3FLEX™

SURFACE CHARACTERIZATION ANALYZER

CALCULATIONS

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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.

$$\alpha_{\mathrm{i}} = \frac{Q_i}{Q_{0.4}}$$

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

A least-squares analysis fit is performed on the (α_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:

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

Pore size is calculated as:

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

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

BET SURFACE AREA

The BET1) transformation is calculated as:

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

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):

$$A_{\mathrm{s}} = \frac{A_{\mathrm{m}} N_{\mathrm{A}}}{V_{\mathrm{m}}\left(s + y_0\right)} \times 10^{-18} m^2 / nm^2$$

BET C value:

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

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

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

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).

BET SURFACE AREA FOR TCD

Surface area is calculated as the number of molecules in the monolayer times the area of a molecule. The result is divided by sample mass to give the specific surface area.

$$A_{BET} = Q_{m,mol,} N_A A_{\alpha} / m$$

The quantity of adsorbate in the monolayer is determined by fitting BET-transformed data from multiple experiments.

$$B_i = \frac{P_{rel,i}}{Q_i\left(1 - P_{rel,i}\right)}$$

$$P_{rel,i} = c_i \frac{P_\alpha}{P_0}$$

The slope s and offset *y0* of the best-fit line through B_i vs. $P_{rel,i}$ are found.

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

$$C = s / y_0 - 1$$

Uncertainty in the surface area is estimated from the uncertainty in the fit parameters.

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

where

ABET = specific BET surface area
$Q_{m,mol}$ = quantity of adsorbate in the monolayer in moles
N_A = Avogadro constant: 6.02214129 × 10^{23} mol^{-1}
A_α = adsorbate cross-sectional area
m = sample mass
B_i = BET transform of the data from experiment *i*
Q_i = cumulative quantity adsorbed for all peaks in experiment $i
$P_{rel,i}$ = relative pressure for experiment *i*
P_α = entered ambient pressure
P_0 = entered saturation pressure for the active gas
c_i = active gas concentration in experiment *i*
C = BET C value
s = slope of best-fit line

y_0 = intercept of best-fit line
$u(x)$ = uncertainty of x

SINGLE-POINT

For single experiment the monolayer quantity calculation becomes

$$s = B / P_{rel}$$

$$y_0 = 0$$

$$Q_m = Q\left(1 - P_{rel}\right)$$

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 Kelvin1) 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 Halenda2) 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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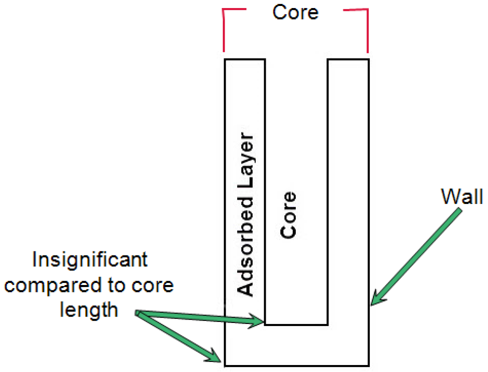
1) Kelvin, J. (published under the name of Sir William Thomson), *Phil. Mag. 42*, 448-452 (1871).
2) Barrett, E.P.; Joyner, L.S.; and Halenda, P.P., J. *Am. Chem. Soc. 73*, 373-380 (1951).



CALCULATIONS

The quantities adsorbed (*Qa*) are converted to the liquid equivalent volumes (*Vl*, cm^3/g):

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

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 (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 72***.

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 72***.

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:

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

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_j is greater than the current increment of volume desorbed (VI_i - $V1_{i+1}$), desorption from walls only is occurring. Total surface of walls exposed thus far (cm^2/g) is calculated as:

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

   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:

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

   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 (VI_i-VI_{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:

   $$Vc_i = (VI_i - VI_{i+1}) - Vd_i$$

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

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

   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:

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

$D_{avg,k}$ 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 $D_{avg,k}$ is calculated as:

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

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

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

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:

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

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

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

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:

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

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

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

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

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

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

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:

$$Dp_j = 2\left(Rc_j\right)$$

for all Rc_j including Rc_{k+1}.

The remaining calculations are based on Dp_i, $D_{avg,i}$, and LP_i. These calculations are only done for $D_{avg,i}$ 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):

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

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

$$VP_{cum,i} = \sum_j Vp_j for\left(J \le 1\right)$$

(3) Incremental Surface Area (SA_i, m^2/g):

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

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

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

(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/dlog(D)* pore volume (*dV/dlog(D)$_i$*, cm^{3}g):

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

(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/dlog(D)* pore area [*dA/dlog(D)$_i$*, m^2/g]:

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

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):

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

where *INTERP(x)* is the value interpolated from the function $X = Dp_{j+i}$ and

$Y = VP_{cum,i}$, using an AKIMA semi-spline interpolation.

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

$$VpF_i = VpF_{cum,i} - VpF_{cum,i-1}$$

where $VpF_{cum,0} = 0$.

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

$$SAF_{cum,i} = INTERP\left(DpF_{i+1}\right)$$

where *INTERP*(*x*) is the value interpolated from the function $X = Dp_{j+i}$ and

$Y = SA_{cum,j}$.

(5) Incremental Surface Area (SAF_i, m^2/g):

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

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

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

$$\frac{dV}{dDpF_i} = INTERP\left(DpF_{i+1}\right)$$

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

(7) *dV/dlog(D)* pore volume [$dV/dlog(DpF_i)$, cm^3/g]:

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

where *INTERP(x)* is the value interpolated from the function $X = D_{avg,j}$ and $Y = dV/dlog(D)_j$.

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

$$\frac{dA}{dDpF1} = INTERP\left(DpF_{i+1}\right)$$

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

(9) *dA/dlog(D)* pore area [$dA/dlog(DpF_i)$, m^2/g]:

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

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

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

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

Where

k = shape factor; 6 for sphere, 5 for cube
$\bar{\rho}$ = weighted average density of the active metals

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 Olivier1) 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:

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

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:

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

where

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

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

f(ε) = 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

The integrations in equations (2) and (3) are carried out over all surface energies or pore sizes in the model. The functions *q(p,ε)* and *q(p,H)*, which we call the kernel functions, are contained in numeric form as model isotherms. Because, in general, there is no analytic solution for equation (1), the problem is best solved in a discrete form; the integral equation for any distributed property Z becomes a summation

$$Q\left(p\right) = \sum_i q\left(p, Z_i\right) f\left(Z_i\right) \tag{4}$$

Given a set of model isotherms, *q(p,Z)*, from a model chosen from the models library and an experimental isotherm, *Q(p),* contained in a sample information file, the software determines the set of positive values *f(Z)* that most nearly, in a least squares sense, solves equation (4). The distributed property, surface energy or pore size, is then displayed on the *Report Options* window as a selection of tables or graphs.

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 ADSORPTION

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:

$$D_i = 2r_k P_i + tP_i$$

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

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

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

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

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

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

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

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
$\overline{r_k}$ = Average Kelvin radius
$\bar{t}$ = Average thickness

DUBININ-ASTAKHOV

The Dubinin-Astakhov equation is:

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

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 (cm^3/g STP)
Q_0 = the micropore capacity (cm^3/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 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):

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

Characteristic Energy (KJ/mol):

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

Modal Equivalent Pore Diameter (Å):

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

where

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

Maximum Differential Pore Volume (cm^3/g-Å):

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

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

Mean Equivalent Pore Width (Å):

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

Micropore surface area (m^2/g):

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

Γ is calculated by a polynomial approximation over the domain $0 \le x \le 1$:

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

---

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):

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

dV/dD Pore Volume (cm^3/g-Å):

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

DUBININ-RADUSHKEVICH

The Dubinin-Radushkevich(1) equation is:

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

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:

$$LV = log(Q)$$

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

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):

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

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

where

P = pressure

R = a constant that depends on the units of n

For n in cm^3, STP $R = \frac{P_{STD}}{T_{STD}}$

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

T = temperature

V = volume

z = compressibility factor for the gas at the given pressure and temperature

The real gas equation of state

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

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.

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

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

FIRST ORDER KINETICS FOR TCD

Heat of desorption is calculated from experiments with different temperature ramp rates. The general equation is

$$\ln\left(\frac{\beta}{T_p^{\;2}}\right) = -\frac{E_d}{RT_p} + \ln\left(\frac{E_d\;Q_s}{RC}\right)$$

Heat of desorption is proportional to the slope *s* of $2\ln T_p - \ln\beta$ vs $1/Tp$.

$$E_d = sR$$

The slope is determined by a least-squares fit.

where

β = ramp rate in K/min
E_d = heat of desorption in kJ/mol
R = ideal gas constant
T_p = temperature at peak maximum
s = slope of best-fit line
Q_s = quantity adsorbed at saturation
C = constant related to the desorption rate

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:

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

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

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

HORVATH-KAWAZOE

A relative pressure lower limit is determined such that $L\text{-}d_0$ 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.

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

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 ($6.02214129 \times 10^{23}\ \text{mol}^{-1}$)

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.

$$ln\left(\frac{P}{P_0}\right) = \frac{3}{4}\frac{\pi N_A}{RT} \times \frac{IPx10^{32}}{d_0{}^4} \times \sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{d_0}{r_p}\right)^{2k} \times \left\{\frac{21}{32}\alpha_k\left(\frac{d_0}{r_p}\right)^{10} - \beta_k\left(\frac{d_0}{r_p}\right)^4\right\}\right]$$

where

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

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

---

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

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 *Po and Temperature Options* window

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.

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

where

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

ε^*_{12} = $\frac{Å_S}{4d_s^{\,6}}, where Å_s = \frac{6\left(mc^2\right)\alpha_S\alpha_A}{\frac{\alpha_S}{\chi_S}+\frac{\alpha_A}{\chi_A}}$

ε^*_{22} = $\frac{A_A}{4D_A^{\,6}}, where\ Å_A = \frac{3\left(mc^2\right)\left(\alpha_A\right)\left(\chi_A\right)}{2}$

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 $(L\text{-}d_0)^2N_A$, 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)

---

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

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

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

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

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

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

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:

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

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)

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

  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 39*** 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^3/g):

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

where

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

dV/dD Pore Volume (cm^3/g-Å):

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

Median Pore Width (Å):

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

$$D_{\mathrm{med}} = exp\left(ln\,D_\iota + (ln\,D_g - lnD_\iota)\frac{ln\,V_{\mathrm{half}} - ln\,V_\iota}{ln\,V_g - ln\,V_\iota}\right)$$

where

D_1 = pore width (L_i) that corresponds to V_l
D_g = pore width (L_i) that corresponds to V_g
$V_{cum,n}$ = 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

$\mathrm{D_A}$ = 2.95
$\mathrm{N_A}$ = 7.608×10^{14}
$\mathrm{X_A}$ = 3.22×10^{-29}
$\mathrm{\alpha_A}$ = 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] .

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[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}

INJECTION LOOP CALIBRATION FOR TCD

$$Q_l = Q_s \frac{A_l}{A_s}$$

The effective loop volume at 0 °C is

$$V_{l,\mathrm{eff}} = Q_{l,STP} \frac{P_{STD}}{P_l}$$

$$= Q_{s,STP} \frac{A_l}{A_s} \frac{T_i}{T_a}$$

where

Q_l = quantity of gas in loop injection
Q_s = quantity of gas in syringe injection
A_l = peak area from loop injection
A_s = peak area from syringe injection
T_l = temperature of loop in kelvins

LANGMUIR SURFACE AREA FOR CHEMICAL ADSORPTION

TRANSFORM FOR CHEMICAL ADSORPTION

The Langmuir isotherm is

$$\frac{Q}{Q_m} = \frac{bP}{1+bP}$$

The isotherm is transformed so that *P/Q* is plotted as a function of pressure. The transformed data are fitted with a straight line. the slope (*m*) and intercept (y_0) of the fit line are used in the calculations below.

SURFACE AREA

$$A_{Lang} = \frac{\overline{A}_{atom}\overline{S}N_A}{V_{mol}m} \cdot 10^{-18}\frac{m^2}{nm^2}$$

MONOLAYER CAPACITY

$$Q_{m=\frac{1}{m}}$$

LANGMUIR b VALUE

$$\mathrm{b} = \frac{1}{\mathrm{y_0Q_m}}$$

DISSOCIATIVE CHEMICAL ADSORPTION

The Langmuir isotherm may be derived for dissociative chemical adsorption.

$$\frac{Q}{Q_m} = \frac{b\sqrt{P}}{1+b\sqrt{P}}$$

The calculations are performed with the slope and intercept of a fit of $\frac{\sqrt{P}}{Q}$ as a function of $\sqrt{P}$.

LANGMUIR SURFACE AREA FOR PHYSICAL ADSORPTION

For each point designated for surface area calculations, the Langmuir1) transformation is calculated as:

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

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:

a. Slope (*S* g/cm^3 STP)
b. Y-intercept (Y_{int} g/cm^3 STP)
c. Error of the slope (S_{err} g/cm^3 STP)
d. Error of the y-intercept (YI_{err} g/cm^3 STP)
e. Correlation coefficient

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

Langmuir Surface Area (m^2/g):

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

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):

Langmuir b Value:

$$b = Y_{int} V_m$$

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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).

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

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

LANGMUIR SURFACE AREA FOR TCD

Surface area is calculated as the number of molecules in the monolayer times the area of a molecule. The result is divided by sample mass to give the specific surface area.

$$A_{Lang} = Q_{m,mol,} N_A A_{\alpha} / m$$

The quantity of adsorbate in the monolayer is determined by fitting Langmuir-transformed data from multiple experiments.

$$L_i = \frac{P_i}{Q_i}$$

$$P_i = c_i P_0$$

The slope *s* and offset y_0 of the best-fit line through L_i vs. P_i are found.

$$Q_m = 1 / s$$

$$b = y_0 / s$$

Uncertainty in the surface area is estimated from the uncertainty in the slope.

$$u(A_{Lang}) = A_{Lang} \frac{u(s)}{s}$$

where

A_{Lang} = specific Langmuir surface area
$Q_{m,mol}$ = quantity of adsorbate in the monolayer in moles
N_A = Avogadro constant: $6.02214129 \times 10^{23}$ mol^{-1}
A_α = adsorbate cross-sectional area
m = sample mass
L_i = Langmuir transform for experiment *i*
P_i = absolute pressure from experiment *i*
Q_i = cumulative quantity adsorbed for all peaks in experiment *i*
c_i = active gas concentration in experiment *i*
b = Langmuir *b* value
P_0 = entered saturation pressure for the active gas

s = slope of best-fit line

y_0 = intercept of best-fit line

$u(x)$ = uncertainty of x

METAL DISPERSION FOR CHEMICAL ADSORPTION

$$D = 100\% \cdot 100\% \frac{Q_o \overline{S}}{V_{mol} \Sigma \frac{P_i}{W_i}}$$

where

$V_{mol} \simeq 22414 cm^3 / mol$ = the molar volume of an ideal gas at standard temperature and pressure

METALLIC SURFACE AREA FOR CHEMICAL ADSORPTION

The metallic surface area is the total active metal surface area available for interaction with the adsorbate.

$$A_{metal} = \frac{N_A Q_o \overline{SA}_{atom}}{V_{mol}}$$

where

$N_A \simeq 6.023 \times 10^{23}$ = the number of atoms per mole

METALLIC SURFACE AREA FOR TCD

$$A_{metal} = Q_{\alpha,mol} S A_{cs} N_A / m$$

where

$Q_{a,mol}$ = cumulative quantity adsorbed in moles
S = weighted stoichiometry factor
A_{cs} = weighted atomic cross-sectional area
NA = Avogadro constant: $6.02214129 \times 10^{23}$ mol^{-1}
m = sample mass

MP-METHOD

With the (t_i,Q_i) data pairs1) , 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 (m^2/g):

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

where

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

Incremental pore surface area occluded for the ith point (m^2/g):

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

Cumulative pore surface area occluded for the ith point (m^2/g):

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

dA/dR pore surface area for the ith point (m^2/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 (cm³/g):

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

Cumulative pore volume occluded for the ith point (cm³/g):

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

dV/dR pore volume for the ith point (cm³/g-Å):

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

PARTICLE SIZE FOR TCD

See ***Crystallite Size for Chemical Adsorption on page 14*** .

PEAK AREA QUANTITY FOR TCD

$$Q_p = \sum_{i=0}^{N} a_i A_p^i$$

where

Q_p = quantity of gas represented by the peak
a_i = coefficients determined by line fit to polynomial of degree *N*
A_p = area between the peak and the baseline

PERCENT DISPERSION FOR TCD

$$D = 100\,\% Q_{\alpha,\,mol} SM / m$$

where

$Q_{\alpha,mol}$ = cumulative quantity adsorbed in moles
S = Stoichiometry factor
M = molecular weight
m = sample mass

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.

$$n_a = n_d - n_f$$

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

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

where

α and β = constants that determine the relative weights of the manifold and port temperatures

n_a = 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

For the i^{th} dose, the quantity dosed is

$$n(i)_{dosed,i} = n_{dosed,i-1} + n\left(P_1, V_m, T_1\right) - n\left(P_2, V_m, T_2\right)$$

The pressure, volume, and temperature are those of the dosing manifold before and after expanding into the sample tube.

$$n_{ads,i} = n_{dosed,i} - n_{fs,i}$$

The quantity of gas in the free space is

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

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

The specific quantity adsorbed is

$$Q_{ads,i} = \frac{n_{ads,i}}{m}$$

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

FREE SPACE - MEASURED

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

$$V_{fw} = \frac{V_{man}}{T_{man}}\left(\frac{P_1}{P_2} - 1\right)T_{STD}$$

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

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.

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

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

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

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_{man} = system manifold temperature before dosing helium onto sample (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_{man} = manifold volume (cm^3)

V_s = sample volume

V_{wb} = volume of warm free space of the empty tube (cm^3 at standard temperature)

QUANTITY ADSORBED FOR TCD

The quantity adsorbed is the amount of gas removed from a loop or syringe injection by the sample.

$$Q_\alpha = NQ_i - Q_n$$

where

Q_α = quantity adsorbed
N = number of injections
Q_i = injection quantity
Q_n = quantity detected, not adsorbed

QUANTITY OF GAS FOR TCD

The quantity of gas in an injection is found by the equation of state. In moles

$$Q_{mol} = V\frac{P_\alpha}{zRT_\alpha}$$

In cm^3 at standard temperature and pressure (cm^3 STP)

$$Q_{STP} = V\frac{P_\alpha}{zT_\alpha}\frac{T_{STD}}{P_{STD}}$$

where

V = volume in cm^3
P_α = entered atmospheric pressure
z = compressibility factor at P_α and T_α for the injected gas
T_α = entered ambient temperature in kelvins
R = ideal gas constant
T_{STD} = standard temperature: 273.15 K
P_{STD} = standard pressure: 101.325 kPa, 760 mmHg

REAL GAS EQUATION OF STATE FOR CHEMICAL ADSORPTION

All chemical adsorption gas accounting calculations utilize the real gas equation of state and compressibility factor data traceable to NIST.

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

where

n = quantity of gas
P = pressure
T = temperature
V = volume
$z(P,T)$ = compressibility factor for the gas of interest at the given pressure and temperature

Quantity of gas in cm^3 STP is given by

$$Q = n\frac{T_{STD}}{P_{STD}}$$

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:

$$P_{rel} = \frac{P}{Po}$$

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.
2. The saturation pressure is measured in the sample tube after all adsorption data points have been collected. This pressure is used as P_0 for all data points.
3. P_0 is measured for all points as with #1. After all adsorption points have been taken P_0 is measured in the sample tube. The measured P_0 points are shifted so that the P_0 measured in the P_0 tube matches the P_0 measured in the sample tube. That is, $Po_i = Po_i + Po_s - Po_n$ where Po_n is the P_0 measured in the P_0 tube when P_0 in the sample tube (Po_s) was measured.
4. Determine P_0 from pressure measured over the dosing source. Note that the *Adsorptive Properties* must specify dosing from Psat tube, Sample port 3, or Vapor source.
5. The saturation pressure of a gas is measured in the P_0 tube for each data point. The bath temperature is found by looking up the temperature for the measured saturation pressure in the fluid properties. P_0 of the analysis gas is found from the bath temperature as in #6. If dosing is done from the Psat tube, P_0 is determined once at the beginning of the analysis and used for all data points. Otherwise, P_0 is measured for each data point.
6. P_0 is found by looking up the saturation pressure for the entered bath temperature in the fluid property information.

   Lookup of saturation pressure in the fluid properties is done by interpolating the Psat data using the Clausius-Clapeyron equation, $ln\left(P\right) = \frac{\alpha}{T} + b$. The constants α and b are determined from the pressures and temperatures that bound the bath temperature.

   Temperature lookup is done by solving for T, $T = \frac{\alpha}{ln(P) - b}$, where α and b are determined from the pressures that bound the given saturation pressure.

7. If entered, P_0 = user-entered value.

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.

$$\bar{\chi} = \frac{\Sigma \chi_i}{N}$$

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

$$Slope = \frac{\Sigma(\chi_i - \bar{\chi})(y_i - \bar{y})}{\Sigma(\chi_i - \bar{\chi})^2}$$

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

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

$$\sigma_{\chi} = \sqrt{\frac{\Sigma(\chi_i - \bar{\chi})^2}{N}}$$

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

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

$$Correlation\ Coeff = \frac{\mathrm{Cov}(x, y)}{\sigma_x \sigma_y}$$

---

[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

$$Mean = \frac{\Sigma y_i}{N}$$

$$Standard\ Deviation = \sqrt{\frac{\Sigma\left(y_i - \mathrm{Mean}\right)^2}{N - 1}}$$

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

$$+\,\mathrm{n}\,\sigma = \mathrm{Mean} + \mathrm{n}\cdot \mathrm{Standard\ \ Deviation}$$

$$-\,\mathrm{n}\,\sigma = \mathrm{Mean} - \mathrm{n}\cdot \mathrm{Standard\ \ Deviation}$$

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)

$$S_{1PT} = \frac{\left[Q\left(1-P\right)\right] \times CSA\left(6.023 \times 10^{23}\right)}{22414cm^3 \times STP\left(\frac{10^{18}nm^2}{m^2}\right)}$$

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 for Chemical Adsorption on page 43*** and ***Langmuir Surface Area for Physical Adsorption on page 44***

d. t-Plot Micropore Surface Area. See ***t-Plot on page 69***

e. t-Plot External Surface Area. See ***t-Plot on page 69***

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 69***

k. Freundlich. See ***Freundlich Isotherm on page 31***

l. Temkin. See ***Temkin Isotherm on page 70***

m. Alpha-S. See ***Alpha-S Method on page 1***

n. DFT Pore Size and DFT Surface Energy. See ***DFT (Density Functional Theory) on page 15***

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

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

See **MP-Method on page 51** 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

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

See **MP-Method on page 51** 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)

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

w. Horvath-Kawazoe. See **Horvath-Kawazoe on page 32**

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 cm^3/g-Å STP)
b. Y-intercept (Y_{int} cm^3/g STP)
c. Error of the slope (S_{err} cm^3/g-Å 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:

External Surface Area (m^2/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 (m^2/g):

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

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^3 liquid/g):

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

TEMKIN ISOTHERM

The Temkin isotherm has the form:

$$\frac{Q}{Q_m} = \frac{RT}{q_0 \alpha} ln\left(A_o P\right)$$

where

A_0 = adjustable constant

a = 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

$$Q = \frac{RTQ_m}{q_0 \alpha} \left[lnA_0 + ln\, P \right]$$

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 $lnA_0 \frac{RTQ_m}{q_0 a}$.

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.

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

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

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

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

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 $\frac{T_{amb} + T}{2}$

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 ith point

REFERENCE

Interpolated from table.

KRUK-JARONIEC-SAYARI

$$t = \left(\frac{C_1}{C_2 = \log\left(P_{rel,\,i}\right)}\right)^{c3}$$

HALSEY

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

Halsey[1]

HARKINS AND JURA

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

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

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

CARBON BLACK STSA

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

WEIGHTED METAL PARAMETERS

The stoichiometry factor, atomic weight, and density used in calculations are averages weighted by the number of moles of each active metal. For example, the average stoichiometry factor is

$$\overline{S} = \frac{\sum_i n_i S_i}{\sum_i n_i}$$

where

n_i = number of moles or metal

$$n_i = \frac{\alpha\beta X}{XW_m + YW_0}$$

where

α = fraction of sample mass
β = fraction reduced
X = number of metal atoms in the oxide
Y = number of oxygen atoms in the oxide
W_m = atomic weight of metal
W_o = atomic weight of Oxygen

Average density and atomic cross-sectional area are calculated similarly.