ASAP® 2020

ACCELERATED SURFACE AREA AND POROSIMETRY SYSTEM

micromeritics®

CALCULATIONS

Apr 2024

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ALPHA-S METHOD

The alpha-S curve is calculated from the reference isotherm by dividing each quantity adsorbed by the quantity adsorbed at 0.4 relative pressure.

$$\alpha_i = \frac{Q_i}{Q_{0.4}}$$

where $Q_{0.4}$ is found by linear interpolation.

A least-squares analysis fit is performed on the $(\alpha_i, Q_{ads,i})$ data pairs where α_i is the independent variable and $Q_{ads,i}$ is the dependent variable. The following are calculated:

   a. Slope (S cm^3/g STP)
   b. Y-intercept (Q_0 cm^3/g STP)
   c. Error of the slope (cm^3/g STP)
   d. Error of the Y-intercept (cm^3/g STP)
   e. Correlation coefficient

Surface area is calculated as:

$$A_s = \frac{A_{ref} S}{Q_{0.4}}$$

Pore size is calculated as:

$$\frac{Q_0 V_{mol}}{22414 \text{cm}^3 \text{STP}}$$

where V_{mol} is liquid molar volume from the fluid property information.

BET SURFACE AREA

The BET[1] transformation is calculated as:

$$y = \frac{1}{Q(\rho^0/\rho - 1)}$$

A least-squares fit is performed on the P_{rel}, y. The following are calculated:

   a. Slope (S cm^3/g STP)
   b. Y-intercept (y_0 cm^3/g STP))
   c. Uncertainty of the slope (u(s) cm^3/g STP))
   d. Uncertainty of the Y-intercept ($u(y_0)$ cm^3/g STP))
   e. Correlation coefficient

Using the results of the above calculations, the following can be calculated:

BET Surface Area (m^2/g):

$$A_s = \frac{A_m N_A}{V_m(s+y_0)} \times 10^{-18} m^2/nm^2$$

BET C value:

$$C = \frac{s}{y_0} + 1$$

Quantity in the Monolayer (cm^3/g STP):

$$Q_m = \frac{1}{Cy_0} = \frac{1}{s+y_0}$$

Error of the BET Surface Area (m^2/g):

$$u(A_s) = \frac{\sqrt{u^2(s)+u^2(y_0)}}{s+y_0}$$

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[1] Brunauer, S.; Emmett, P.H.; and Teller, E., *J. Am. Chem. Soc. 60*, 309 (1938).

BJH PORE VOLUME AND AREA DISTRIBUTION

For adsorption data, the relative pressure and quantity adsorbed data point pairs collected during an analysis must be arranged in reverse order from which the points were collected during analysis. All calculations are performed based on a desorption model, regardless of whether adsorption or desorption data are being used.

The data used in these calculations must be in order of strictly decreasing numerical value. Points which do not meet this criterion are omitted. The remaining data set is composed of relative pressure (P), quantity adsorbed (Q) pairs from (P_1, Q_1) to (P, Q_n) where ($P_n = 0$, $Q_n = 0$) is assumed as a final point. Each data pair represents an interval boundary (or desorption step boundary) for intervals i=1 to i=n-1 where n = total number of (P, Q) pairs.

Generally, the desorption branch of an isotherm is used to relate the amount of adsorbate lost in a desorption step to the average size of pores emptied in the step. A pore loses its condensed liquid adsorbate, known as the core of the pore, at a particular relative pressure related to the core radius by the Kelvin[1] equation. After the core has evaporated, a layer of adsorbate remains on the wall of the pore. The thickness of this layer is calculated for a particular relative pressure from the thickness equation. This layer becomes thinner with successive decreases in pressure, so that the measured quantity of gas desorbed in a step is composed of a quantity equivalent to the liquid cores evaporated in that step plus the quantity desorbed from the pore walls of pores whose cores have been evaporated in that and previous steps. Barrett, Joyner, and Halenda[2] developed the method (known as the BJH method) which incorporates these ideas. The algorithm used is an implementation of the BJH method.

EXPLANATION OF TERMS

A pore filled with condensed liquid nitrogen has three zones:

- **Core.** The *core* — evaporates all at once when the critical pressure for that radius is reached; the relationship between the core radius and the critical pressure is defined by the Kelvin equation.
- **Adsorbed layer.** The *adsorbed layer* — composed of adsorbed gas that is stripped off a bit at a time with each pressure step; the relationship between the thickness of the layer and the relative pressure is defined by the thickness equation.
- **Walls of the cylindrical pore.** The *walls of the cylindrical pore* — the diameter of the empty pore is required to determine the pore volume and pore area. End area is neglected.

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[1] Kelvin, J. (published under the name of Sir William Thomson), *Phil. Mag. 42*, 448-452 (1871).

[2] Barrett, E.P.; Joyner, L.S.; and Halenda, P.P., *J. Am. Chem. Soc. 73*, 373-380 (1951).
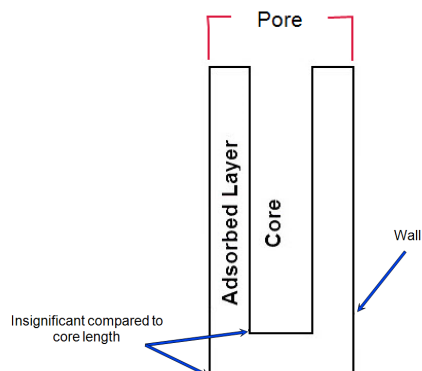
CALCULATIONS

The quantities adsorbed (Q_a) are converted to the liquid equivalent volumes (V_l, cm^3/g)

$$Vl_i = \frac{Q_i V_{\text{mol}}}{22414 \text{cm}^3 \text{STP}}$$

where V_{mol} is the liquid molar volume from the fluid property information.

The relative pressure (P_i) is assumed to be close to unity so that substantially all the pores in the sample are filled.

The corresponding Kelvin core radius is calculated. Only pores smaller than this size will be included:

$$Rc_i = \frac{-A}{(l+F)\ln(P_i)}$$

where

    A   =   adsorbate property factor (from the *BJH Adsorptive Options* window)

    F   =   fraction of pores open at both ends (from the *BJH Adsorption Report Options* window or the *BJH Desorption Report Options* window); assumed to be zero for desorption

    Rc   =   Kelvin radius (Å) of core

This radius will be adjusted for the thickness of the adsorbed layer during subsequent calculation steps.

The following calculations (a-c) are made for each relative pressure interval based on the increment of volume desorbed during that interval:

where

i	=	interval number, that is i=1 for the first interval from P_1 to P_2, and so on
j	=	each previous interval during which new pores were found
k	=	the total number of intervals in which new pores have been found. It is also the number of lines reported on the BJH table for collected data

a. The thickness of the adsorbed layer at the end of the interval is calculated using the equation located in *Thickness Curve on page 64*.

For the last pressure interval from the lowest Pr_i to zero relative pressure, reference the calculations from the equations in *Thickness Curve on page 64*.

For the first pressure interval, there are no previously opened pores so the volume of liquid desorbed from walls of previously opened pores is zero ($Vd_1 = 0$), and the remainder of Step (a) is skipped.

The change in thickness of the wall layer due to desorption from previously opened pores is calculated as:

$$\Delta Tw = Tw_1 - Tw_{i+1}$$

The annular cross-sectional area of the wall layer desorbed is calculated for all previously opened pores:

$$CSA_j = \pi\left[\left(Rc_j = \Delta Tw\right)^2 - Rc_j^2\right]\left(10^{-16}\frac{cm^2}{Å^2}\right)$$

The total volume of gas desorbed from walls of previously opened pores is calculated:

$$Vd_i = \sum_j (LP_j)(CSAa_j) \qquad \text{for all previously opened pores}$$

where LP_j = length of previously opened pores as calculated in Step b(2).

b. The physical processes occurring for this pressure interval are determined as:

1. If Vd_i is greater than the current increment of volume desorbed $(Vl_i - Vl_{i+1})$, desorption from walls only is occurring. Total surface of walls exposed thus far (cm^2/g) is calculated as:

$$SA_w = \sum_j \pi(LP_j)(D_{avg,j})\left(\frac{10^{-8} cm}{\text{Å}}\right)$$
for all previously opened pores

where

$D_{avg,j}$ = weighted average pore diameter calculated in Step b.2.

A new layer thickness (ΔTw) that will not overcompensate for the actual volume desorbed in this interval is calculated:

$$\Delta Tw = \frac{(Vl_i - Vl_{i+1})(10^8 \frac{\text{Å}}{cm})}{SAw_i}$$

Since no cores are evaporated in this pressure interval, no new pores are revealed. Thus no ending Kelvin radius and average pore diameter are calculated for this interval. Note that this means the report may have fewer tabulated intervals on the collected data report than experimental pressure intervals.

2. If Vd_i is less than the volume increment desorbed during this interval $(Vl_i - Vl_{i+1})$, the remaining volume is due to new pores with core evaporation taking place in this interval. K, the number of intervals with new pores exposed, is increased by 1. (For the interval from the lowest Pr_1 to zero relative pressure, no new pore volume is calculated and the rest of Step b is skipped.)

The volume desorbed from newly opened pores in this interval is calculated as:

$$Vc_i = (Vl_i - Vl_{i+1}) - Vd_i$$

The Kelvin radius for the end of the interval is calculated as:

$$Rc_{k+1} = \frac{-A}{(1+F)\ln(P_{i+1})}$$

All new pores opened in this interval are represented by one pore having a length-weighted average pore diameter and a corresponding length sufficient to account for the required volume of adsorbate. The weighted average pore diameter is calculated as:

$$D_{\text{avg,k}} = \frac{2(Rc_k + Rc_{k+1})(Rc_k)(Rc_{k+1})}{Rc_k{}^2 + Rc_{k+1}{}^2}$$

$D_{\text{avg,k}}$ is the diameter of a pore which would have a surface area that is the average of the areas for pores radius Rc_k and Rc_{k+1}, if its length was the mean of the lengths at those radii.

The relative pressure corresponding to $D_{\text{avg,k}}$ is calculated as:

$$P_{\text{avg,k}} = \exp\left[\frac{-2A}{(1+F)(D_{\text{avg,k}})}\right]$$

The thickness of the adsorbed layer at this pressure is calculated as:

$$Tw_{\text{avg,k}} = HP1\left[\frac{HP2}{ln(P_{\text{avg,k}})}\right]^{HP3}$$

The decrease in thickness of the wall layer by desorption from the walls of new pores during the lower portion of the pressure interval is calculated as:

$$\Delta Td = Tw_{\text{avg,k}} - Tw_{i+1}$$

The cross-sectional area of the newly opened pores is calculated as:

$$CSAc_k = \left[\frac{D_{\text{avg,k}}}{2} + \Delta Td\right]^2 \left(\frac{10^{-16}\,\text{cm}^2}{\text{Å}^2}\right)$$

The length of the newly opened pores is calculated as:

$$LP_k = \frac{Vc_i}{CSAc_k}$$

Pore diameters and radii are adjusted for the change in thickness of the adsorbed wall layer during this interval. If new pores were opened during this interval, the average diameter is adjusted by the change in layer thickness during the second portion of the desorption interval as:

$$D_{\text{avg,k,new}} = D_{\text{avg,k,old}} + 2(\Delta Td)$$

The layer thickness change during the whole interval is added to diameters of previously opened pores as:

$$D_{\mathrm{avg,k,new}} = D_{\mathrm{avg,k,old}} + 2(\Delta T dw)$$

(not including $D_{\mathrm{avg,k}}$)

The layer thickness change desorbed during this interval also is added to the radii corresponding to the ends of the pressure intervals as:

$$Rc_{\mathrm{j,new}} = Rc_{\mathrm{j,old}} + \Delta T w$$

for all except Rc_{k+1}.

Steps *a* to *c* are repeated for each pressure interval.

After the above calculations have been performed, the diameters corresponding to the ends of the intervals are calculated as:

$$Dp_{\mathrm{j}} = 2(Rc_{\mathrm{j}})$$

for all Rc_{j}. including Rc_{k+1}.

The remaining calculations are based on Dp_i, $D_{\mathrm{avg,i}}$, and LP_i. These calculations are only done for $D_{\mathrm{avg,i}}$ values that fall between the Minimum BJH diameter and the Maximum BJH diameter specified by the operator on the *BJH Adsorption Report Options* window or the *BJH Desorption Report Options* window.

(1) Incremental Pore Volume (Vp_i, cm^3/g):

$$Vp_{\mathrm{i}} = \pi(Lp_{\mathrm{i}})\left[\frac{D_{\mathrm{avg,i}}}{2}\right]^2\left[\frac{10^{16}\,\mathrm{cm}^2}{\mathring{A}^2}\right]$$

(2) Cumulative Pore Volume ($VP_{\mathrm{cum,i}}$, cm^3/g):

$$VP_{\mathrm{cum,i}} = \sum_{j} VP_{\mathrm{j}} \ \ \mathrm{for} \ \ (J \le 1)$$

(3) Incremental Surface Area $SA_{\mathrm{cum,i}}$, m^2g-A):

$$SA_{\mathrm{i}} = \pi\left(LP_{\mathrm{i}}\right)\left(\frac{10^{-2}\,\mathrm{m}}{\mathrm{cm}}\right)\left(D_{\mathrm{avg,i}}\right)\left(\frac{10^{-10}\,\mathrm{m}}{\mathring{A}}\right)$$

(4) Cumulative Surface Area $SA_{cum,i}$,m^2g):

$$SA_{cum,10} = \sum SA_j \, \text{for} \, J \leq 1$$

(5) dV/dD pore volume (dV/dD$_i$, cm^3/g-A):

$$\frac{dV}{dD_i} = \frac{VP_i}{Dp_i - Dp_{i+1}}$$

(6) dV/d log (D) pore volume (dV/d log(D)$_i$, cm^{3}g):

$$\frac{dDv}{d \log D_i} = \frac{VP_i}{\log \left(\frac{Dp_i}{Dp_{i+1}} \right)}$$

(7) dA/dD pore area (dA/dD$_i$,m^2/g-A):

$$\frac{dA}{dDi} = \frac{SA_i}{Dp_i - Dp_{i+1}}$$

(8) *dA/d log(D)* pore area [*dA/d log(D)i*, m^2/g]:

$$\frac{dA}{d \log D_i} = \frac{SA_i}{\log \left(\frac{Dp_i}{Dp_{i+1}} \right)}$$

For fixed pore size tables (if selected), the following calculations are performed

(1) Average Fixed Pore Size (DF$_{avg,j}$,A):

$$DF_{avg,j} = \frac{Dp_{F_j} + Dp_{F_{j+1}}}{2}$$

calculated for all intervals in the fixed pore size table.

For the intervals with between the Minimum BJH diameter and the Maximum BJH diameter.

(2) Cumulative Pore volume (VpF$_{cum,i}$, cm^3/g):

$$V_P F_{cum,i} = \text{INTERP}(D_P F_{i+1})$$

where INTERP(x) is the value interpolated from the function X=dP$_{j+1}$ and Y=VP$_{cum,i}$, using an AKIMA semi-spline interpolation.

(3) Incremental Pore Volume (VpF$_i$, cum^3/g):

$$V_P F_i = V_P F_{\mathrm{cum,i}} - V_P F_{\mathrm{cum,i-1}}$$

where VpF$_{\mathrm{cum,0}}$=0

(4) Cumulative Surface Area (SAF$_{\mathrm{cum,i}}$, m^2/g):

$$SAF_{\mathrm{cum,i}} = \mathrm{INTERP}(D_P F_{\mathrm{i+1}})$$

where *INTERP(x)* is the value interpolated from the function $X = Dp_{\mathrm{j+1}}$ and Y=SA$_{\mathrm{cum,j}}$.

(5) Incremental Surface Area (*SAF$_i$*, m^2/g):

$$SAF_{\mathrm{i}} = SAF_{\mathrm{cum,i}} - SAF_{\mathrm{cum,i-1}}$$

where *SAF$_{cum,0}$* = 0.

(6) dV/dD pore volume (*dV/dDpF$_i$*, cm^3/g-A):

$$\frac{dV}{dDpF_{\mathrm{i}}} = \mathrm{INTERP}(DpF_{\mathrm{i+1}})$$

where *INTERP(x)* is the value interpolated from the function $X = D_{\mathrm{avg,j}}$ and Y=dV/d D$_{\mathrm{j}}$

(7) dV/d log(D) pore volume [*dV/d log(DpF$_i$)*, cm^3/g]:

$$\frac{dV}{d\log(DpF_{\mathrm{i}})} = \mathrm{INTERP}(DpF_{\mathrm{i+1}})$$

where INTERP(x) is the value interpolated from the function$X = D_{\mathrm{avg,j}}$ and Y=dV/d log(D)$_{\mathrm{j}}$

(8) dA/dD pore area (*dA/dDpF$_i$*, m^2/g-A):

$$\frac{dA}{dDpF_{\mathrm{i}}} = \mathrm{INTERP}(DpF_{\mathrm{i+1}})$$

where *INTERP(x)* is the value interpolated from the function$X = D_{\mathrm{avg,j}}$ and Y=dA/dD$_{\mathrm{j}}$.

(9) dA/d log(D) pore area [dA/d log(DpF$_i$), m^2/g]:

$$\frac{dA}{d\log(DpF_i)} = \text{INTERP}(DpF_{i+1})$$

where *INTERP(x)* is the value interpolated from the function *X = D$_{avg,j}$* and *Y=dA/d log(D)$_j$*.

COMPENDIUM OF VARIABLES

ΔTd	=	thickness of layer desorbed from walls of newly opened pores (Å)
ΔTw	=	thickness of adsorbed layer desorbed during interval (Å)
A	=	adsorbate property factor; from the *BJH Adsorptive Options* window
CSA	=	analysis gas molecular cross-sectional area (nm^2), user-entered on the *Adsorptive Properties* window
CSAa	=	annular cross-sectional area of the desorbed layer (cm^2)
CSAc	=	cross-sectional area of opening of newly opened pores (cm^2)
D$_{avg}$	=	average pore diameter (Å)
Dp	=	pore (or core) diameter (Å)
F	=	fraction of pores open at both ends; from the *BJH Adsorption Report Options* window or the *BJH Desorption Report Options* window
LP	=	length of pore (cm/g)
P	=	relative pressure
Q	=	quantity adsorbed expressed as a volume (cm^3/g STP)
Rc	=	Kelvin radius (Å) of core
SAw	=	total surface area of walls exposed (cm^2/g)
Tw	=	thickness of remaining adsorbed wall (Å)
Vc	=	volume desorbed from cores of newly opened pores (cm^3/g)
Vd	=	volume of gas desorbed from walls of previously opened pores (cm^3/g)
Vl	=	liquid equivalent volume of volume adsorbed (cm^3/g)
V$_{mol}$	=	liquid molar volume, from the fluid property information

CRYSTALLITE SIZE FOR CHEMICAL ADSORPTION

$$d_{\mathrm{xtal}} = \frac{1000k}{\bar{\rho} A_{\mathrm{metal}}}$$

Where

k = shape factor; 6 for sphere, 5 for cube

$\bar{\rho}$ = weighted average density of the active metals

DATA SMOOTHING FOR CHEMICAL ADSORPTION

The data smoothing feature of the chemical adsorption program was developed to cope with noise and drift of pressure readings at very low pressures — usually at pressures well under 1 mmHg and very low gas volumes adsorbed. Data smoothing in the chemical adsorption program requires eleven points to satisfy the technique employed. However, most chemical adsorption analyses are performed with fewer than eleven points and at pressures higher than 1 mmHg, and so the data smoothing option is turned off by default. It may be enabled if required

TECHNIQUE

The analysis information consists of absolute pressure and volume adsorbed data pairs (P,V). In order to account for negative transducer shift, all coordinate pairs are scanned for points with pressures less than or equal to zero. If such points exist, then all pressure data are shifted by an amount large enough to convert the smallest pressure to a nominally small positive value.

After examination of the low pressure data is complete, the entire data set is subdivided into equally spaced intervals along the volume axis and corresponding pressures for these volumes are interpolated. The pressure data are smoothed by passing them through an eleven-point Blackman[1] convolution array. Once the smoothing is complete, the volume adsorbed values from the original data set are used to interpolate back to the corresponding smoothed analysis pressures. This amended set of data, consisting of the original volume adsorbed values and the fully smoothed pressure values, forms the isotherm data from which all subsequent report data are based. Coefficients for the Blackman convolution array are given below.

$$
\begin{aligned}
P_{smoothed} = {} & 0.0029918P_{i-5} + 0.020005P_{i-4} + 0.0618580P_{i-3} + \\
& 0.1250300P_{i-2} + 0.1850900P_{i-1} + 0.2100500P_i + \\
& 0.1850900P_{i+1} + 0.1250300P_{i+2} + 0.061850P_{i+3} + \\
& (0.0200050)P_{i+4} + 0.0029918P_{i-5}
\end{aligned}
$$

where

$P_{smoothed}$ = i^{th} smoothed pressure

P_i = pressure coordinate from the ith equally spaced data point

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[1] Blackman, R.B. and Tukey, J.S., "The Measurement of Power Spectra," Dover (1958).

DFT (DENSITY FUNCTIONAL THEORY)

The adsorption isotherm is known to convey a great deal of information about the energetic heterogeneity and geometric topology of the sample under study. The data of physical adsorption have been used for many years as the basis for methods to characterize the surface area and porosity of adsorbents. Real solid surfaces rarely approach ideal uniformity of structure. It is accepted that in general, the surface of even a nonporous material presents areas of greater or lesser attraction for adsorbed molecules.

This energetic heterogeneity greatly affects the shape of the adsorption isotherm with the result that simple theories such as the Langmuir and BET formulas can, at best, give only approximate estimates of surface area. Porous solids virtually are never characterized by a single pore dimension, but instead exhibit a more or less wide distribution of sizes. The observed adsorption isotherm for a typical material is therefore the convolution of an adsorption process with the distribution of one or more properties which affect that process. This was first stated mathematically by Ross and Olivier[1] for the case of surface energy distribution and has become known as the integral equation of adsorption.

THE INTEGRAL EQUATION OF ADSORPTION

In a general form for a single component adsorptive, the integral equation of adsorption can be written as:

$$Q(p) = \int da\,db\,dc \ldots q(p, a, b, c \ldots) \int (a, b, c \ldots)$$

(1)

where

$Q(p)$	=	the total quantity adsorbed per unit weight at pressure p,
$a,b,c,...$	=	a set of distributed properties,
$f(a,b,c,...)$	=	the distribution function of the properties, and
$q(p,a,b,c,...)$	=	the kernel function describing the adsorption isotherm on unit surface of material with fixed properties $a,b,c,...$

Equation (1), a Fredholm integral of the first kind, is a member of a class of problems known as ill-posed, in that there are an infinite number of functional combinations inside the integral that will provide solutions. Even when the kernel function is known, experimental error in the data can make solving for even a single distribution function a difficult task. Solving for multiple distribution functions requires more data than provided by a single adsorption isotherm.

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[1] Ross and Olivier, J.P., "On Physical Adsorption," J. Wiley and Sons, New York (1964).

APPLICATION TO SURFACE ENERGY DISTRIBUTION

Under certain conditions, an energetically heterogeneous surface may be characterized by a distribution of adsorptive energies. The conditions are that the sample is not microporous, i.e., that adsorption is taking place on essentially a free surface with no pore filling processes at least to about 0.2 relative pressure. Secondly, that each energetically distinct patch contributes independently to the total adsorption isotherm in proportion to the fraction of the total surface that it represents. This condition is satisfied if the patches are relatively large compared to an adsorptive molecule, or if the energy gradient along the surface is not steep. In mathematical terms, this concept is expressed by the integral equation of adsorption in the following form:

$$Q(p) = \int d\epsilon \; q(p, \epsilon) \, f(\epsilon) \tag{2}$$

where

$Q(p)$ = the experimental quantity adsorbed per gram at pressure p,

$q(p,\epsilon)$ = the quantity adsorbed per unit area at the same pressure, p, on an ideal free surface of energy ϵ, and

$f(\epsilon)$ = the total area of surface of energy ϵ in the sample.

The exact form of the energy-dependent term depends on the form of the model isotherms expressed in the kernel function and is provided in the model description.

APPLICATION TO PORE SIZE DISTRIBUTION

Similarly, a sample of porous material may be characterized by its distribution of pore sizes. It is assumed in this case that each pore acts independently. Each pore size present then contributes to the total adsorption isotherm in proportion to the fraction of the total area of the sample that it represents. Mathematically, this relation is expressed by:

$$Q(p) = \int dH \; q(p, H) \, f(H) \tag{3}$$

where

$Q(p)$ = the experimental quantity adsorbed at pressure p,

$q(p,H)$ = the quantity adsorbed per unit area at the same pressure, p, in an ideal pore of size H, and

$f(H)$ = the total area of pores of size H in the sample.

Numerical values for the kernel functions in the form of model isotherms can be derived from modern statistical mechanics such as density functional theory or molecular simulations, or can be calculated from one of various classical theories based on the Kelvin equation. Several types are found in the models library.

PERFORMING THE DECONVOLUTION WITH AN ADVANCED MICROMERITICS SPLINE (AMS) DECONVOLUTION

In the previous section, the solution to the integral equations (2) and (3) are obtained directly by discretizing the system and solving the resulting matrix equation (4). An alternative method to this deconvolution was first developed by Jacek Jagiello[1]. This method involves a preliminary step of decomposing both the kernel functions $q(p, Z)$ and the desired function $f(Z)$ in a convenient set of basis functions.

$$f(Z) = \sum_i d_i v_i(Z)$$

$$q(p, Z) = \sum_i t_i(p) v_i(Z)$$

where $v_i(Z)$ are the basis functions and $t_i(p)$ are expansion coefficients obtained by a least squares curve fitting of the known kernel functions $q(p, Z)$. The d_i coefficients are unknowns in the above but may be solved by expressing the original integral equation in the new basis and truncating the expansion in the index i so that the kernel functions $q(p, Z)$ are suitably appoximated. The choice of basis functions $v_i(Z)$ employed in the footnote referenced below are a set of cardinal b-spline functions.

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[1] Jagiello, Jacek. "Stable numerical solution of the adsorption integral equation using splines." \textit{Langmuir} 10, no. 8 (1994): 2778-2785.

REGULARIZATION

DFT allows a selectable regularization (also referred to as smoothing) constraint to be applied during the deconvolution process to avoid over-fitting in the case of noisy data or ill-fitting models. The method used is based on co-minimization of the second derivative of the distribution. The relative weight given to this term is determined by the value of the regularization parameter, which is set on the *DFT Pore Size* or *Surface Energy* window and also is shown in the header of reports. The value of the regularization parameter varies from zero (for no second derivative constraint) to ten (indicating a weight equal to minimizing the residuals), or even larger. When the distribution and residuals obtained change little with the value of the regularization parameter, it indicates that the chosen model provides a good representation of the data. Conversely, a large sensitivity to the regularization parameter might indicate inadequate data or a poor choice of model to represent the data.

DOLLIMORE-HEAL PORE VOLUME AND AREA DISTRIBUTION

The calculations for the Dollimore-Heal reports are the same as those for BJH, except for the calculation of average pore diameter and pore length.

PORE DIAMETER

Pore diameter is determined from the Kelvin radius and thickness equation:

$$D_i = 2r_k P_i + t P_i$$

The average pore diameter is the arithmetic mean of the diameters that bound the interval.

$$\overline{D_i} = \left(\frac{D_i + D_{i+1}}{2} \right)$$

PORE LENGTH

$$l_i = \frac{A_{p,i} + 10^8}{\pi \overline{D_i}}$$

$$A_{p,i} = \frac{4 \times (10^8 \Delta V_p)}{\overline{D_i}}$$

$$\Delta V_p = Cv(D(Q_{i-1} - Qi) - \Delta t \times 10^8 (A_{p,cum} - 2\pi \bar{t} l_{i,cum}))$$

$$Cv = \left(\frac{\bar{D_i}}{2(\bar{\pi}_k + t(P_i) - t(P_{i+1}))} \right)^2$$

$$\bar{t} = \frac{\bar{D_i}}{2 - \bar{r}_k}$$

$$\bar{r}_k = \frac{(r_{k,i} + r_{k,i+1})}{2}$$

where

ΔV_p	=	Change in pore volume
$A_{p,i}$	=	Pore surface area
$A_{p,i,cum}, l_{i,cum}$	=	Summations over the lengths and areas calculated so far
Cv	=	Volume correction factor
D	=	Density conversion factor
$\bar{r}_k$	=	Average Kelvin radius
$\bar{t}$	=	Average thickness

DUBININ-ASTAKHOV

The Dubinin-Astakhov equation is:

$$\log(Q) = \log(Q_0) - \left(\frac{RT}{\beta E_0}\right)^N \times \left(\log \frac{P_0}{P}\right)^N$$

where

β	=	the affinity coefficient of the analysis gas relative to the P_0 gas, from the *Dubinin Adsorptive Options* window
E_0	=	characteristic energy *(kj/mol)*
N	=	Astakhov exponent, may be optimized or user entered from the *Dubinin Report Options* window
P	=	equilibrium pressure
P_0	=	saturation vapor pressure of gas at temperature T
Q	=	quantity adsorbed at equilibrium pressure (cm³/g STP)
Q_0	=	the micropore capacity (cm³/g STP)
R	=	the gas constant (0.0083144 kj/mol)
T	=	analysis bath temperature (K)

For each point designated for Dubinin-Astakhov calculations, the following calculations are done:

$$LV = \log(Q)$$

$$LP = \log(\frac{P_0}{P})^N$$

A least-squares fit is performed on the (*LP,LV*) designated pairs where *LP* is the independent variable and *LV* is the dependent variable. If the user selected *Yes* for the *Optimize Astakhov Exponent* prompt, a systematic search for the optimum value of *N* is conducted by recalculating the linear regression and selecting the value of *N* that gives the smallest standard error of the y-intercept. The exponent *N* is optimized to within 10^{-4}. If the optimum value for *N* is not found in this range, an exponent of 2 is used. The following are calculated:

a. Slope (S cm^3/g STP)
b. Y-intercept (YI cm^3/g STP)
c. Error of the slope (S$_{err}$ cm^3/g STP)
d. Error of the y-intercept (YI$_{err}$ cm^3/g STP)

e. Correlation coefficient
f. Optimized Astakhov exponent (N)

Using the results of the above calculations, the following can be calculated:

Monolayer Capacity (cm^3/g STP):

$$Q_0 = 10^{YI}$$

Micropore Volume (cm^3/g):

$$V_i = \frac{Q_i V_{mol}}{22414}$$

where

V_{mol} =   liquid molar volume conversion factor from the fluid property information

Limiting Micropore Volume (cm^3/g):

$$V_0 = \frac{Q_0 V_{mol}}{22414 cm^3 STP}$$

where

V_{mol} =   liquid molar volume from the fluid property information

Error of Limiting Micropore Volume (cm^3/g):

$$V_{0,err} = W_0 (10 YI_{err} - 1.0)$$

Characteristic Energy (KJ/mol):

$$E = \frac{2.303(RT)}{\beta(2.303 \times S)^{1/N}}$$

Modal Equivalent Pore Diameter (Å):

$$D_{\mathrm{mode}} = 2\left\{\left[\frac{3N}{3N+1}\right]^{1/N} \times \left[\frac{10^3 nm^3/\mathring{A}^3}{\beta \cdot E_0}\right]\right\}^{1/3}$$

where

β = affinity coefficient of the analysis gas relative to the P_0 gas from the *Dubinin Adsorptive Options* window

Maximum Differential Pore Volume (cm³/g-Å):

This value is also known as *frequency of the mode*[1] .

$$\frac{dV}{dD_{\mathrm{mode}}}\mathrm{Max} = 0.5(3N+1)W_0\left[\frac{3N+1}{3N}\right]^{1/3N}\left[\frac{\beta \cdot E_0}{((10^3 nm^3)/\mathring{A}^3)}\right]^{1/3}\exp\left(-\left[\frac{3N+1}{3N}\right]\right)$$

Mean Equivalent Pore Width (Å):

$$D_{\mathrm{mean}} = 2 \times \frac{\left[\frac{(10^3 nm^3)\mathring{A}^3}{\beta \cdot E_0}\right]^{1/3}}{\tau(\frac{3N+1}{3N})}$$

Micropore surface area (m²/g):

$$SDA = 1000 \times 2.0 \times W_0 \times \left[\frac{E_0}{k}\right]^{1/3} \times \tau\left(\frac{3N+1}{3N}\right)$$

Γ is calculated by a polynomial approximation over the domain 0 ≤ × ≤ 1:

$$\tau(x+1) = 1 + b_1 x + b_2 x^2 + b_3 x^3 + b_4 x^4 + b_5 x^5 + b_6 x^6 + b_7 x^7 + b_8 x^8$$
$$+\varepsilon x |\varepsilon x| \leq 3(10^{-7})$$

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[1] Ross and Olivier, J.P., "On Physical Adsorption," J. Wiley and Sons, New York (1964).

where

b_1 = -0.57719 1652

b_2 = 0.98820 5891

b_3 = -0.89705 6937

b_4 = 0.91820 6857

b_5 = -0.75670 4078

b_6 = 0.48219 9394

b_7 = -0.19352 7818

b_8 = 0.03586 8343

and where

$$x + 1 = \left(\frac{3N+1}{3N} \right)$$

Equivalent Pore Diameter (Å):

$$D_i = 2 \left[\frac{-\left(\frac{10^3\,\mathrm{nm}^3/\mathring{A}^3}{\beta \cdot E_0} \right)^N}{\ln(W_i) - \ln(W_0)} \right]^{1/3N}$$

dV/dD Pore Volume (cm^3/g-Å):

$$\frac{dV}{dD_i} = 0.5 \times W_0 \times 3N \left(\frac{10^3\,\mathrm{nm}^3/\mathring{A}^{3N}}{\beta \cdot E_0} \right) \left(\frac{D_i}{2} \right)^{-(3N+1)}$$

$$\times \exp\left[-\left(\frac{10^3\,\mathrm{nm}^3/\mathring{A}^3}{\beta \cdot E_0} \right)^N \left(\frac{D_i}{2} \right)^{-3N} \right]$$

DUBININ-RADUSHKEVICH

The Dubinin-Radushkevich[1] equation is:

$$\log(Q) = \log(Q_0) - \frac{BT^2}{\beta} \times \left[\log \frac{P_0}{P}\right]^2$$

where

β	=	the affinity coefficient of analysis gas relative to P_0 gas (for this application β is taken to be 1)
B	=	a constant
P_0	=	saturation vapor pressure of gas at temperature T
P	=	equilibrium pressure
Q	=	quantity adsorbed at equilibrium pressure (cm^3/g STP)
Q_0	=	the micropore capacity (cm^3/g STP)
T	=	analysis bath temperature (K), from the P_0 and Temperature Options window

For each point designated for Dubinin-Radushkevich calculations, the following calculations are done:

$$LV = \log(Q)$$

$$LP = \log(\frac{P_0}{P})^2$$

The intercept, *log(Vo)* can be found by performing a least-squares fit on the (*LP,LV*) designated pairs where *LP* is the independent variable and *LV* is the dependent variable. Assuming the adsorption of gas is restricted to a monolayer, *Vo* is the monolayer capacity. Based on this assumption, the following are calculated:

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[1] Dubinin, M., *Carbon 21*, 359 (1983); Dubinin, M., *Progress in Surface and Membrane Science 9*, 1, Academic Press, New York (1975); Dubinin, M. and Astakhov, V., *Adv. Chem. Ser. 102*, 69 (1971); Lamond, T. and Marsh, H., *Carbon 1*, 281, 293 (1964); Medek, J., *Fuel 56*, 131 (1977); Polanyi, M., *Trans. Faraday Soc. 28*, 316 (1932); Radushkevich, L., *Zh. fiz. Kemi. 33*, 2202 (1949); Stoeckli, H., *et al, Carbon 27*, 125 (1989).

a. Slope (S cm^3/g STP)

b. Y-intercept (YI cm$^{3/}$g STP)

c. Error of the slope (S_{err} cm^3/g STP)

d. Error of the y-intercept (YI_{err} cm^3/g STP)

e. Correlation coefficient

Using the results of the above calculations, the following can be calculated:

Monolayer Capacity (cm^3/g STP):

$$Q_0 = 10^{YI}$$

Error of Monolayer Capacity (cm^3/g STP):

$$Q_{0,err} = Q_0 \left(10^{YI,err} - 1.0 \right)$$

Micropore surface area (m^2/g):

$$SDP = \frac{\sigma Q_0 N_A}{22414 \text{cm}^3 \left(\frac{10^{18} \text{nm}^2}{\text{m}^2} \right)}$$

where

σ = molecular cross sectional area of gas (nm^2) from the *Adsorptive Properties* window

EQUATION OF STATE

The ideal gas law relates pressure, volume, temperature, and quantity of gas.

$$n = \frac{PV}{RT}$$

where

P	=	pressure
V	=	volume
R	=	a constant that depends on the units of *n*

For *n* in cm^3 , STP, R = P_{STD} / T_{STD}

For *n* in moles, *R* = 8.3145 J mol^{-1} K^{-1}

T	=	temperature

The non-ideality correction is made by replacing *P* with *P(1 + aP)*, where *a* is the non-ideality factor. This gives

$$n = \frac{PV}{RT}(1 + \alpha P)$$

The real gas equation of state uses

$$n = \frac{PV}{RT_z(P,T)}$$

where *z(P,T)* is the compressibility factor for the gas at the given pressure and temperature.

EQUILIBRATION

Equilibration is reached when the pressure change per equilibration time interval (first derivative) is less than 0.01% of the average pressure during the interval. Both the first derivative and average pressure are calculated using the Savitzky-Golay[1] convolution method for polynomial functions. The following equations are those used to compute weighted average and first derivative, respectively, for the 6th point of an 11-point window:

$$P_{avg} = \frac{-36(P_{11}+P_1)+9(P_{10}+P_2)+44(P_9+P_3)+69(P_8+P_4)+84(P_7+P_5)+89(P_6)}{429}$$

$$P_{chg} = \frac{5(P_{11}-P_1)+4(P_{10}-P_2)+3(P_9-P_3)+2(P_8-P_4)+(P_7-P_5)}{110}$$

$$P_{pcp,i} = 100\% \frac{P_{chg}}{P_{avg}}$$ pressure change per equilibration time interval

where the numerical constants are from the Savitzky-Golay convolution arrays, and

P_{avg} =   average pressure
P_{chg} =   change in pressure
$P_{pcp,i}$ =   percent change per interval
P_i = ith pressure reading taken at equilibrium intervals

If a non-zero value that is too small is entered for the maximum equilibration time, the points are collected before equilibration is reached.

If P_{avg} is greater than 0.995 times the current P_0, equilibration will not take place until the *Minimum equilibration delay for P/P$_0$ 0.995* has expired, in addition to the standard equilibration criteria.

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[1] Savitzky, A. and Golay, M.J.E., *Anal. Chem. 36*, 1627 (1964).

F-RATIO METHOD

The *f*-Ratio is the quantity adsorbed divided by the quantity adsorbed in a reference isotherm at the same pressure.

$$f_i = \frac{Q_i}{Q_{\mathrm{ref}} P_i}$$

The reference quantity adsorbed is found by spline interpolation of the reference isotherm.

FREE SPACE FOR CHEMICAL ADSORPTION

$$V_{\mathrm{FS}} = \frac{V_{\mathrm{LOW}}}{T_1} \times \left[\frac{P_1}{P_2} - 1 \right] \times T_{\mathrm{STD}}$$

where

P_1	=	system manifold pressure before dosing helium onto sample (μmHg)
P_2	=	system manifold pressure after dosing helium onto sample (μmHg)
T_1	=	system manifold temperature before dosing helium onto sample (K)
T_2	=	system manifold temperature after raising Dewar and equilibrating with helium (K)
T_{STD}	=	standard temperature (273.13 K)
V_{FS}	=	volume of free space (cm^3 at standard temperature)
V_{LOW}	=	lower manifold volume (cm^3)

FREE SPACE FOR CHEMICAL ADSORPTION

The free space is the physical volume below the sample valve. The different temperatures in the sample tube, stem, and port must be accounted for.

Free space volumes are calculated as:

$$n_p = \frac{P_s V_p}{z(P_s T_p) T_p}$$

$$n_s = n_d - n_P$$

$$V_s = \frac{n_s z(P_s, T_s) T_s}{P_s}$$

The reported free space is

$$V_f = V_p = V_s$$

The quantity of gas in the free space for a given data point is:

$$n_p = P_s \left(\frac{V_p}{z(P_s, T_p) T_p} + \frac{V_s}{z(P_s, T_s) T_s} \right)$$

where

n_d	=	quantity of gas dosed
n_p	=	quantity of gas in the port
n_s	=	quantity of gas in the sample tube
P_s	=	sample (and port) pressure
T_p	=	port temperature
T_s	=	sample temperature
V_p	=	volume of the sample port
V_s	=	volume of the sample tube
$z(P,T)$	=	gas compressibility factor P and temperature T for the gas used

FREUNDLICH ISOTHERM

The Freundlich isotherm has the form:

$$\frac{Q}{Q_{\mathrm{m}}} = CP^{\frac{1}{\mathrm{m}}}$$

where

C	=	temperature-dependent constant
m	=	temperature-dependent constant
P	=	equilibrated collected pressure measured by gauge at temp T_{amb}
Q	=	quantity of gas adsorbed
Q_m	=	quantity of gas in a monolayer

The pressure is absolute; typically, m > 1. In terms of quantity adsorbed,

$$Q = Q_{\mathrm{m}}CP^{\frac{1}{\mathrm{m}}}$$

Taking the log of both sides yields

$$\log Q = \log Q_{\mathrm{m}}C + \frac{1}{\mathrm{m}}\log P$$

HEAT OF ADSORPTION FOR PHYSICAL ADSORPTION

The adsorption isostere is represented by

$$\ln\left(\frac{P}{P_0}\right) = \frac{q_i}{RT} + C$$

where

q_i	=	isosteric heat of adsorption
C	=	unknown constant
R	=	gas constant
T	=	analysis temperature

The isosteric heat of adsorption, q_i, is determined by finding the slope of *ln (P/P0)* as a function of *1/RT* for a set of isotherms measured at different temperatures.

HORVATH-KAWAZOE

A relative pressure lower limit is determined such that L-d_0 never equals zero. All pressure points less than this limit are discarded. For each collected relative pressure point, values of L are chosen in an iterative manner, and the relative pressure (P/P_0) determined by solving one of the following equations:

- Slit Pore Geometry (original Horvath-Kawazoe)
- Cylinder Pore Geometry (Saito / Foley)
- Sphere Pore Geometry (Cheng / Yang)

SLIT PORE GEOMETRY (ORIGINAL HORVATH-KAWAZOE)

When using the original Horvath-Kawazoe[1] method, the following equation is solved for each value of P. The value of L is determined when the solved-for relative pressure is within 0.1% of the collected absolute pressure:

$$\ln \frac{P}{P_0} = \frac{N_A}{RT} \frac{IP \times 10^{32}}{\sigma^4 L - 2d_0} \frac{\sigma_4}{3L - d_0{}^3} - \frac{\sigma^{10}}{9L - d_0{}^9} - \frac{\sigma^4}{3d_0{}^3} + \frac{\sigma^{10}}{9d_0{}^9}$$

where

10^{32} = the number of cm^4 that are equal to $Å^4$

σ = gas solid nuclear separation at zero interaction energy (Å), $\frac{Z_s + Z_A}{2}$

d_0 = $\frac{D_A + D_s}{2}$

where

D_A = molecular diameter (Å) from the *Horvath-Kawazoe Physical Properties* window

D_S = diameter of sample atom (Å) from the *Horvath-Kawazoe Physical Properties* window

IP = interaction parameter (erg-cm^4) from the *Horvath-Kawazoe Report Options* window

N_A = Avogadro Constant ($6.02214129 \times 10^{23}$ mol^{-1})

L = pore width (nucleus to nucleus) (Å)

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[1] Horvath, G. and Kawazoe, K., *J. Chem. Eng. Japan 16(6)*, 470 (1983).

P   = equilibrium pressure

P_0 = saturation pressure

R   = gas constant (8.31441×10^7 erg/mol K)

T   = analysis bath temperature (K), from an entered or calculated value on the *P_0 and Temperature Options* window

where:

Z_s =   sample equilibrium diameter at zero interaction energy (Å) from the *Horvath-Kawazoe Physical Properties* window

Z_A =   zero interaction energy diameter from the *Horvath-Kawazoe Physical Properties* window

CYLINDER PORE GEOMETRY (SAITO/FOLEY)

When using the Saito/Foley[1] method, the following equation is solved for each value of *P*. The value of *L* is determined when the solved-for relative pressure is within 0.1% of the collected absolute pressure:

$$\ln\left(\frac{P}{P_0}\right) = \frac{3}{4}\frac{\pi N_A}{RT} \times \frac{IP \times 10^{32}}{d_0{}^4} \times \sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1 - \frac{d_0}{r_p}\right)^{2k} \times \right.$$
$$\left.\left\{\frac{21}{32}\alpha_k\left(\frac{d_0}{r_p}\right)^{10} - \beta_k\left(\frac{d_0}{r_p}\right)^4\right\}\right]$$

where

10^{32} =   the number of Å^4 that are equal to 1 cm^4

β_k = $\left(\frac{-1.5-k}{k}\right)^2 \beta_{k-1}, \beta_0 = 1.0$

α_k = $\left(\frac{-4.5-k}{k}\right)^2 \alpha_{k-1}, \alpha_0 = 1.0$

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[1] Saito, A. and Foley, H. C., *AlChE Journal 37(3)*, 429 (1991).

$$d_0 = \frac{D_A D_s}{2}$$

where

D_A	=	molecular diameter (Å) from the *Horvath-Kawazoe Physical Properties* window
D_S	=	diameter of sample atom (Å) from the *Horvath-Kawazoe Physical Properties* window

IP = interaction parameter (10^{-43} erg-cm^4) from the *Horvath-Kawazoe Report Options* window

N_A = Avogadro Constant ($6.02214129 \times 10^{23}$ mol^{-1})

L = pore width (nucleus to nucleus) (Å)

P = equilibrium pressure

P_o = saturation pressure

R = gas constant (8.31441×10^7 erg/mol *K)*

r_p = radius of the cylindrical pore, $\frac{L}{2}$

T = analysis bath temperature (*K*), from an entered or calculated value on the *P_0 and Temperature Options* window

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SPHERE PORE GEOMETRY (CHENG/YANG)

When using the Cheng / Yang[1] method, the following equation is solved for each value of *P*. The value of *L* is determined when the solved-for relative pressure is within 0.1% of the collected absolute pressure:

$$\ln\left(\frac{P}{P_0}\right) = \frac{6N_1\epsilon^*{}_{12}+N_2\epsilon^*{}_{22}L^3\times10^{32}}{RTL-d_0{}^3}\left[-\left(\frac{d_0}{L}\right)^6\left(\frac{T_1}{12}+\frac{T_2}{8}\right)+\left(\frac{d_0}{L}\right)^{12}\left(\frac{T_3}{90}+\frac{T_4}{80}\right)\right]$$

where

$\frac{10}{32}$ = the number of cm^4 that are equal to $Å^4$

$\epsilon^*{}_{12}$ = $\frac{\dot{A}_S}{4d_s{}^6}$, where $\dot{A}_s = \frac{6(mc^2)\alpha_S\alpha_A}{\frac{\alpha_S}{x_S}+\frac{\alpha_A}{x_A}}$

$\epsilon^*{}_{22}$ = $\frac{\dot{A}_A}{4D_A{}^6}$, where $\dot{A}_A = \frac{3(mc^2)(\alpha_A)(\chi_A)}{2}$

d_0 = $\frac{D_A+D_S}{2}$

where

D_A = molecular diameter (Å) from the *Horvath-Kawazoe Physical Properties* window

D_S = diameter of sample atom (Å) from the *Horvath-Kawazoe Physical Properties* window

L = pore width (nucleus to nucleus) (Å)

N_1 = 4π L_2N_S, where N_s = number of sample atoms/cm^2 at monolayer

N_2 = 4π $(L-d_0)^2N_A$, where N_S = number of gas molecules/cm^2

P = equilibrium pressure

P_0 = saturation pressure

R = gas constant (8.31441 × 10^7 erg/mol K)

T = analysis bath temperature (*K*), from an entered or calculated value on the *P_0 and Temperature Options* window

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[1] Cheng, Linda S. and Yang, Ralph T., *Chemical Engineering Science 49(16)*, 2599-2609 (1994).

$$T_1 = \frac{1}{(1-S)^3} - \frac{1}{(1+S)^3}$$

$$T_2 = \frac{1}{(1+S)^2} - \frac{1}{(1-S)^2}$$

$$T_3 = \frac{1}{(1-S)^9} - \frac{1}{(1+S)^9}$$

$$T_4 = \frac{1}{(1+S)^8} - \frac{1}{(1-S)^8}$$

where $\quad S = \frac{L-d_0}{L}$

CHENG/YANG CORRECTION

This factor corrects for the nonlinearity of the isotherm. It adds an additional term to the equations for the different geometrics:

$$\ln\left(\frac{P}{P_0}\right) = G(L) - \left[1 - \frac{1}{\theta}\ln\left(\frac{1}{1-\theta}\right)\right]$$

where

$G(L)$	=	one of the Horvath-Kawazoe equations given above
θ	=	degree of void filling; θ is estimated by first computing the monolayer capacity (Q_m) with the Langmuir equation over the range of data points from relative pressure 0.02 to 0.2 or the maximum relative pressure included in the Horvath-Kawazoe analysis. θ is computed as the quantity adsorbed over Q_m.

INTERACTION PARAMETER

The interaction parameter (IP) results from the following calculations:

The Kirkwood-Muller dispersion coefficients

$$A_S = \frac{6mc^2 \alpha_S \alpha_A}{\frac{\alpha_S}{\chi_S} + \frac{\alpha_A}{\chi_A}}$$

$$A_A = \frac{3mc^2 \alpha_A \chi_A}{2}$$

where

α_A	=	polarizability of gas molecule (cm^3)
α_S	=	polarizability of sample atoms (cm^3)
mc^2	=	kinetic energy of electron (0.8183×10^{-6} erg)
X_A	=	diamagnetic susceptibility of gas molecule (cm^3)

$$IP = (N_M A_A) + (N_S A_S)$$

where:

N_M	=	number of gas molecules/cm^2 at monolayer from the *Horvath-Kawazoe Physical Properties* window
N_S	=	number of sample atoms/cm^2 from the *Horvath-Kawazoe Physical Properties* window
X_S	=	diamagnetic susceptibility of sample atom (cm^3)

See *Interaction Parameter Components Table on page 40* for recommended values.

ADDITIONAL CALCULATIONS

Based on the previous calculations, the following can be calculated:

Adjusted Pore Width (Å):

(Shell to Shell)

$$AL_i = L_i - D_S$$

Cumulative Pore Volume (cm³/g):

$$V_{cum,i} = \frac{Q_i V_{mol}}{22414 cm^3 STP}$$

where

V_{mol} = liquid molar volume from the fluid property information

dV/dD Pore Volume (cm³/g-Å):

$$\frac{dV}{dD_i} = \frac{V_{cum,i} - V_{cum,i-1}}{AL_i - AL_{i-1}}$$

Median Pore Width (Å):

$$V_{half} = \frac{V_{cum,n}}{2}$$

$$D_{med} = \exp\left(\ln D_l + (\ln D_g - \ln D_l)\frac{\ln V_{half} - \ln V_l}{\ln V_g - \ln V_l} \right)$$

where

D_l	=	pore width (L_i) that corresponds to V_l
D_g	=	pore width (L_i) that corresponds to V_g
$V_{cum,n}$	=	total cumulative pore volume ($V_{cum,i}$) for points designated for Horvath-Kawazoe calculations
V_g	=	cumulative pore volume ($V_{cum,i}$) for first point greater than V_{half}
V_{half}	=	50% of total cumulative pore volume
V_l	=	cumulative pore volume ($V_{cum,i}$) for first point less than V_{half}

Interaction Parameter Components Table

Gas	Bath Temperature (K)	Sample Type	Interaction Parameter Calculated Value *
Argon	87.3	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	2.61 5.89 3.19
Carbon Dioxide	298.15	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	4.20 9.20 5.08
	273.15	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	4.34 9.35 5.22
	194.65	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	4.72 9.72 5.60
Nitrogen	77.15	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	2.84 6.53 3.49
* The interaction parameter is entered in the *Horvath-Kawazoe Report Options* window in the following field: Interaction parameter: (calculated value) × 10^{-43} erg-cm^4			

The following values were used to calculate the values in the previous table.

Carbon-Graphite

D_S	=	3.40
N_S	=	3.845×10^{15}
X_S	=	1.05×10^{-29} (Ross/Olivier)
		13.5×10^{-29} (Horvath/Kawazoe, implicit)
α_s	=	1.02×10^{-24}

Zeolite

D_S	=	3.04
N_S	=	3.75×10^{15}
X_S	=	1.94×10^{-29}
α_s	=	0.85×10^{-24}

Nitrogen

D_A	=	3.00
N_A	=	6.71×10^{14}
X_A	=	3.6×10^{-29}
α_A	=	1.76×10^{-24}

Argon

D_A	=	2.95
N_A	=	7.608×10^{14}
X_A	=	3.22×10^{-29}
α_A	=	1.63×10^{-24}

Carbon Dioxide

D_A	=	3.23
N_A	=	4.567×10^{14} (25 °C)
		5.45×10^{14} (0 °C)
		7.697×10^{14} (-78 °C)
X_A	=	5.0×10^{-29}
α_A	=	2.7×10^{-24}

D_A values are from van der Waal's constant.

N_A values are from liquid densities.

X and α values are derived from data found in Ross and Olivier[1].

[1] Ross and Olivier, J.P., "On Physical Adsorption," J. Wiley and Sons, New York (1964)

The physical parameters referenced in Saito/Foley are:

Aluminophosphate

D_S = 2.60

N_S = 1.48×10^{15}

X_S = 1.3×10^{-29}

α_s = 2.5×10^{-24}

Aluminosilicate

D_S = 2.76

N_S = 1.31×10^{15}

X_S = 1.3×10^{-29}

α_s = 2.5×10^{-24}

LANGMUIR SURFACE AREA FOR PHYSICAL ADSORPTION

For each point designated for surface area calculations, the Langmuir[1] transformation is calculated as:

$$L = \frac{P_{\text{rel}}}{N_{\text{ads}}}$$

where L is in units of g/cm^3 STP.

A least-squares fit is performed on the (P_{rel}, L) designated pairs where P_{rel} is the independent variable and L is the dependent variable. The following are calculated:

Slope (S g/cm^3 STP)

Y-intercept (Y_{int} g/cm^3 STP)

Error of the slope (S_{err} g/cm^3 STP)

Error of the y-intercept (YI_{err} g/cm^3 STP)

Correlation coefficient

Using the results of the above calculations, the following can be calculated:

Langmuir Surface Area (m^2/g):

$$SA_{\text{LAN}} = \frac{\text{CSA}_{\times} N_A}{(22414\,\text{cm}^3\text{STP})(\frac{10^{18} nm^2}{m^2})S}$$

where

CSA	=	analysis gas molecular cross-sectional area (nm^2), user-entered on the *Adsorptive Properties* window
N_A	=	Avogadro constant (6.02214129 × 10^{23} mol^{-1})

Quantity of the Monolayer (cm^3/g STP):

$$Q_m = \frac{1}{s}$$

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[1] Langmuir, I., J. *Am. Chem. Soc. 38*, 2267 (1916); J. Am. Chem. Soc. 40, 1361 (1918); Phys. Rev 8, 149 (1916).

Langmuir b Value:

$$b = Y_{\text{int}} V_m$$

Error of the Langmuir Surface Area (m^2/g):

$$LAN_{\text{err}} = \frac{SA_{\text{Lan}} S_{\text{err}}}{S}$$

METAL DISPERSION FOR CHEMICAL ADSORPTION

The metal dispersion is the percentage of the active metal available for interaction with the adsorbate.

$$\%M_{\text{DISP}} = \frac{100\% \times 100\%}{22414^*} \times \frac{Q_0 \times SF_{\text{CALC}}}{\frac{\%weight1}{W_{\text{ATOMIC1}}} + \frac{\%weight2}{W_{\text{ATOMIC2}}} + \frac{\%weight3}{W_{\text{ATOMIC3}}}}$$

where

$\%M_{\text{DISP}}$	=	metal dispersion (%)
$\%weight_1$	=	% of sample weight for first metal
$\%weight_2$	=	% of sample weight for second metal
$\%weight_3$	=	% of sample weight for third metal
Q_0	=	quantity adsorbed intercept of the best fit to the primary, repeat, or difference data. For the Sinfelt report, Q_0 is the difference of the primary and repeat intercepts.
SF_{CALC}	=	calculated stoichiometry factor
W_{ATOMIC1}	=	atomic weight of first metal (g/mole)
W_{ATOMIC2}	=	atomic weight of second metal (g/mole)
W_{ATOMIC3}	=	atomic weight of third metal (g/mole)

* The volume one mole of gas occupies (cm^3 STP/mole of gas).

METALLIC SURFACE AREA

The metallic surface area per gram of sample is the total active metal surface area available for interaction with the adsorbate.

$$\mathrm{Msa} = \frac{6.023 \times 10^{23}}{22414^*} \times V \times SF_{\mathrm{CALC}} \times A_{\mathrm{AREA}}$$

where

A_{AREA}	=	effective area of 1 active metal atom (m^2/atom)
Msa	=	metallic surface area (m^2/g sample)
SF_{CALC}	=	calculated stoichiometry factor
V	=	(cm^3/g STP)

If Msa is being calculated from analysis data, then V is the volume intercept derived form the best line fit of the points selected for line fit by the user. If Msa is being calculated from difference data, then V is the average of the volume differences (V^{DIFF}) for the points selected for line fit.

V_{DIFF}	=	difference in volume between the first analysis and the repeat analysis

* The volume one mole of gas occupies (cm^3 STP/mole of gas)

Assuming that all species of metals disperse evenly, the metallic surface area per gram of metal is

$$N_{\mathrm{sa}} = MSA\left(\frac{100\%}{\%\mathrm{weight1} + \%\mathrm{weight2} + \%\mathrm{weight3}}\right)$$

where

%weight1	=	% of sample weight for first metal
%weight2	=	% of sample weight for second metal
%weight3	=	% of sample weight for third metal
MSA	=	metallic surface area (m^2/g sample)
Nsa	=	metallic surface area (m^2/g metal)

MP-METHOD

With the (t_i, Q_i) data pairs[1], the Akima semi-spline interpolation method is used to interpolate quantity adsorbed values based on thickness values that are evenly spaced 0.2 angstrom apart starting at the first outlier point. Outliers are defined as those points that have the maximum instantaneous slope within an iteratively shrinking subset of all points. The remaining pore surface area calculation result is the slope of the line defined by two consecutive interpolated points. The slopes of each pair of consecutive points from the origin to the last point must be monotonically decreasing and non-negative. With the interpolated points set the following can be calculated:

Average pore hydraulic radius (Å):

$$R_i = \frac{t_i + t_{i-1}}{2}$$

Remaining pore surface area for the ith point (m²/g):

$$S_i = \frac{Q_i - Q_{i-1}}{t_i - t_{i-1}} \frac{V_{mol}}{22414 \text{cm}^3 \text{STP}} \times 10^4$$

where

10^4	=	unit conversions
V_{mol}	=	liquid molar volume from the fluid property information

Incremental pore surface area occluded for the ith point (m²/g):

$$S_{inc,i} = S_{i-1} - S_i$$

Cumulative pore surface area occluded for the ith point (m²/g):

$$S_{cum_i} = S_{inc,i} + S_{inc,i-1} + \ldots + S_{inc,i}$$

dA/dR pore surface area for the ith point (m²/g-Å):

$$\frac{dA}{dR_i} = \frac{S_{inc_i}}{t_i - t_{i-1}}$$

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[1] Mikhail, R., Brunauer, S. and Bodor, E., *J. Colloid and Interface Sci. 24*, 45 (1968).

Incremental pore volume occluded for the ith point (cm^3/g):

$$V_{\text{inc,i}} = S_{\text{inc,i}} R_i \times 10^{-4}$$

Cumulative pore volume occluded for the ith point (cm^3/g):

$$V_{\text{cum,i}} = V_{\text{inc,i}-1} + V + \ldots + V_{\text{inc,i}}$$

dV/dR pore volume for the ith point (cm^3/g-Å):

$$\frac{dV}{dR_i} = \frac{V_{\text{inc},i}}{t_i - t_{i-1}}$$

QUANTITY ADSORBED FOR CHEMICAL ADSORPTION

For the ith dose:

$$N_{\text{gas}_i} = N_{\text{gas}_{i-1}} + V_{\text{LOW}} \times \left[\frac{P_{\text{sys1}_i}}{T_{\text{sys1}_i}} - \frac{P_{\text{sys2}_i}}{T_{\text{sys2}_i}} \right] \times \frac{T_{\text{STD}}}{P_{\text{STD}}}$$

$$N_{ads_i} = \frac{N_{gas_i} - P_{sam}}{P_{STD} \times V_{FS}}$$

$$Q_i = \frac{N_{ads_i}}{Msam}$$

where

M_{sam}	=	mass of sample (g)
N_{ads}	=	amount of gas adsorbed after equilibrating i^{th} dose (cm^3 STP)
$N_{\text{gas\_i}}$	=	total amount of gas dosed into sample tube after i^{th} dose (cm^3 STP)
$P_{\text{sam\_i}}$	=	sample pressure after equilibrating i^{th} dose of gas onto sample (mmHg)
P_{STD}	=	standard pressure (760 mmHg)
$P_{\text{sys1\_i}}$	=	system manifold pressure before i^{th} dose of gas onto sample (mmHg)
$P_{\text{sys2\_i}}$	=	system manifold pressure after i^{th} dose of gas onto sample (mmHg)
Q_i	=	amount of gas adsorbed per gram of sample (cm^3/g STP)
T_{STD}	=	standard temperature
$T_{\text{sys1\_i}}$	=	system manifold temperature before i^{th} dose of gas onto sample (K)
$T_{\text{sys2\_i}}$	=	system manifold temperature after i^{th} dose of gas onto sample (K)
Vfs	=	free space
V_{LOW}	=	volume of lower manifold

QUANTITY ADSORBED FOR CHEMICAL ADSORPTION

A portion of the dosing volume may be at a slightly elevated temperature due to heating of the sample ports. The manifold volume is partitioned into a volume at the temperature of the manifold block and a volume at the average temperature of the ports.

$$n_\alpha - n_d - n_f$$

$$n_d = P_{1m} C(P_{1m}, T_{1m}, \bar{T}_{1p}) - P_{2m} C(P_{2m}, T_{2m}, \bar{T}_{2p})$$

$$c(P, T_m, T_p) = V_m \left(\frac{\alpha}{z(P, T_m) T_m} + \frac{\beta}{z(P, T_p) T_p} \right)$$

where

α and β	=	constants that determine the relative weights of the manifold and port temperatures
n_α	=	quantity of gas adsorbed
n_d	=	quantity of gas dosed
n_f	=	quantity of gas in the free space
P_{1m}	=	manifold pressure before dosing onto the sample
P_{2m}	=	manifold pressure after dosing
T_{1m}	=	manifold temperature before dosing onto the sample
T_{1p}	=	average of all port temperatures before dosing onto the sample
T_{2m}	=	manifold temperature after dosing
T_{2m}	=	average of all port temperatures after dosing
V_m	=	volume of the dosing manifold

QUANTITY ADSORBED FOR PHYSICAL ADSORPTION

The quantity of gas in the free space is

$$n_{fs,i} = \frac{P_{s,i}}{T_{\mathrm{STD}}} \left(\frac{V_{\mathrm{bath}}}{z(P_{s,i}, T_{\mathrm{bath}})} + \frac{V_{\mathrm{amb}}}{z(P_{s,i}, T_{\mathrm{amb}})} \right)$$

with the real gas equation of state. Here, P_s is the sample pressure.

FREE SPACE - MEASURED

Measured free-space volumes are calculated using the following equations:

$$V_{fc} = V_{fw} \left(\frac{P_2}{P_3} \right)$$

FREE SPACE - CALCULATED

The calculated free space is determined by subtracting the gas capacity of the volume occupied by the sample from the measured free space of the empty tube.

$$V_{fw} = V_{wb} - V_s \left(\frac{T_{\text{STD}}}{T_{\text{amb}}} \right)$$

$$V_{\text{bath}} = \frac{V_{fc} - V_{fw}}{1 - \frac{T_{\text{bath}}}{T_{\text{amb}}}}$$

$$V_s = \frac{m}{\rho}$$

COMPENDIUM OF VARIABLES

ρ	=	sample density
m	=	sample mass
P_i	=	equilibrated sample pressure
P_1	=	system manifold pressure before dosing onto sample
P_2	=	system manifold pressure after dosing onto sample
P_3	=	sample pressure after raising Dewar and equilibrating with helium
T_{amb}	=	approximate room temperature (298 K)
T_{bath}	=	analysis bath temperature (K)
T_{STD}	=	standard temperature (273.15 K)
V_{amb}	=	volume of cold free space (cm^3 at standard temperature)
V_{bath}	=	volume of cold free space at analysis bath temperature (cm^3 at standard temperature)
V_{cb}	=	volume of cold free space of the empty tube (cm^3 at standard temperature)
V_{fc}	=	volume of cold free space (cm^3 at standard temperature)
V_{fw}	=	volume of warm free space (cm^3 at standard temperature)
V_s	=	sample volume
V_{wb}	=	volume of warm free space of the empty tube (cm^3 at standard temperature)

RELATIVE PRESSURE

Relative pressure is defined as:

$$P_{\mathrm{rel},i} = \frac{P_i}{P_{0,i}}$$

$P_{0,i}$ depends on the method selected in the P_0 and Temperature options

If P_0 was measured for each point, $P_{0,i}$ is the saturation pressure measured when P_i was equilibrated.

If P_0 was measured at intervals, $P_{0,i}$ is found by linear interpolation.

$$P_{0,i} = P_{0,i-1} + \left(P_{0,i+1} - P_{0,i-1} \right) \frac{t_i - t_{i-1}}{t_{i+1} - t_{i-1}}$$

The last measured P_0 is only for points taken after the last P_0 measurement.

If P_0 was calculated from measured Psat or entered temperature the calculated P_0 is used for all data points.

If P_0 was entered, the entered P_0 is used for all data points.

SATURATION PRESSURE

Saturation pressure (P_0) is selected on the *P_0 and Temperature Options* window. It may be entered or measured in the P_0 tube. The analyzer uses the following methods to get P_0:

1. P_0 is measured in the P_0 tube for each isotherm point. This method can be used only if the instrument has a dedicated P_0 transducer.
2. P_0 is measured at a specified time interval using the 1000 mmHg manifold transducer.
3. The saturation pressure of a gas is measured in the P_0 tube for prior to data collection. The bath temperature is found by looking up the temperature for the measured saturation pressure in the Psat vs. T table. P_0 is found by looking up the calculated bath temperature in the adsorptive properties Psat vs. T table.

4. P_0 is found by looking up the entered bath temperature in the adsorptive properties Psat vs. T table.
5. P_0 is entered.

SPC REPORT VARIABLES

REGRESSION CHART VARIABLES

The line of best fit for the Regression Chart is calculated by the usual least squares method. [1] If there is only a single point or all *N* points have the same x-value, there can be no line of best fit in the standard form.

$$\bar{x} = \frac{\sum x_i}{N}$$

$$\bar{y} = \frac{\sum y_i}{N}$$

$$\text{Slope} = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2}$$

$$\text{Intercept} = \bar{y} - \text{Slope} \cdot \bar{x}$$

The coefficient of correlation for this line is also calculated in the usual way. [2]

$$\sigma_x = \sqrt{\frac{\sum (x_i - \bar{x})^2}{N}}$$

$$\sigma_y = \sqrt{\frac{\sum (y_i - \bar{y})^2}{N}}$$

$$\text{Cov}(x, y) = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{N}$$

$$\text{CorrelationCoeff} = \frac{\text{Cov}(x, y)}{\sigma_x \sigma_y}$$

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[1] *BASIC Scientific Subroutines Vol II*, by F.R. Ruckdeschel, Copyright 1981 BYTE Publications/McGraw Hill, p. 16.
[2] *Mathematical Handbook for Scientists and Engineers*, G.A. Korn and T.M. Korn, McGraw Hill, Sec. 18.4. (1968)

CONTROL CHART VARIABLES

$$\text{Mean} = \frac{\sum y_i}{N}$$

$$\text{StandardDeviation} = \sqrt{\frac{\sum(y_i - \text{Mean})^2}{N-1}}$$

$$\text{C.V.} = \frac{\text{StdDev}}{\text{Mean}}$$

$$+n\sigma = \text{Mean} + n \cdot \text{StandardDeviation}$$

$$-n\sigma = \text{Mean} - n \cdot \text{StandardDeviation}$$

STOICHIOMETRY FACTOR FOR CHEMICAL ADSORPTION

The calculated stoichiometry factor is a weighted average. It is dependent on both the individual stoichiometry factor and number of moles of each active metal.

$$SF_{\mathrm{CALC}} = \frac{\frac{\%weight1 \times SF1}{W_{\mathrm{ATOMIC1}}} + \frac{\%weight2 \times SF2}{W_{\mathrm{ATOMIC2}}} + \frac{\%weight3 \times SF3}{W_{\mathrm{ATOMIC3}}} + ... + \frac{\%weightn \times SFn}{W_{\mathrm{ATOMICn}}}}{\frac{\%weight1}{W_{\mathrm{ATOMIC1}}} + \%weight2 W_{\mathrm{ATOMIC2}} + \frac{\%weight3}{W_{\mathrm{ATOMIC3}}} + ... + \frac{\%weightn}{W_{\mathrm{ATOMICn}}}}$$

where

SF_{CALC}	=	calculated stoichiometry factor
SF_1	=	stoichiometry factor for first metal
SF_2	=	stoichiometry factor for second metal
SF_3	=	stoichiometry factor for third metal
SF_n	=	stoichiometry factor for n^{th} metal
$\%weight_1$	=	% of sample weight for first metal
$\%weight_2$	=	% of sample weight for second metal
$\%weight_3$	=	% of sample weight for third metal
$\%weight_n$	=	% of sample weight for n^{th} metal
$WATOMIC_1$	=	atomic weight of first metal (g/mole)
$WATOMIC_2$	=	atomic weight of second metal (g/mole)
$WATOMIC_3$	=	atomic weight of third metal (g/mole)
$WATOMIC_n$	=	atomic weight of nth metal (g/mole)

SUMMARY REPORT

The following calculations and the results of previous calculations (as noted) are used to generate the summary report:

a. Single-point Surface Area (m^2/g)

$$S_{1PT} = \frac{[Q(1-P)] \times CSA(6.023 \times 10^{23})}{22414\text{cm}^2 \times \text{STP}\left(\frac{10^{18}\text{nm}^2}{\text{m}^2}\right)}$$

where

        P   =   pressure closest to 0.3 of the relative pressure points designated for surface area calculations

        Q   =   quantity adsorbed corresponding to *P*

b. Multi-point Surface Area. See *BET Surface Area on page 2* .
c. Langmuir Surface Area. See
d. t-Plot Micropore Surface Area.
e. t-Plot External Surface Area.
f. BJH Cumulative Adsorption
g. BJH Cumulative Desorption
h. Adsorption Total Pore Volume
i. Desorption Total Pore Volume
j. t-Plot Micropore Pore Volume.
k. Freundlich. See *Freundlich Isotherm on page 31*.
l. Temkin. See *Temkin Isotherm on page 62*.
m. Alpha-S. See .
n. DFT Pore Size and DFT Surface Energy. See *DFT (Density Functional Theory) on page 14*.
o. Nanoparticle Size

$$d = \frac{6 \times 10^4}{A\rho}$$

where

        ρ =   sample density

        A   =   BET surface area

        d   =   side length (for cubic particles or diameter (for spherical particles)

p. Dubinin-Astakhov Micropore Surface Area. See *Dubinin-Astakhov on page 20*.
q. Dubinin-Astakhov Micropore Volume. See *Dubinin-Astakhov on page 20*.

r. Dubinin-Radushkevich Micropore Surface Area. See ***Dubinin-Radushkevich on page 24*** .

s. Dubinin-Radushkevich Monolayer Capacity. See ***Dubinin-Radushkevich on page 24*** .

t. MP-Method Cumulative Surface Area of Pores

$$S_{\text{total}} = S_{\text{cum,i}}$$

See for the last collected data point used in the MP-method Calculations, and the range of hydraulic pore radii over which the cumulative surface area was computed.

u. MP-Method Cumulative Pore Volume of Pores

$$V_{\text{total}} = V_{\text{cum,i}}$$

See for the last collected data point used in the MP-method calculations, and the range of hydraulic pore radii over which the cumulative pore volume was computed.

v. Average Pore Hydraulic Radius (Å)

$$\bar{r} = \frac{V_{\text{total}}}{S_{\text{total}}} \times 10^4$$

w. Horvath-Kawazoe. See ***Horvath-Kawazoe on page 33***.

T-PLOT

A least-squares analysis fit is performed on the $(t_i, N_{ads,i})$ data pairs where t_i is the independent variable and $N_{ads,i}$ is the dependent variable. Only the values of t_i between t_{min} and t_{max}, the minimum and maximum thickness, are used. The following are calculated:

a. Slope (S cm³/g-Å STP)

b. Y-intercept (Y_{int} cm³/g STP)

c. Error of the slope (S_{err} cm³/g-Å STP)

d. Error of the Y-intercept (YI_{err} cm³/g STP)

e. Correlation coefficient

Using the results of the above calculations, the following can be calculated:

External Surface Area (m²/g):

$$\frac{SV_{mol}}{F \times 22414 cm^3 STP} \times 10^4$$

where

10^4	=	unit conversions
F	=	surface area correction factor, user-entered on the *t-Plot Report Options* window
V_{mol}	=	liquid molar volume, from the fluid property information

Micropore Surface Area (m²/g):

$$SA_{\mu\rho} = SA_{total} + SA_{ext}$$

where SA_{total} is the BET surface area if the user enabled the BET report exclusively, or Langmuir surface area if the user enabled the Langmuir report exclusively. If neither report has been selected, SA_{total} is the BET surface area value calculated using a set of default parameters.

Micropore Volume (cm³ liquid/g):

$$\frac{Y_{int} V_{mol}}{22414 cm^3 STP}$$

TEMKIN ISOTHERM

The Temkin isotherm has the form:

$$\frac{Q}{Q_m} = \frac{RT}{q_0 \alpha} \ln(A_0 P)$$

where

A_0	=	adjustable constant
α	=	adjustable constant
P	=	equilibrium pressure measured by gauge at temp T_{amb}
q_0	=	the differential heat of adsorption at zero surface coverage
Q	=	quantity of gas adsorbed
Q_m	=	quantity of gas in a monolayer
R	=	molar gas constant $8.31441 \times 10^{-3} \frac{kJ}{molK}$
T	=	bath temperature

In terms of quantity adsorbed

$$Q = \frac{RTQ_m}{q_0 \alpha}[\ln A_0 + \ln P]$$

Thus, the plot of the natural log of absolute pressure vs. quantity adsorbed yields a straight line with slope $\frac{RTQ_m}{q_0}$ and intercept $\ln A_0 \frac{RTQ_m}{q_0 \alpha}$

THERMAL TRANSPIRATION CORRECTION

During data reduction, thermal transpiration correction is applied to the data if the user selected *Apply thermal transpiration correction* from the *Report Options* window. Starting with the first collected pressure, the following calculations are performed until the pressure ratio (PC/P) is greater than or equal to 0.99.

$$Y = \left(\frac{P \times \text{SD} \times \text{MD}^2}{2.33 \times T} \right) 10^3$$

$$\mu = \frac{(1+G)Y}{(1+H)Y}$$

$$F = \frac{1}{\alpha Y^2 + \beta Y + \mu}$$

$$P = \left(1 - F \left(1 - \sqrt{\frac{T_{\text{bath}}}{T_{\text{amb}}}} \right) \right)$$

where

α	=	Weber's coefficient, 0.033
β	=	Weber's coefficient, 0.245
F, Y, μ	=	intermediate values for subsequent calculations
G	=	Weber's coefficient, 2.5
H	=	Weber's coefficient, 2
MD	=	thermal transpiration hard sphere diameter of gas (Å), from the *Adsorptive Properties* window
P	=	equilibrated collected pressure measured by gauge at temp T_{amb}
SD	=	inside diameter of sample tube (mm) from the *Report Options* window
T	=	average temperature $\frac{T_{\text{bath}} + T}{2}$
T_{amb}	=	room temperature (298 K)
T_{bath}	=	analysis bath temperature (*K*), from the *P$_0$ and Temperature Options* window

THICKNESS CURVE

For each point designated, the following parameters are used in thickness curve calculations:

C_1 = parameter #1

C_2 = parameter #2

C_3 = parameter #3

$P_{rel,\,i}$ = relative pressure for the ith point (mmHg)

t_i = thickness for i^{th} point

REFERENCE

Interpolated from table.

KRUK-JARONIEC-SAYARI

$$t_i = \left(\frac{C_2}{C_2 - \log(P_{rel,i})} \right)^{c_3}$$

HALSEY

$$t_i = C_1 \left[\frac{C_2}{\ln(P_{rel,i})} \right]^{C_3}$$

Halsey[1]

HARKINS AND JURA

$$t_i = \left[\frac{C_1}{C_2 - \log(P_{rel,i})} \right]^{C_3}$$

Harkins and Jura[2]

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[1] Halsey, G., J. *Chem. Phys. 16*, 931-937 (1948).

[2] Harkins, W.D. and Jura, G., J. *Chem. Phys. 11*, 431 (1943).

BROEKOFF-DE BOER

$$\log(P_{\text{rel,i}}) = \frac{C_1}{t^2_{,i}} + C_2 \exp(c_3 t_i)$$

CARBON BLACK STSA

$$t_i = C_1 (P_{\text{rel,i}})^2 + C_2 (P_{\text{rel,i}}) + C_3$$