# Gas Adsorption Theory

Presented by Micromeritics Instrument Corporation

Adsorption Defined

Similiar to surface tension, adsorption is a consequence of surface energy. Most atoms that make up a solid are bound on all sides by other atoms in the bulk of the solid. The atoms on the surface of the solid, however, are incompletely bound. Due to van der Waals forces of interaction, these surface atoms are more reactive and they attract gas, vapor, and liquids to satisfy the imbalance of atomic forces.
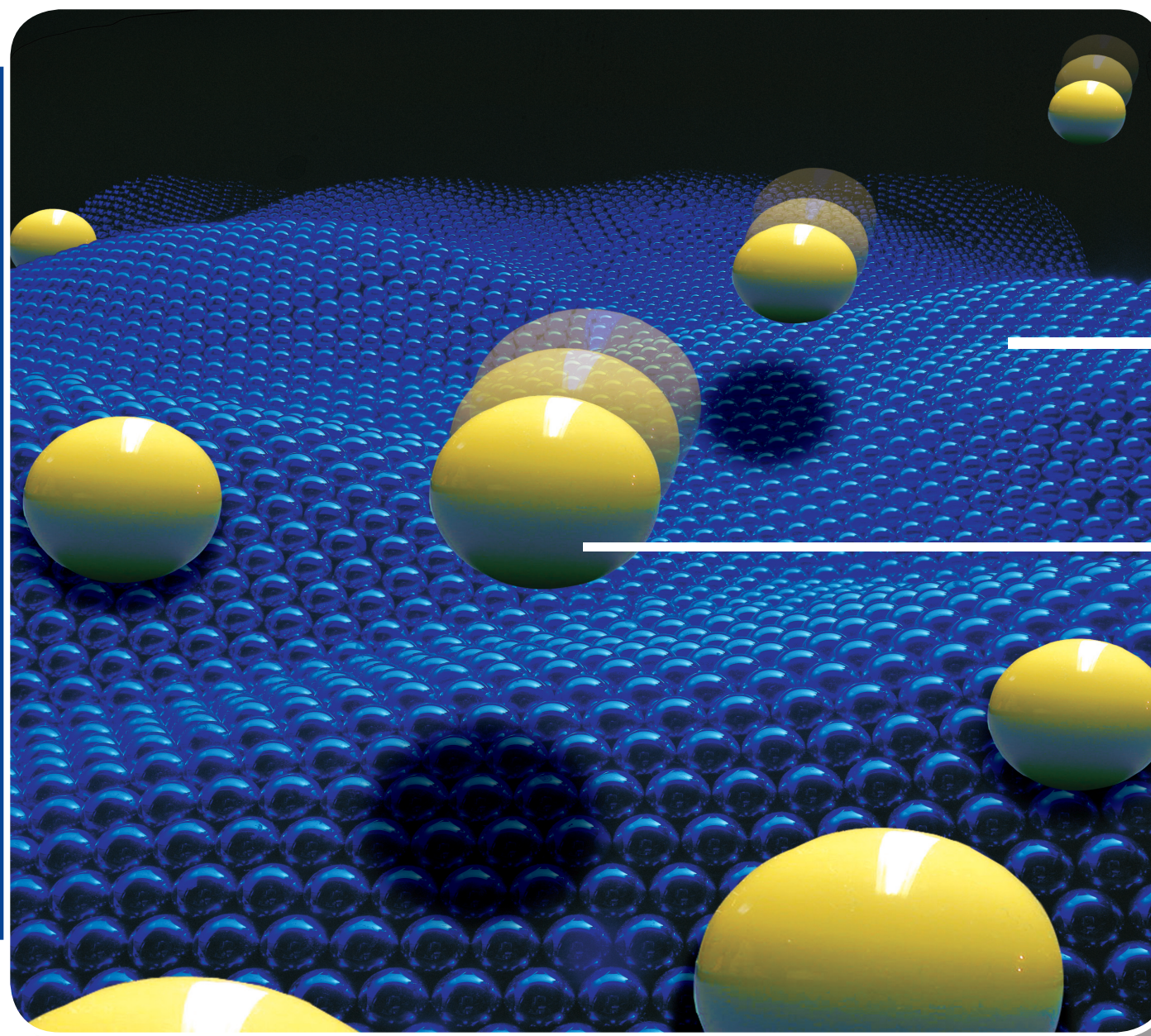
These surface molecules (in blue) are experiencing a bond deficiency, thus it is energetically favorable for them to adsorb molecules. (in yellow).

Stage 1 in diagram below.

Surface Area

Surface area helps determine such things as how solids burn, dissolve, and react with other materials. To determine the surface area, solid samples are pretreated by applying some combination of heat, vacuum, and /or flowing gas to remove adsorbed contaminants acquired (typically water and carbondioxide) from atmospheric exposure. The solid is then cooled, under vacuum, usually to cryogenic temperature (77 k, -195 °C). An adsorptive (typically nitrogen) is dosed to the solid in controlled increments. After each dose of adsorptive, the pressure is allowed to equilibrate and the quantity adsorbed is calculated. The quantity adsorbed at each pressure (and temperature) defines an adsorption isotherm, from which the quantity of gas required to form a monolayer over the external surface of the solid is determined. With the area covered by each adsorbed gas molecule known, the surface area can be calculated.
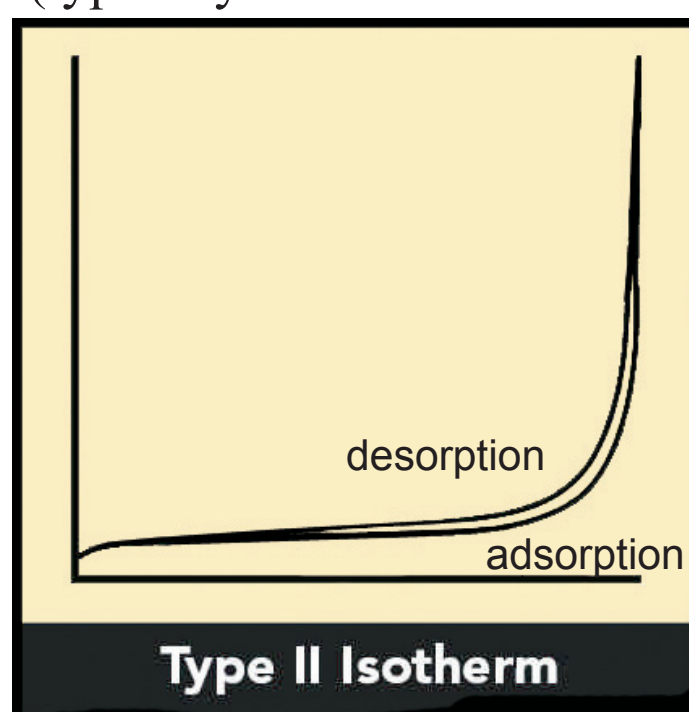
desorption
adsorption
Type II Isotherm

Porosity, Pore Sizes and Pore Distributions

Surface area determinations involve creating the conditions required to adsorb an average monolayer of molecules onto a sample. By extending this process so that the gas is allowed to condense in the pores, the sample's fine pore structure can be evaluated. As pressure increases, the gas condenses first in the pores with the smallest dimensions. The pressure is increased until saturation is reached, at which time all pores are filled with liquid. The adsorptive gas pressure then is reduced incrementally, evaporating the condensed gas from the system. Evaluation of the adsorption and desorption branches of these isotherms and the hysteresis between them reveals information about the size, volume, and area.
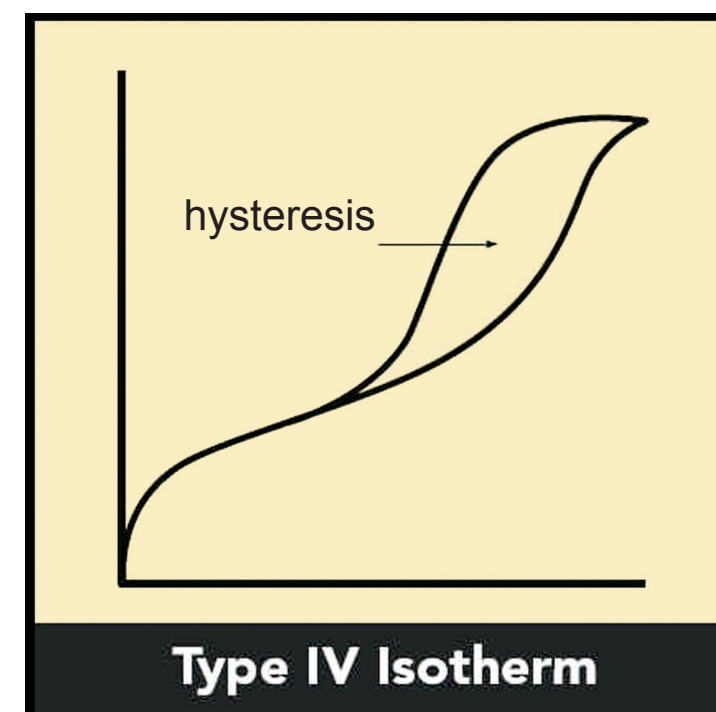
hysteresis
Type IV Isotherm

Chemisorption Determinations

Chemisorption is used to determine the percent metal dispersion, active metal surface area, size of active particles, and surface acidity of catalyst materials. The dispersion is the ratio of active sites to total sites on a catalyst.
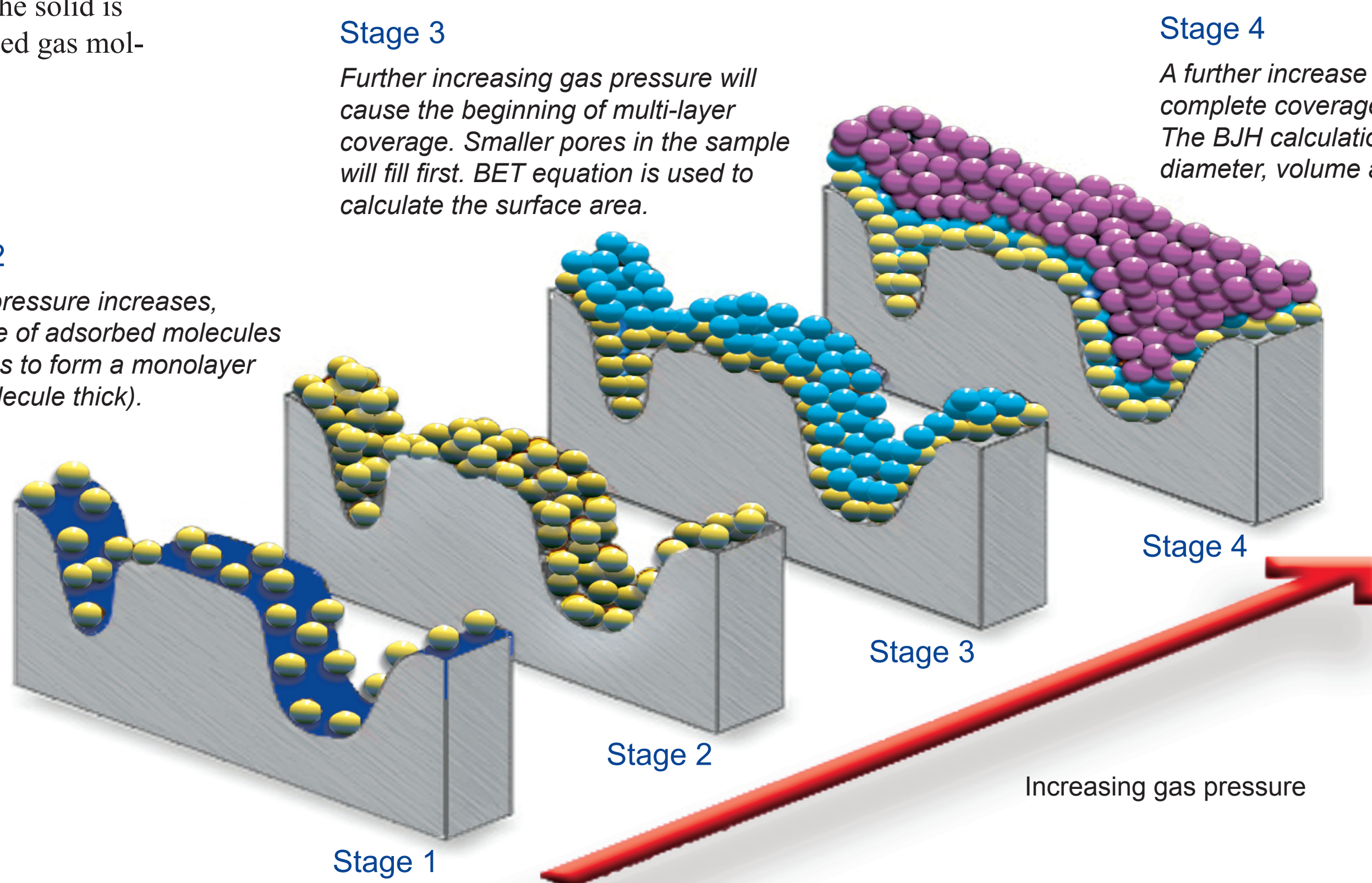
Active Metal Dispersions

Chemisorption is the interaction of an active gas and a solid surface, involving the sharing of electrons between the adsorptive molecule and the solid surface. It is generally assumed that a chemisorbed layer will not exceed a single molecule in thickness. The efficiency of a catalyst in promoting a chemical reaction is related directly to the density of active sites on is surface.

Stage 3

Further increasing gas pressure will cause the beginning of multi-layer coverage. Smaller pores in the sample will fill first. BET equation is used to calculate the surface area.

Stage 4

A further increase in the gas pressure will cause complete coverage of the sample and fill all the pores. The BJH calculation can be used to determine pore diameter, volume and distribution.

Stage 2

As gas pressure increases, coverage of adsorbed molecules increases to form a monolayer (one molecule thick).

Stage 1

Isolated sites on the sample surface begin to adsorb gas molecules at low pressure.

Stage 4
Stage 3
Stage 2
Stage 1

Increasing gas pressure

Data Reduction Methods

Langmuir
provides a means of determining surface area based on a monolayer coverage of the solid surface by the adsorptive.

BET
the method of Brunauer, Emmet, and Teller is employed to determine surface area on a model of adsorption which incorporates multilayer coverage.

BJH
the method of Barrett, Joyner, and Halenda is a procedure for calculating pore size distributions from experimental isotherms using the Kelvin model of pore filling. It applies only to the mesopore and small macropore size range.

deBoer t-Plot
is most commonly used to determine the external surface area and micropore volume of microporous materials. It is based on standard isotherms and thickness curves which describe the statistical thickness of the film of adsorptive on a non-porous reference surface.

MP-Method
is an extension of the t-Plot method. It extracts micropore volume distribution information from the experimental isotherm.

Dubinin Plots
relate the characteristic energy of adsorption to micropore structure.

Medek
uses Dubinin plots to determine micropore volume distributions by pore size.

Horvath-Kawazoe Technique
provides a means by which the micropore volume distribuiton by size is extracted from the experimental isotherm. The original H-K method is based on slit-shaped pores, however additions by Saito-Foley and Cheng-Yang extend the method to apply to cylindrical and spherical pores, respectively.

Deconvolution by Classical Model Fitting
this method determines the best fit (in a least squares sense) of a set of single-mode model isotherms to the experimental isotherm. The solution set represents the pore volume distribution by size for the solid on which the isotherm was developed.

DFT Plus
density functional theory provides a method by which the total expanse of the experimental isotherm can be analyzed to determine both microporosity and mesoporosity in a continuous distribution of pore volume in respect to pore size.

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