GEMINI® VII KEYPAD

CALCULATIONS

May 2021

CORPORATE PROFILE

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BET SURFACE AREA

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

$$B_I = \frac{P_{rel_I}}{(1.0 - P_{rel_I}) \times N_{ads_I}}$$

where

      B_I =   units of g/cm^3 STP

      $P_{rel,I}$ =   relative pressure

      $N_{ads,I}$ =   amount of gas adsorbed after equilibrating I^{th} dose (cm^3 STP)

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

- Slope (S g/cm^3 STP)
- Y-intercept (Y_{INT} g/cm^3 STP)
- Error of the slope (S_{ERR} g/cm^3 STP)
- Error of the y-intercept (YI_{ERR} g/cm^3 STP)
- Correlation coefficient (C_C)

Using the results of the above calculations, the following are calculated:

BET SURFACE AREA (SA_{BET} M²/G):

$$SA_{\text{BET}} = \frac{CSA \times (6.023 \times 10^{23})}{(22414 \ cm^3 \ STP) \times (10^{18} nm^2/m^2) \times (S + Y_{INT})}$$

where

      CSA   =   adsorbate molecular cross-sectional area (nm^2)

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

BET C VALUE:

$$C = \frac{S + Y_{INT}}{Y_{INT}}$$

VOLUME OF THE MONOLAYER (CM³/G STP):

$$V_M = \frac{1}{C \times Y_{INT}} = \frac{1}{S + Y_{INT}}$$

ERROR OF THE BET SURFACE AREA (M²/G):

$$BET_{ERR} = \frac{SA_{BET} \times (S_{ERR}{}^2 + YI_{ERR}{}^2)^{0.5}}{Y_{INT} + S}$$

SINGLE POINT SURACE AREA (M²/G):

$$S1PT = Va\,(1 - Pr) \times 4.35 \ \times \frac{CSA}{0.162}$$

where

Pr	=	pressure closest to 0.3 of the relative pressure points designated for surface area calculations
Va	=	volume corresponding to *Pr*
0.162	=	nitrogen molecule cross-sectional area (nm^2)

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 (Pr), quantity adsorbed (V_a) pairs from (Pr_I, V_{aI}) to (Pr_N, V_{aN}) where ($Pr_N = 0$, $V_{aN} = 0$) 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 (Pr, V_a) pairs.

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

EXPLANATION OF TERMS

A pore filled with condensed liquid nitrogen has three zones:

- **Core** — 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** — 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 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).
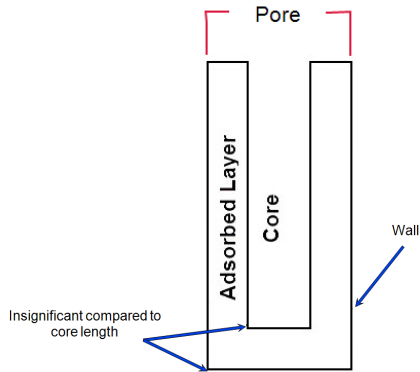
CALCULATIONS

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

$$Vl = (V_{a_I})(D)$$

where D is the Density Conversion Factor.

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

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

$$Rc_I = \frac{-A}{(l+F)\ln(Pr_I)}$$

where

A	=	adsorbate property factor
F	=	fraction of pores open at both ends; assumed to be zero for desorption

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

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

$$TW_I = HP1 \left[\frac{HP2}{ln(Pr_I)} \right]^{HP3}$$

where

HP1, HP2, and HP3 are Halsey Parameters 1, 2, and 3 (respectively) from the Halsey Thickness Equation prompt.

These calculations illustrate the use of the Halsey thickness equation. If the Harkins and Jura equation was selected, substitute the following wherever the thickness equation appears:

$$T_{W_I} = \left[\frac{HJI}{(HJ2 - log(Pr_I))} \right]^{HJI}$$

where

HJ1, HJ2, and HJ3 are Harkins and Jura Parameters 1, 2, and 3 (respectively) from the Harkins-Jura Thickness Equation prompt.

The following calculations (a-c) are made for each relative pressure interval based on the increment of volume desorbed during that interval. The variable I refers to the interval number, that is I=1 for the first interval from Pr_1 to Pr_2, and so on. J refers to each previous interval during which new pores were found. K refers to the total number of intervals in which new pores have been found. K 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 as:

$$TW_{I+1} = HP1\left[\frac{HP2}{ln(Pr_{I+1})}\right]^{HP3}$$

(For the last pressure interval from the lowest Pr_I to zero relative pressure, $TW_{I+1}=0$.)

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:

$$CSA_J = \pi[(RC_j + \Delta Tw)^2 - RC_j{}^2](10^{-16} cm^2/A^2)$$

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

$$Vd_I = \sum(LP_J)(CSAa_J) \qquad \text{for all previously opened pores}$$

where LP_J = length of previously opened pores as calculated in Step b-2.

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

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

$$SA_W = \sum \pi (LP_J)(D_{avg_J})(10^{-8} cm/A)$$

for all previously opened pores

where

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

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

$$\Delta Tw = \frac{(Vl_I - Vl_{I+l})(10^8 \frac{A}{cm})}{SAw_I}$$

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

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

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

$$Vc_I = (Vl_I - Vl_{I+1}) - Vd_I$$

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

$$Rc_{k+1} = \frac{-A}{(1+F)[\ln(Pr_I+1)]}$$

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:

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

$D_{\mathrm{avg,K}}$ 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 $Rc_{\mathrm{K+1}}$, if its length was the mean of the lengths at those radii.

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

$$P_{avg_K} = ln^{-1} \left[\frac{-2A}{(1+F)(D_{\mathrm{avg_K}})} \right]$$

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

$$Tw_{\mathrm{avg_K}} = HP1 \left[\frac{HP2}{ln(P_{\mathrm{avg_K}})} \right]^{HP3}$$

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:

$$\Delta Td = Tw_{\mathrm{avg_K}} - Tw_{\mathrm{I+1}}$$

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

$$CSAc_{\mathrm{K}} = \left[\frac{D_{\mathrm{avg_K}}}{2} + \Delta Td \right]^2 \left(\frac{10^{-16}\,\mathrm{cm}^2}{\mathrm{\AA}^2} \right)$$

The length of the newly opened pores is calculated as:

$$LP_{\mathrm{K}} = \frac{Vc_{\mathrm{i}}}{CSAc_{\mathrm{K}}}$$

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:

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

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

$$D_{\text{avg}_{J\,new}} = D_{\text{avg}_{J\,old}} + 2(\Delta Tw)$$

(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:

$$Dp_J = 2(rc_J)$$

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 report options.

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

$$Vp_I = \pi(Lp_I)\left[\frac{D_{\text{avg}_I}}{2}\right]^2 \left[\frac{10^{16}\,cm^2}{\mathring{A}^2}\right]$$

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

$$VP_{cum_I} = \sum VP_J \ \text{ for } \ (J \le 1)$$

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

$$\text{SA}_I = \pi(LP_I)(10^{-2}m/cm)(D_{avg_I})(10^{-10}\ m/A)$$

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

$$SA_{cum_{10}} = \sum SA_J \, \text{for} \, J \leq 1$$

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

$$\frac{dV}{dD_I} = \frac{VP_I}{Dp_I - Dp_{I+1}}$$

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

$$\frac{dDv}{d \log D_I} = \frac{VP_I}{\log \left(\frac{Dp_I}{Dp_{I+1}} \right)}$$

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

$$\frac{dA}{dDI} = \frac{SA_I}{Dp_I - Dp_{I+1}}$$

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

$$\frac{dA}{d \log D_I} = \frac{SA_I}{\log \left(\frac{Dp_I}{Dp_{I+1}} \right)}$$

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

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

$$DF_{avg_J} = \frac{Dp_{F_J} + D_{P_{F_{J+1}}}}{2}$$

calculated for all intervals in the fixed pore size table.

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

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

$$V_P F_{CUM_I} = \text{INTERP}(D_P F_{I+1})$$

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

(3) Incremental Pore Volume (VpFI, cum^3/g):

$$V_P F_i = V_P F_{\text{CUM}_I} - V_P F_{\text{CUM}_{I-1}}$$

where VpF$_{CUM0}$=0

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

$$SAF_{\text{CUM}_I} = \text{INTERP}(D_P F_{I+1})$$

where *INTERP(x)* is the value interpolated from the function $X = Dp_{J+1}$ and Y=SA$_{CUMJ}$.

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

$$SAF_I = SAF_{\text{CUM}_I} - SAF_{\text{CUM}_{I-1}}$$

where *SAF$_{CUM0}$* = 0.

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

$$\frac{dV}{dDpF_I} = \text{INTERP}(DpF_{I+1})$$

where *INTERP(x)* is the value interpolated from the function $X = D_{avgJ}$ and Y=dV/d D$_J$.

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

$$\frac{dV}{d \log(DpF_I)} = \text{INTERP}(DpF_{I+1})$$

where INTERP(x) is the value interpolated from the function$X = D_{avgJ}$ and Y=dV/d log(D)$_J$

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

$$\frac{dA}{dDpF_I} = \text{INTERP}(DpF_{I+1})$$

where *INTERP(x)* is the value interpolated from the function$X = D_{avgJ}$ and *Y=dA/dD$_J$*.

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

$$\frac{dA}{d\log(DpF_I)} = \mathrm{INTERP}(DpF_{I+1})$$

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

COMPENDIUM OF VARIABLES

V$_a$	=	quantity adsorbed expressed as a volume (cm^3/g STP)
V$_l$	=	liquid equivalent volume of volume adsorbed (cm^3/g)
D	=	density conversion factor (cm^3/cm^3 STP)
P$_r$	=	relative pressure
D$_p$	=	pore (or core) diameter (A)
R$_c$	=	Kelvin radius (A) of core
A	=	adsorbate property factor
F	=	fraction of pores open at both ends
ΔTw	=	thickness of adsorbed layer desorbed during interval (A)
Tw	=	thickness of remaining adsorbed wall (A)

HP1, HP2, and HP3 are Halsey Parameters from the Halsey Thickness Equation prompt.

HJ1, HJ2, and HJ3 are Harkins and Jura Parameters from the Harkins and Jura Thickness Equation prompt.

Vd	=	volume of gas desorbed from walls of previously opened pores (cm^3/g)
D$_{avg}$	=	average pore diameter (Å)
CSAa	=	annular cross-sectional area of the desorbed layer (cm^2)
CSAc	=	cross-sectional area of opening of newly opened pores (cm^2)
SAw	=	total surface area of walls exposed (cm^2/g)
ΔTd	=	thickness of layer desorbed from walls of newly opened pores (Å)
Vc	=	volume desorbed from cores of newly opened pores (cm^3/g)
L$_P$	=	length of pore (cm/g)

FREE-SPACE CORRECTION ALGORITHMS

Free space differential compensation for the Gemini is accomplished in two steps. First, the free space correction, C_f (cm^3 STP/mmHg) is determined. Second, the correction is applied to quantities adsorbed during analysis.

DETERMINING THE FREE-SPACE CORRECTION

The free space correction C_f (cm^3 STP/mmHg) can be *Measured* or *Calculated*.

MEASURED

Evacuate the sample and balance ports, charge the reservoirs with helium, and dose to 760 mmHg. Measure the gas quantity differential, Q_h (cm^3 STP), and the absolute sample pressure, P_h (mmHg). Record the free space correction:

$$C_f = \frac{Q_h}{P_h}$$

CALCULATED

> 🖉   This method requires using a bath of liquid nitrogen temperature. It should not be selected for free-space correction if a liquid nitrogen bath is not being used.

Measure the free space correction as above, except use an empty sample tube of the same volume as that to be used during subsequent sample analyses. Calculate and record the system volume correction Q_{sys} (cm^3 STP):

$$Q_{sys} = 760 \; mmHg \times \frac{Q_h}{P_h}$$

Calculate the sample quantity Q_{sam} (cm^3) from independently determined sample mass M_{sam} (g) and sample density D_{sam} (g/cm^3):

$$Q_{sam} = \frac{M_{sam}}{D_{sam}}$$

Calculate the quantity of gas displaced by the sample at liquid nitrogen temperature and standard pressure:

$$Q_{gas} = Q_{sam} \times \frac{273.13K}{77.15K}$$

Calculate the free space correction due to both the system volume correction and the gas displaced by the sample in cm³ STP/mmHg:

$$C_f = \frac{Q_{sys} - Q_{gas}}{760\ mmHg}$$

APPLYING THE FREE-SPACE CORRECTION TO QUANTITIES ADSORBED

Measure the uncorrected quantity adsorbed Q_{raw} (cm³ STP) and the pressure at which this quantity is adsorbed P_{ads} (mmHg). Use the independently determined adsorbate nonideality correction C_n (%/atm) and the free space correction C_f (cm³ STP/mmHg) to calculate the adsorbate quantity correction Q_{cor} (cm³ STP) for this point:

$$Q_{cor} = C_f \times P_{ads} \times \left[1 + \left(\frac{P_{ads}(C_n)}{100\% \times \frac{760\ mmHg}{atm}} \right) \right]$$

Apply the correction to the uncorrected quantity adsorbed to obtain the corrected quantity adsorbed Q_{ads} (cm³ STP):

$$Q_{ads} = Q_{raw} - Q_{cor}$$

HORVATH-KAWAZOE

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

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

SLIT PORE GEOMETRY (ORIGINAL HORVATH-KAWAZOE)

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

$$\ln \frac{P}{Po} = \frac{K}{RT} \times \frac{IP \times 10^{32} JA^4/J\,cm^4}{\sigma^4 \times (L - 2 \times d_0)} \times \left[\frac{\sigma^4}{3 \times (L - d_o)^3} - \frac{\sigma^{10}}{9 \times (L - d_o)^9} - \frac{\sigma^4}{3 \times d_o^3} + \frac{\sigma^{10}}{9 \times d_o^9} \right]$$

where

K	=	Avogadro's number (6.023×10^{23})
R	=	gas constant (8.31441×10^7 ergs/mol K)
T	=	analysis bath temperature (K), from an entered or calculated value
σ	=	gas solid nuclear separation at zero interaction energy (Å), $\frac{Z_S + Z_A}{2}$

    where

Z_S	=	sample equilibrium diameter at zero interaction energy (Å)
Z_A	=	zero interaction energy diameter

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

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

where

D_A =   molecular diameter of adsorbate (Å)

D_S =   diameter of sample atom (Å)

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

P   =   equilibrium pressure (mmHg)

P_o =   saturation pressure (mmHg)

IP   =   interaction parameter (10^{-43} ergs-cm^4)

CYLINDER PORE GEOMETRY (SAITO/FOLEY)

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

$$\ln\left(\frac{P}{P_0}\right) = \frac{3}{4}\frac{\pi N_A}{RT} \times \frac{IP \times 10^{32}\, J A^4/J\, cm^4}{d_0{}^4} \times \sum_{k=0}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{d_0}{r_p}\right)^{2k} \times\right.$$

$$\left.\left\{\frac{21}{32}\alpha_k\left(\frac{d_0}{r_p}\right)^{10} - \beta_k\left(\frac{d_0}{r_p}\right)^4\right\}\right]$$

where

N_A = Avogadro's number (6.023×10^{23})

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

T = analysis bath temperature (K), from an entered or calculated value

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

P = equilibrium pressure (mmHg)

P_o = saturation pressure (mmHg)

IP = interaction parameter (10^{-43} ergs-cm^4)

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

    where

      D_A = molecular diameter of adsorbate (Å)

      D_S = diameter of sample atom (Å)

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

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

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

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

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:

$$\ln\left(\frac{P}{P_0}\right) = \frac{6(N_1\epsilon^*{}_{12}+N_2\epsilon^*{}_{22})L^3\times10^{32}JA^4/J\ cm^4}{RT(L-d_0)^3}\left[-\left(\frac{d_0}{L}\right)^6\left(\frac{1}{12}T_1+\frac{1}{8}T_2\right)+\left(\frac{d_0}{L}\right)^{12}\left(\frac{1}{90}T_3+\frac{1}{80}T_4\right)\right]$$

where

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

T = analysis bath temperature (*K*), from an entered or calculated value

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

where

D_A = molecular diameter of adsorbate (Å)

D_S = diameter of sample atom (Å)

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

N_1 = $4\pi L^2 N_S$, where N_s = number of sample atoms/cm^2 at monolayer

P equilibrium pressure (mmHg)

Po saturation pressure (mmHg)

N_1 $4\pi L^2 N_S$, where N_S = number of sample atoms/cm^2 at monolayer

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

$\epsilon^*{}_{12}$ = $\frac{A_S}{4D_S{}^6}$, $where\ A_S = \frac{6\times MC^2\times\alpha_S\times\alpha_A}{\frac{\alpha_S}{\chi_S}+\frac{\alpha_A}{\chi_A}}$

$\epsilon^*{}_{22}$ = $\frac{A_A}{0Dd_A{}^6}$, $where\ A_A = \frac{3\times MC^2\times\alpha_A\times\chi_A}{2}$

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

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

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

$$T3 \quad = \quad \frac{1}{(1-S)^9} - \frac{1}{(1+S)^9}$$

$$T4 \quad = \quad \frac{1}{(1+S)^8} - \frac{1}{(1-S)^8}$$

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

CHENG/YANG CORRECTION

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

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

where

$G(L)$ = one of the Horvath-Kawazoe equations given above

θ = degree of void filling; θ is estimated by first computing the monolayer capacity (V_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 V_m.

INTERACTION PARAMETER

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

The Kirkwood-Muller dispersion coefficients:

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

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

where

MC^2	=	kinetic energy of electron (0.8183 × 10⁻⁶ erg)
α_S	=	polarizability of sample atoms (cm³)
α_A	=	polarizability of gas molecule (cm³)
X_A	=	diamagnetic susceptibility of gas molecule (cm³)

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

where:

N_A = number of gas molecules/cm² at monolayer

N_S = number of sample atoms/cm²

See *Interaction Parameter Components on page 22* for recommended values.

ADDITIONAL CALCULATIONS

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

Adjusted Pore Width (Å):

(Shell to Shell)

$$AL_I = L_I - DS$$

Cumulative Pore Volume (cm^3/g):

$$V_{CUM,I} = V_I \times D$$

where

$\quad D \quad = \quad$ density conversion factor (cm^3 liquid/cm^3 STP)

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):

$$V_{HALF} = \frac{V_{CUM_N}}{2}$$

$$D_{MED} = \exp\left[\ln(D_L) + [\ln(V_{HALF}) - \ln(V_L)] \times \frac{\ln(D_G) - \ln(D_L)}{\ln(V_G) - \ln(V_L)} \right]$$

where

$\quad V_{CUM,N} \quad = \quad$ total cumulative pore volume ($V_{CUM,I}$) for points designated for Horvath-Kawazoe calculations

$\quad V_{HALF} \quad = \quad$ 50% of total cumulative pore volume

$\quad V_L \quad = \quad$ cumulative pore volume ($V_{CUM,I}$) for first point less than V_{HALF}

$\quad V_G \quad = \quad$ cumulative pore volume ($V_{CUM,I}$) for first point greater than V_{HALF}

$\quad D_L \quad = \quad$ pore width (L_I) that corresponds to V_L

$\quad D_G \quad = \quad$ pore width (L_I) that corresponds to V_G

Interaction Parameter Components

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 Report Options:*

Interaction parameter: (calculated value) $\times 10^{-43}$ ergs-cm^4

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

Carbon-Graphite

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

Zeolite

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

Nitrogen

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

Argon

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

Carbon Dioxide

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

D_A values are from van der Waal's constant.

N_A values are from liquid densities.

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

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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			**Aluminosilicate**		
D_S	=	2.60	D_S	=	2.76
N_S	=	1.48×10^{15}	N_S	=	1.31×10^{15}
X_S	=	1.3×10^{-29}	X_S	=	1.3×10^{-29}
α_s	=	2.5×10^{-24}	α_s	=	2.5×10^{-24}

SPERICAL PARAMETERS

The spherical parameters result from the following calculations:

Adsorptive spherical parameter = $N_A \times \alpha_A \times \chi_A$

Adsorbent spherical parameter = $N_S \times \dfrac{\alpha_S \times \alpha_A}{\dfrac{\alpha_S}{\chi_S} + \dfrac{\alpha_A}{\chi_A}}$

where

N_A	=	number of gas molecules/cm^2 at monolayer
N_S	=	number of sample atoms/cm^2
α_A	=	polarizability of gas molecule (cm^3)
α_S	=	polarizability of sample atoms (cm^3)
X_A	=	diamagnetic susceptability of gas molecule (cm^3)
X_S	=	diamagnetic susceptability of sample atom (cm^3)

Adsorptive and Adsorbent Sperical Parameters

Gas	Bath Temp. (K)	Sample Type	Spherical Parameter	
			Adsorptive	**Adsorbent**
Argon	87.3	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	3.99313 3.99313 3.99313	4.32629 11.00271 5.50177
Carbon Dioxide	298.15	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	6.16545 6.16545 6.16545	7.00604 17.22493 8.79855
	273.15	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	7.35750 7.35750 7.35750	7.00604 17.22493 8.79855
	194.65	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	10.39095 10.39095 10.39095	7.00604 17.22493 8.79855
Nitrogen	77.15	Carbon (Ross/Olivier value) Carbon (Horvath/Kawazoe value) Zeolite	4.25146 4.25146 4.25146	4.72674 12.24482 6.05156

* The spherical parameters are entered *in Report Options:*

Spherical parameter: (calculated value) $\times 10^{-38}$ cm^4

LANGMUIR SURFACE AREA

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

$$L_I = \frac{P_{rel_I}}{N_{ads_I}}$$

where L_I is in units of g/cm^3 STP

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

- Slope (S g/cm^3 STP)
- Y-intercept (Y_{INT} g/cm^3 STP)
- Error of the slope (S_{ERR} g/cm^3 STP)
- Error of the y-intercept (YI_{ERR} g/cm^3 STP)
- Correlation coefficient (C_C)

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

LANGMUIR SURFACE AREA (M^2/G):

$$SA_{LAN} = \frac{CSA \times (6.023 \times 10^{23})}{(22414 \; cm^3 \; STP) \times (10^{18} \; nm^2/m^2) \times S}$$

where

CSA   =   analysis gas molecular cross-sectional area (nm^2)

VOLUME OF THE MONOLAYER (CM^3/G STP):

$$V_M = \frac{1}{S}$$

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

LANGMUIR C VALUE:

$$C = [(Y_{INT}) (V_m)]^{-1}$$

ERROR OF THE LANGMUIR SURFACE AREA (M^2/G):

$$\text{LAN}_{ERR} = \frac{\text{SA}_{LAN} \times S_{ERR}}{S}$$

SINGLE-POINT TOTAL PORE VOLUME

The liquid equivalent of the designated quantity adsorbed is calculated; this is the total pore volume (cm^3/g):

$$V_{TOT} = (Q_a)(D)$$

where

D	=	density conversion factor
Q_a	=	volume adsorbed

T-METHOD

For each point designated for t-Plot[1] calculations, the following calculations are made:

Thickness for the Ith point (Å):

$$t_I = HPI \times \left[\frac{HP2}{\ln(P_{rel_I})} \right]^{HP3}$$ (Halsey[2])

or

$$t_I = \left[\frac{HJP1}{HJP2 - \log(P_{rel_I})} \right]^{HJP3}$$ (Harkins and Jura[3])

or

$$T_I = CB1(Prel_l \times Po)^2 + CB2(Prel_l \times Po) + CB3$$ (Magee-STSA[4])

where

t_I	=	thickness for I[th] point
HP1	=	Halsey parameter #1
HP2	=	Halsey parameter #2
HP3	=	Halsey parameter #3
HJP1	=	Harkins and Jura parameter #1
HJP2	=	Harkins and Jura parameter #2
HJP3	=	Harkins and Jura parameter #3
MP1	=	Magee-STSA parameter #1
MP2	=	Magee-STSA parameter #2
MP3	=	Magee-STSA parameter #3
$P_{rel,I}$	=	relative pressure for the Ith point (mmHg)

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[1] Magee, Ricky, Columbian Chemicals Company, personal communications

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

[3] Harkins, W.C. and Jura, G., J. Chem. Phys 11, 431 (1943)

[4] Magee, Ricky, Columbian Chemicals Company, personal communications

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

> Slope (S cm^3/g-Å STP)
>
> Y-intercept (Y_{INT} cm^3/g STP)
>
> Correlation coefficient (Cc)

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

External Surface Area (m^2/g):

$$ \mathrm{SA}_{EXT} = \frac{(S\ cm^3/g - A\ STP) \times (10^{10}\ A/m) \times (D\ cm^3\ liquid/cm^3\ STP)}{F \times (10^6\ cm^3/m^3)} $$

where

> F $\quad$ = $\quad$ surface area correction (Report Options)
>
> D $\quad$ = $\quad$ density conversion factor (cm^3 liquid/cm^3 STP)

Micropore Surface Area (m^2/g):

$$ SA\mu P = SA_{TOT} + SA_{EXT} $$

where SA_{TOT} is the BET surface area if a BET report was requested, or Langmuir surface area.

Micropore Volume (cm^3 liquid/g):

$$ V_{\mu P} = (Y_{INT}\, cm^3/g\ STP) \times (D\ cm^3\ liquid/cm^3\ STP) $$