer gas adsorption (artists rendition)

alpha-S 

Multi-layer formation (adsorbed amount as function of relative pressure) is compared graphically with normalized reference isotherm of a non-porous analog of sample under test. The linear range lies between monolayer and capillary condensation. The slope of the alpha-S plot is equal to the ratio of “external” areas of sample under test and of reference i.e. the areas of those pores that are NOT micropores. Mesopores, macropores and the outside surface are able to form a multilayer, whereas micropores, which have already been filled, cannot contribute further to the adsorption process. Standard alpha-S reference isotherms are available for nitrogen and argon on different oxides. It is recommended to initially select P/Po range 0.2 – 0.5, and subsequently adjust it to find the best linear plot. Does not yield quantitative surface area information directly.

BJH 

Modified Kelvin equation. Kelvin equation predicts pressure at which adsorptive will spontaneously condense (and evaporate) in a cylindrical pore of a given size. Condensation occurs in pores that already have some multilayers on the walls. Therefore, the pore size is calculated from the Kelvin equation and the selected statistical thickness (t-curve) equation. Severely underestimates size of small to medium mesopores. Acceptable for broad size distributions of medium to large mesopores. Largely superseded by DFT.

DH

Extremely similar calculation to BJH, which gives very similar results. Essentially differs only in minor mathematical details. No advantage to BJH.

NOTE on Linear Fitting Methods

BET, Langmuir, t-plot and DR all use linear regression (least squares) to fit their respective data sets. Each model can be considered to be successful in characterizing the material under test if a good correlation coefficient results. BET and Langmuir have an additional restriction; the y-intercept must be positive. The slope of a DR plot should be negative (or zero). The best t-curve is that which yields a non-negative y-intercept and linearizes over a wide P/Po range.

Other Methods

FRACTAL DIMENSION

The geometric topography of the surface structure of many solids can be characterized by the fractal dimension D, which is a kind of roughness exponent. When considering a *Euclidean* surface, D is 2, however for an irregular (real) surface D may vary between 2 and 3 and expresses so the degree of roughness of the surface and/or porous structure. The determination of the surface roughness can be investigated by means of the modified Frenkel-Halsey Hill method, which is applied in the range of multilayer adsorption.

Glossary

Capillary condensation: formation of liquid like phase (complete with meniscus) in the confines of a mesopore.

Euclidean: planar, flat, (*c.f.* three-dimensional curved geometry)

M41S: a class of materials having a regular array of pores of narrow size distribution, often referred to as mesoporous molecular sieves.

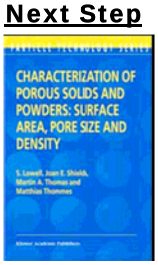
Mesopore: by definition, a pore between 2 and 50 nm diameter or width.

Micropore: a pore of molecular dimensions, by definition less than 2nm diameter or width.

Monolayer: a layer of adsorbed gas one molecule thick (a monomolecular layer).

Multilayer: an adsorbed film of adsorbed gas two or more molecules thick (a multimolecular layer).

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 and pore size.