

# **TRISTAR<sup>®</sup> II PLUS**

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**SURFACE AREA AND POROSITY ANALYZER**



**micromeritics<sup>®</sup>**

***CALCULATIONS***

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Apr 2024

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## ***Table of Contents***

<b>Alpha-S Method</b>	<b>1</b>
<b>BET Surface Area</b>	<b>2</b>
<b>BJH Pore Volume and Area Distribution</b>	<b>3</b>
<b>DFT (Density Functional Theory)</b>	<b>12</b>
<b>Dollimore-Heal Pore Volume and Area Distribution</b>	<b>16</b>
<b>Dubinin-Astakhov</b>	<b>18</b>
<b>Dubinin-Radushkevich</b>	<b>22</b>
<b>Equilibration</b>	<b>24</b>
<b>f-Ratio Method</b>	<b>25</b>
<b>Freundlich Isotherm</b>	<b>26</b>
<b>Heat of Adsorption for Physical Adsorption</b>	<b>27</b>
<b>Horvath-Kawazoe</b>	<b>28</b>
<b>Langmuir Surface Area</b>	<b>38</b>
<b>MP-Method</b>	<b>40</b>
<b>Quantity Adsorbed</b>	<b>42</b>
<b>Relative Pressure</b>	<b>44</b>
<b>Saturation Pressure</b>	<b>45</b>

SPC Report Variables	46
Summary Report	48
t-Plot	50
Temkin Isotherm	51
Thermal Transpiration Correction	52
Thickness Curve	53

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## ALPHA-S METHOD

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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  $(\alpha_i, Q_{\text{ads},i})$  data pairs where  $\alpha_i$  is the independent variable and  $Q_{\text{ads},i}$  is the dependent variable. The following are calculated:

- Slope ( $S \text{ cm}^3/\text{g STP}$ )
- Y-intercept ( $Q_0 \text{ cm}^3/\text{g STP}$ )
- Error of the slope ( $\text{cm}^3/\text{g STP}$ )
- Error of the Y-intercept ( $\text{cm}^3/\text{g STP}$ )
- Correlation coefficient

Surface area is calculated as:

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

Pore size is calculated as:

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

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

## BET SURFACE AREA

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The BET<sup>1)</sup> 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:

- Slope (S cm<sup>3</sup>/g STP)
- Y-intercept ( $y_0$  cm<sup>3</sup>/g STP)
- Uncertainty of the slope ( $u(s)$  cm<sup>3</sup>/g STP)
- Uncertainty of the Y-intercept ( $u(y_0)$  cm<sup>3</sup>/g STP)
- Correlation coefficient

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

**BET Surface Area (m<sup>2</sup>/g):**

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

**BET C value:**

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

**Quantity in the Monolayer (cm<sup>3</sup>/g STP):**

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

**Error of the BET Surface Area (m<sup>2</sup>/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***

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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<sup>1)</sup> 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<sup>2)</sup> 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***

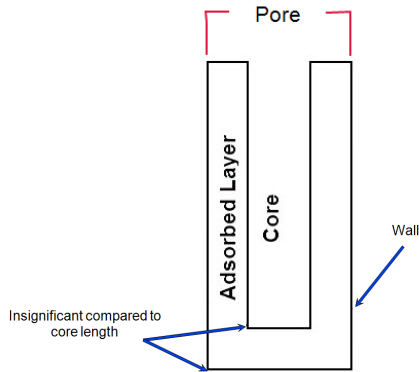
A pore filled with condensed liquid nitrogen has three zones:

- **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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<sup>1)</sup> Kelvin, J. (published under the name of Sir William Thomson), *Phil. Mag.* 42, 448-452 (1871).

<sup>2)</sup> 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 ( $V_l$ ,  $\text{cm}^3/\text{g}$ )

$$V_l = \frac{Q_a V_{mol}}{22414 \text{cm}^3 \text{STP}}$$

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:

$$Rc_i = \frac{-A}{(1+F) \ln(P_i)}$$

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 ( $\text{\AA}$ ) 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 P1 to P2, 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 53](#).

For the last pressure interval from the lowest  $P_{r_i}$  to zero relative pressure, reference the calculations from the equations in [Thickness Curve on page 53](#).

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:

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

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

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

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 ( $\text{cm}^2/\text{g}$ ) is calculated as:

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

where

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

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

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

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:

$$D_{\text{avg},k} = \frac{2(R_{c_k} + R_{c_{k+1}})(R_{c_k})(R_{c_{k+1}})}{R_{c_k}^2 + R_{c_{k+1}}^2}$$

$D_{\text{avg},k}$  is the diameter of a pore which would have a surface area that is the average of the areas for pores radius  $R_{c_k}$  and  $R_{c_{k+1}}$ , 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:

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

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:

$$\Delta T d = T w_{\text{avg},k} - T w_{i+1}$$

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

$$CSA_{c_k} = \left[ \frac{D_{\text{avg},k}}{2} + \Delta T d \right]^2 \left( \frac{10^{-16} \text{cm}^2}{\text{\AA}^2} \right)$$

The length of the newly opened pores is calculated as:

$$L P_k = \frac{V_{c_i}}{CSA_{c_k}}$$

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:

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

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

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

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

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

$$Rc_{j,\text{new}} = Rc_{j,\text{old}} + \Delta Tw$$

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:

$$Dp_j = 2(Rc_j)$$

for all  $Rc_j$ , including  $Rc_{k+1}$ .

The remaining calculations are based on  $Dp_i$ ,  $D_{\text{avg},i}$ , and  $LP_i$ . These calculations are only done for  $D_{\text{avg},i}$  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 ( $Vp_i$ ,  $\text{cm}^3/\text{g}$ ):

$$Vp_i = \pi(LP_i) \left[ \frac{D_{\text{avg},i}}{2} \right]^2 \left[ \frac{10^{16} \text{cm}^2}{\text{\AA}^2} \right]$$

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

$$VP_{\text{cum},i} = \sum_j VP_j \text{ for } (J \leq i)$$

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

$$SA_i = \pi(LP_i) \left( \frac{10^{-2} \text{m}}{\text{cm}} \right) \left( D_{\text{avg},i} \right) \left( \frac{10^{-10} \text{m}}{\text{\AA}} \right)$$

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

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

(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 ( $dA/dD_i$ ,  $m^2/g-A$ ):

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

(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 ( $VpF_{cum,i}$ ,  $cm^3/g$ ):

$$VpF_{cum,i} = \text{INTERP}(DpF_{i+1})$$

where  $\text{INTERP}(x)$  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 ( $V_p F_i$ ,  $\text{cum}^3/\text{g}$ ):

$$V_p F_i = V_p F_{\text{cum},i} - V_p F_{\text{cum},i-1}$$

where  $V_p F_{\text{cum},0} = 0$

(4) Cumulative Surface Area ( $SAF_{\text{cum},i}$ ,  $\text{m}^2/\text{g}$ ):

$$SAF_{\text{cum},i} = \text{INTERP}(D_p F_{i+1})$$

where  $\text{INTERP}(x)$  is the value interpolated from the function  $X = D_{p,j+1}$  and  $Y = SA_{\text{cum},j}$ .

(5) Incremental Surface Area ( $SAF_i$ ,  $\text{m}^2/\text{g}$ ):

$$SAF_i = SAF_{\text{cum},i} - SAF_{\text{cum},i-1}$$

where  $SAF_{\text{cum},0} = 0$ .

(6)  $dV/dD$  pore volume ( $dV/dD_p F_i$ ,  $\text{cm}^3/\text{g-A}$ ):

$$\frac{dV}{dD_p F_i} = \text{INTERP}(D_p F_{i+1})$$

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

(7)  $dV/d \log(D)$  pore volume [ $dV/d \log(D_p F_i)$ ,  $\text{cm}^3/\text{g}$ ]:

$$\frac{dV}{d \log(D_p F_i)} = \text{INTERP}(D_p F_{i+1})$$

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

(8)  $dA/dD$  pore area ( $dA/dD_p F_i$ ,  $\text{m}^2/\text{g-A}$ ):

$$\frac{dA}{dD_p F_i} = \text{INTERP}(D_p F_{i+1})$$

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



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

## COMPENDIUM OF VARIABLES

$\Delta Td$	=	thickness of layer desorbed from walls of newly opened pores (Å)
$\Delta Tw$	=	thickness of adsorbed layer desorbed during interval (Å)
$A$	=	adsorbate property factor; from the <i>BJH Adsorptive Options</i> window
$CSA$	=	analysis gas molecular cross-sectional area ( $nm^2$ ), user-entered on the <i>Adsorptive Properties</i> window
$CSAa$	=	annular cross-sectional area of the desorbed layer ( $cm^2$ )
$CSAc$	=	cross-sectional area of opening of newly opened pores ( $cm^2$ )
$D_{\text{avg}}$	=	average pore diameter (Å)
$Dp$	=	pore (or core) diameter (Å)
$F$	=	fraction of pores open at both ends; from the <i>BJH Adsorption Report Options</i> window or the <i>BJH Desorption Report Options</i> 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 ( $cm^3/g$ )
$VI$	=	liquid equivalent volume of volume adsorbed ( $cm^3/g$ )
$V_{\text{mol}}$	=	liquid molar volume, from the fluid property information

## ***DFT (DENSITY FUNCTIONAL THEORY)***

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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<sup>1</sup>) 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:

$$Q(p) = \int da db dc \dots q(p, a, b, c, \dots) f(a, b, c, \dots) \quad (1)$$

where

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

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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<sup>1</sup>) 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:

$$Q(p) = \int d\epsilon q(p, \epsilon) f(\epsilon) \quad (2)$$

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  $\epsilon$ , and
- $f(\epsilon)$  = the total area of surface of energy  $\epsilon$  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:

$$Q(p) = \int dH q(p, H) f(H) \quad (3)$$

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<sup>1</sup>). 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 approximated. 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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<sup>1</sup>) Jagiello, Jacek. "Stable numerical solution of the adsorption integral equation using splines." *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***

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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.

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

### ***PORE LENGTH***

$$l_i = \frac{A_{p,i} + 10^8}{\pi \bar{D}_i}$$

$$A_{p,i} = \frac{4 \times (10^8 \Delta V_p)}{\bar{D}_i}$$

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

$$C\nu = \left( \frac{\bar{D}_i}{2(\bar{r}_k + t(P_i) - t(P_{i+1}))} \right)^2$$

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

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

where

$\Delta V_p$	=	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
$C_v$	=	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

- $\beta$  = 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 ( $\text{cm}^3/\text{g}$  STP)
- $Q_0$  = the micropore capacity ( $\text{cm}^3/\text{g}$  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:

$$LV = \log(Q)$$

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

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 ( $S \text{ cm}^3/\text{g STP}$ )
- b. Y-intercept ( $YI \text{ cm}^3/\text{g STP}$ )
- c. Error of the slope ( $S_{\text{err}} \text{ cm}^3/\text{g STP}$ )
- d. Error of the y-intercept ( $YI_{\text{err}} \text{ cm}^3/\text{g STP}$ )
- e. Correlation coefficient
- f. Optimized Astakhov exponent ( $N$ )

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

**Monolayer Capacity ( $\text{cm}^3/\text{g STP}$ ):**

$$Q_0 = 10^{YI}$$

**Micropore Volume ( $\text{cm}^3/\text{g}$ ):**

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

where

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

**Limiting Micropore Volume ( $\text{cm}^3/\text{g}$ ):**

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

where

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

**Error of Limiting Micropore Volume ( $\text{cm}^3/\text{g}$ ):**

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

**Characteristic Energy (KJ/mol):**

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

**Modal Equivalent Pore Diameter (Å):**

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

where

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

**Maximum Differential Pore Volume (cm<sup>3</sup>/g-Å):**

This value is also known as *frequency of the mode*<sup>1)</sup>.

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

**Mean Equivalent Pore Width (Å):**

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

**Micropore surface area (m<sup>2</sup>/g):**

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

$\Gamma$  is calculated by a polynomial approximation over the domain  $0 \leq x \leq 1$ :

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

---

<sup>1)</sup> Ross and Olivier, J.P., "On Physical Adsorption," J. Wiley and Sons, New York (1964).

where

$$\begin{aligned}
 b_1 &= -0.57719\ 1652 \\
 b_2 &= 0.98820\ 5891 \\
 b_3 &= -0.89705\ 6937 \\
 b_4 &= 0.91820\ 6857 \\
 b_5 &= -0.75670\ 4078 \\
 b_6 &= 0.48219\ 9394 \\
 b_7 &= -0.19352\ 7818 \\
 b_8 &= 0.03586\ 8343
 \end{aligned}$$

and where

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

**Equivalent Pore Diameter (Å):**

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

**dV/dD Pore Volume (cm<sup>3</sup>/g-Å):**

$$\begin{aligned}
 \frac{dV}{dD_i} &= 0.5 \times W_0 \times 3N \left( \frac{10^3 \text{ nm}^3 / \text{Å}^3}{\beta \cdot E_0} \right)^{3N} \left( \frac{D_i}{2} \right)^{-(3N+1)} \\
 &\quad \times \exp \left[ - \left( \frac{10^3 \text{ nm}^3 / \text{Å}^3}{\beta \cdot E_0} \right)^N \left( \frac{D_i}{2} \right)^{-3N} \right]
 \end{aligned}$$

## ***DUBININ-RADUSHKEVICH***

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The Dubinin-Radushkevich<sup>1)</sup> equation is:

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

where

- $\beta$  = the affinity coefficient of analysis gas relative to  $P_0$  gas (for this application  $\beta$  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 ( $\text{cm}^3/\text{g}$  STP)
- $Q_0$  = the micropore capacity ( $\text{cm}^3/\text{g}$  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:

$$LV = \log(Q)$$

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

The intercept,  $\log(V_0)$  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,  $V_0$  is the monolayer capacity. Based on this assumption, the following are calculated:

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<sup>1)</sup> 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 ( $S \text{ cm}^3/\text{g STP}$ )
- b. Y-intercept ( $YI \text{ cm}^3/\text{g STP}$ )
- c. Error of the slope ( $S_{\text{err}} \text{ cm}^3/\text{g STP}$ )
- d. Error of the y-intercept ( $YI_{\text{err}} \text{ cm}^3/\text{g STP}$ )
- e. Correlation coefficient

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

**Monolayer Capacity ( $\text{cm}^3/\text{g STP}$ ):**

$$Q_0 = 10^{YI}$$

**Error of Monolayer Capacity ( $\text{cm}^3/\text{g STP}$ ):**

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

**Micropore surface area ( $\text{m}^2/\text{g}$ ):**

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

where

$\sigma$  = molecular cross sectional area of gas ( $\text{nm}^2$ ) from the *Adsorptive Properties* window

## 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<sup>1)</sup> convolution method for polynomial functions. The following equations are those used to compute weighted average and first derivative, respectively, for the 6<sup>th</sup> point of an 11-point window:

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

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

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

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

$P_{\text{avg}}$	=	average pressure
$P_{\text{chg}}$	=	change in pressure
$P_{\text{pcp},i}$	=	percent change per interval
$P_i$	=	$i^{\text{th}}$ 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  $P_{\text{avg}}$  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.

<sup>1)</sup> Savitzky, A. and Golay, M.J.E., *Anal. Chem.* 36, 1627 (1964).

## ***F-RATIO METHOD***

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

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

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

## ***FREUNDLICH ISOTHERM***

---

The Freundlich isotherm has the form:

$$\frac{Q}{Q_m} = CP^{\frac{1}{m}}$$

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,

$$Q = Q_m CP^{\frac{1}{m}}$$

Taking the log of both sides yields

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



## ***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  $\ln (P/P_0)$  as a function of  $1/RT$  for a set of isotherms measured at different temperatures.

## ***HORVATH-KAWAZOE***

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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<sup>1)</sup> 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  $\text{cm}^4$  that are equal to  $\text{\AA}^4$

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

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

where

$D_A$  = molecular diameter ( $\text{\AA}$ ) from the *Horvath-Kawazoe Physical Properties* window

$D_S$  = diameter of sample atom ( $\text{\AA}$ ) from the *Horvath-Kawazoe Physical Properties* window

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

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

$L$  = pore width (nucleus to nucleus) ( $\text{\AA}$ )

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<sup>1)</sup> Horvath, G. and Kawazoe, K., *J. Chem. Eng. Japan* 16(6), 470 (1983).

- P = equilibrium pressure  
 P<sub>0</sub> = saturation pressure  
 R = gas constant (8.31441 × 10<sup>7</sup> erg/mol K)  
 T = analysis bath temperature (K), from an entered or calculated value on the *P<sub>0</sub> and Temperature Options* window

where:

- Z<sub>s</sub> = sample equilibrium diameter at zero interaction energy (Å) from the *Horvath-Kawazoe Physical Properties* window  
 Z<sub>A</sub> = zero interaction energy diameter from the *Horvath-Kawazoe Physical Properties* window

### CYLINDER PORE GEOMETRY (SAITO/FOLEY)

When using the Saito/Foley<sup>1)</sup> 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:

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

where

10<sup>32</sup> = the number of Å<sup>4</sup> that are equal to 1 cm<sup>4</sup>

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

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

---

<sup>1)</sup> Saito, A. and Foley, H. C., *AIChE 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<sup>4</sup>) from the *Horvath-Kawazoe Report Options* window

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

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

P = equilibrium pressure

$P_0$  = saturation pressure

R = gas constant ( $8.31441 \times 10^7$  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<sub>0</sub> and Temperature Options* window

## SPHERE PORE GEOMETRY (CHENG/YANG)

When using the Cheng / Yang<sup>1)</sup> 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:

$$\ln \left( \frac{P}{P_0} \right) = \frac{6N_1 \epsilon_{12}^* + N_2 \epsilon_{22}^* L^3 \times 10^{32}}{RTL - d_0^3} \left[ - \left( \frac{d_0}{L} \right)^6 \left( \frac{T_1}{12} + \frac{T_2}{8} \right) + \left( \frac{d_0}{L} \right)^{12} \left( \frac{T_3}{90} + \frac{T_4}{80} \right) \right]$$

where

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

$$\epsilon_{12}^* = \frac{\dot{A}_S}{4d_S^6}, \text{ where } \dot{A}_S = \frac{6(mc^2)\alpha_S\alpha_A}{x_S + x_A}$$

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

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

where

$D_A$  = molecular diameter ( $\text{\AA}$ ) from the *Horvath-Kawazoe Physical Properties* window

$D_S$  = diameter of sample atom ( $\text{\AA}$ ) from the *Horvath-Kawazoe Physical Properties* window

$L$  = pore width (nucleus to nucleus) ( $\text{\AA}$ )

$N_1$  =  $4\pi L_2 N_S$ , where  $N_S$  = number of sample atoms/cm<sup>2</sup> at monolayer

$N_2$  =  $4\pi (L - d_0)^2 N_A$ , where  $N_S$  = number of gas molecules/cm<sup>2</sup>

$P$  = equilibrium pressure

$P_0$  = saturation pressure

$R$  = gas constant ( $8.31441 \times 10^7$  erg/mol K)

$T$  = analysis bath temperature (K), from an entered or calculated value on the *P<sub>0</sub> and Temperature Options* window

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<sup>1)</sup> 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  $S = \frac{L-d_0}{L}$

### 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
- $\theta$  = degree of void filling;  $\theta$  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.  $\theta$  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

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

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

where

- $\alpha_A$  = polarizability of gas molecule (cm<sup>3</sup>)
- $\alpha_S$  = polarizability of sample atoms (cm<sup>3</sup>)
- $mc^2$  = kinetic energy of electron (0.8183 × 10<sup>-6</sup> erg)
- $\chi_A$  = diamagnetic susceptibility of gas molecule (cm<sup>3</sup>)

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

where:

$N_M$  = number of gas molecules/cm<sup>2</sup> at monolayer from the *Horvath-Kawazoe Physical Properties* window

$N_S$  = number of sample atoms/cm<sup>2</sup> from the *Horvath-Kawazoe Physical Properties* window

$\chi_S$  = diamagnetic susceptibility of sample atom (cm<sup>3</sup>)

See [Interaction Parameter Components Table on page 35](#) 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 (cm<sup>3</sup>/g):

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

where

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

### dV/dD Pore Volume (cm<sup>3</sup>/g-Å):

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

### Median Pore Width (Å):

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

$$D_{\text{med}} = \exp \left( \ln D_1 + (\ln D_g - \ln D_1) \frac{\ln V_{\text{half}} - \ln V_l}{\ln V_g - \ln V_l} \right)$$

where

- $D_1$  = pore width ( $L_i$ ) that corresponds to  $V_l$
- $D_g$  = pore width ( $L_i$ ) that corresponds to  $V_g$
- $V_{\text{cum},n}$  = total cumulative pore volume ( $V_{\text{cum},i}$ ) for points designated for Horvath-Kawazoe calculations
- $V_g$  = cumulative pore volume ( $V_{\text{cum},i}$ ) for first point greater than  $V_{\text{half}}$
- $V_{\text{half}}$  = 50% of total cumulative pore volume
- $V_l$  = cumulative pore volume ( $V_{\text{cum},i}$ ) for first point less than  $V_{\text{half}}$



## Interaction Parameter Components Table

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

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

**Carbon-Graphite**

$$\begin{aligned}
 D_S &= 3.40 \\
 N_S &= 3.845 \times 10^{15} \\
 X_S &= 1.05 \times 10^{-29} \text{ (Ross/Olivier)} \\
 &\quad 13.5 \times 10^{-29} \\
 &\quad \text{(Horvath/Kawazoe, implicit)} \\
 \alpha_S &= 1.02 \times 10^{-24}
 \end{aligned}$$

**Zeolite**

$$\begin{aligned}
 D_S &= 3.04 \\
 N_S &= 3.75 \times 10^{15} \\
 X_S &= 1.94 \times 10^{-29} \\
 \alpha_S &= 0.85 \times 10^{-24}
 \end{aligned}$$

**Nitrogen**

$$\begin{aligned}
 D_A &= 3.00 \\
 N_A &= 6.71 \times 10^{14} \\
 X_A &= 3.6 \times 10^{-29} \\
 \alpha_A &= 1.76 \times 10^{-24}
 \end{aligned}$$

**Argon**

$$\begin{aligned}
 D_A &= 2.95 \\
 N_A &= 7.608 \times 10^{14} \\
 X_A &= 3.22 \times 10^{-29} \\
 \alpha_A &= 1.63 \times 10^{-24}
 \end{aligned}$$

**Carbon Dioxide**

$$\begin{aligned}
 D_A &= 3.23 \\
 N_A &= 4.567 \times 10^{14} \text{ (25 °C)} \\
 &\quad 5.45 \times 10^{14} \text{ (0 °C)} \\
 &\quad 7.697 \times 10^{14} \text{ (-78 °C)} \\
 X_A &= 5.0 \times 10^{-29} \\
 \alpha_A &= 2.7 \times 10^{-24}
 \end{aligned}$$

$D_A$  values are from van der Waal's constant.

$N_A$  values are from liquid densities.

$X$  and  $\alpha$  values are derived from data found in Ross and Olivier<sup>1)</sup> .

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<sup>1)</sup> Ross and Olivier, J.P., "On Physical Adsorption," J. Wiley and Sons, New York (1964)

The physical parameters referenced in Saito/Foley are:

**Aluminophosphate**

$$\begin{aligned}D_S &= 2.60 \\N_S &= 1.48 \times 10^{15} \\X_S &= 1.3 \times 10^{-29} \\a_s &= 2.5 \times 10^{-24}\end{aligned}$$

**Aluminosilicate**

$$\begin{aligned}D_S &= 2.76 \\N_S &= 1.31 \times 10^{15} \\X_S &= 1.3 \times 10^{-29} \\a_s &= 2.5 \times 10^{-24}\end{aligned}$$

## LANGMUIR SURFACE AREA

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For each point designated for surface area calculations, the Langmuir<sup>1)</sup> transformation is calculated as:

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

where  $L$  is in units of  $\text{g}/\text{cm}^3$  STP.

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

- Slope ( $S$   $\text{g}/\text{cm}^3$  STP)
- Y-intercept ( $Y_{\text{int}}$   $\text{g}/\text{cm}^3$  STP)
- Error of the slope ( $S_{\text{err}}$   $\text{g}/\text{cm}^3$  STP)
- Error of the y-intercept ( $Y_{\text{err}}$   $\text{g}/\text{cm}^3$  STP)
- Correlation coefficient

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

### Langmuir Surface Area ( $\text{m}^2/\text{g}$ ):

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

where

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

### Quantity of the Monolayer ( $\text{cm}^3/\text{g}$ STP):

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

---

<sup>1)</sup> 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<sup>2</sup>/g):

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

## MP-METHOD

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With the  $(t_i, Q_i)$  data pairs<sup>1)</sup>, 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  $i^{\text{th}}$  point ( $\text{m}^2/\text{g}$ ):**

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

where

$10^4$  = unit conversions

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

**Incremental pore surface area occluded for the  $i^{\text{th}}$  point ( $\text{m}^2/\text{g}$ ):**

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

**Cumulative pore surface area occluded for the  $i^{\text{th}}$  point ( $\text{m}^2/\text{g}$ ):**

$$S_{\text{cum}_i} = S_{\text{inc},i} + S_{\text{inc},i-1} + \dots + S_{\text{inc},1}$$

**$dA/dR$  pore surface area for the  $i^{\text{th}}$  point ( $\text{m}^2/\text{g}\cdot\text{Å}$ ):**

$$\frac{dA}{dR_i} = \frac{S_{\text{inc}_i}}{t_i - t_{i-1}}$$

---

<sup>1)</sup> Mikhail, R., Brunauer, S. and Bodor, E., *J. Colloid and Interface Sci.* 24, 45 (1968).

Incremental pore volume occluded for the  $i^{\text{th}}$  point ( $\text{cm}^3/\text{g}$ ):

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

Cumulative pore volume occluded for the  $i^{\text{th}}$  point ( $\text{cm}^3/\text{g}$ ):

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

$dV/dR$  pore volume for the  $i^{\text{th}}$  point ( $\text{cm}^3/\text{g}\text{-\AA}$ ):

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

## QUANTITY ADSORBED

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### FREE SPACE - MEASURED

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

$$V_{fw} = \left( \frac{P_1}{P_2} V_{man1} - V_{man2} \right) \frac{T_{STD}}{T_{man}}$$

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

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

### 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.

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

$$V_{fc} = V_{cb} + V_p - V_s \left( \frac{T_{STD}}{T_{bath}} \right)$$



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**COMPENDIUM OF VARIABLES**

$P_1$	=	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)
$T_{man}$	=	system manifold temperature (K)
$T_{STD}$	=	standard temperature (273.15 K)
$V_{bath}$	=	volume of cold free space at analysis bath temperature ( $\text{cm}^3$ at standard temperature)
$V_{cb}$	=	volume of cold free space of the empty tube ( $\text{cm}^3$ at standard temperature)
$V_{fc}$	=	volume of cold free space ( $\text{cm}^3$ at standard temperature)
$V_{fw}$	=	volume of warm free space ( $\text{cm}^3$ at standard temperature)
$V_{man1}$	=	manifold volume ( $\text{cm}^3$ ) before dosing onto sample. May differ from $V_{man2}$ because it includes deflection if 10 mmHg transducer is present.
$V_{man2}$	=	manifold volume ( $\text{cm}^3$ ) after dosing onto sample. May differ from $V_{man1}$
$V_p$	=	port volume
$V_s$	=	sample volume
$V_{wb}$	=	volume of warm free space of the empty tube ( $\text{cm}^3$ at standard temperature)

## ***RELATIVE PRESSURE***

---

If  $P_0$  is measured in the  $P_0$  tube, the current pressure is measured in the  $P_0$  tube when each point is taken, and used to calculate relative pressure for that point:

$$P_{\text{rel}} = \frac{P}{P_0}$$

## ***SATURATION PRESSURE***

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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.

- If entered,  $P_0$  equals user-entered value.
- If measured,  $P_0$  equals equilibrated pressure reading after saturating  $P_0$  tube or the sample tube.  $P_0$  is measured for each data point.

## SPC REPORT VARIABLES

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### REGRESSION CHART VARIABLES

The line of best fit for the Regression Chart is calculated by the usual least squares method. <sup>1)</sup> 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. <sup>2)</sup>

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

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

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

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

---

<sup>1)</sup> *BASIC Scientific Subroutines Vol II*, by F.R. Ruckdeschel, Copyright 1981 BYTE Publications/McGraw Hill, p. 16.

<sup>2)</sup> *Mathematical Handbook for Scientists and Engineers*, G.A. Korn and T.M. Korn, McGraw Hill, Sec. 18.4. (1968)

**CONTROL CHART VARIABLES**

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

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

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

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

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

## SUMMARY REPORT

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

- a. Single-point Surface Area (m<sup>2</sup>/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 [Langmuir Surface Area on page 38](#)  
 d. t-Plot Micropore Surface Area. See [t-Plot on page 50](#).  
 e. t-Plot External Surface Area. See [t-Plot on page 50](#).  
 f. BJH Cumulative Adsorption  
 g. BJH Cumulative Desorption  
 h. Adsorption Total Pore Volume  
 i. Desorption Total Pore Volume  
 j. t-Plot Micropore Pore Volume. See [t-Plot on page 50](#).  
 k. Freundlich. See [Freundlich Isotherm on page 26](#).  
 l. Temkin. See [Temkin Isotherm on page 51](#).  
 m. Alpha-S. See .  
 n. DFT Pore Size and DFT Surface Energy. See [DFT \(Density Functional Theory\) on page 12](#).  
 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 18](#).  
 q. Dubinin-Astakhov Micropore Volume. See [Dubinin-Astakhov on page 18](#).

- r. Dubinin-Radushkevich Micropore Surface Area. See [Dubinin-Radushkevich on page 22](#).
- s. Dubinin-Radushkevich Monolayer Capacity. See [Dubinin-Radushkevich on page 22](#).
- t. MP-Method Cumulative Surface Area of Pores

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

See [MP-Method on page 40](#) 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 [MP-Method on page 40](#) 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 28](#).

- x. Percent Porosity The percent porosity is calculated for each reported pore volume as:

$$P = \frac{V}{\frac{1}{\rho} + V} \cdot 100\%$$

where

P	=	percent porosity
$\rho$	=	sample density
V	=	pore volume

## 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:

- Slope ( $S$  cm<sup>3</sup>/g-Å STP)
- Y-intercept ( $Y_{int}$  cm<sup>3</sup>/g STP)
- Error of the slope ( $S_{err}$  cm<sup>3</sup>/g-Å STP)
- Error of the Y-intercept ( $YI_{err}$  cm<sup>3</sup>/g STP)
- Correlation coefficient

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

### External Surface Area (m<sup>2</sup>/g):

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

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 (m<sup>2</sup>/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 (cm<sup>3</sup> liquid/g):

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



## TEMKIN ISOTHERM

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The Temkin isotherm has the form:

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

where

$A_0$  = adjustable constant

$\alpha$  = 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***

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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.

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

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

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

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

where

- $\alpha$  = Weber's coefficient, 0.033
- $\beta$  = Weber's coefficient, 0.245
- $F, Y, \mu$  = 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  $T_{\text{amb}}$
- $SD$  = inside diameter of sample tube (mm) from the *Report Options* window
- $T$  = average temperature  $\frac{T_{\text{bath}} + T}{2}$
- $T_{\text{amb}}$  = room temperature (298 K)
- $T_{\text{bath}}$  = analysis bath temperature (K), from the *P<sub>0</sub> and Temperature Options* window

## THICKNESS CURVE

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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  $i^{\text{th}}$  point (mmHg)
- $t_i$  = thickness for  $i^{\text{th}}$  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<sup>1)</sup>

### HARKINS AND JURA

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

Harkins and Jura<sup>2)</sup>

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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**

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

**CARBON BLACK STSA**

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