AUTOCHEM® HP 2950

AUTOMATED CATALYST CHARACTERIZATION SYSTEM

CALCULATIONS

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micromeritics®

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ACTIVE PARTICLE SIZE

This equation calculates the active particle size.

$$APS = \frac{6}{(D_{calc}) \times (\frac{W_s}{GMW_{calc}}) \times (6.023 \times 10^{23}) \times (SA_{calc})}$$

APS	=	Active Particle Size
D_{calc}	=	Calculated metal density (g/cm^3)
W_s	=	Sample weight, g
GMW_{calc}	=	Gram molecular weight (g/g-mole)
SA_{calc}	=	Calculated specific surface area (per gram of metal)

BET SURFACE AREA

For each included point i, relative pressure P/Po_i and specific volume adsorbed V_{STPi} are calculated for a single point BET. Then the BET transformation B_i is calculated:

$$B_i = \frac{\frac{P}{Po_i}}{(1-\frac{P}{Po_i})V_{STP_i}}$$

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

A linear least squares fit is performed on the (B_i, P/Po_i) pairs where B_i is the dependent variable and P/Po_i is the independent 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} m^2/g):

$$SA_{\mathrm{BET}} = \frac{CSA\times(6.023\times10^{23})}{(22414\ cm^3STP)\times(10^{18}nm^2/m^2)\times(S+Y_{INT})}$$

CSA=adsorbate molecular cross-sectional area (nm_2)

BET C value:

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

Volume of monolayer (cm^3/g STP):

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

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

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

CALIBRATION ERROR (GOODNESS OF FIT)

Used as a means to determine whether the calibration curve is acceptable.

$$E_{\%} = \sum_{i=0}^{N} \left[\frac{(Q_{m_i} - Q_{c_i})^2}{(N-1)} \right]^{1/2}$$

$E_{\%}$	=	Percent error
Q_m	=	Quantity measured
Q_c	=	Quantity calculated
N	=	Number of measurements

CROSS-SECTIONAL AREA

$$SA_{calc} = \left[\left(\frac{F_1 \times SA_1}{W_{atomic1}}\right) + \left(\frac{F_2 \times SA_2}{W_{atomic2}}\right) + \cdots + \left(\frac{F_N \times SA_N}{W_{atomicN}}\right)\right] \cdot (GMW_{\text{calc}})$$

SA_{calc}	=	Calculated cross-sectional area
F_N	=	Fraction of sample weight for metal N
SA_N	=	Cross-sectional area for metal N
$W_{atomicN}$	=	Gram molecular weight of first metal (g/g-mole)

FIRST ORDER KINETICS FOR TCD

This series of steps calculates the First Order Kinetics (Heat of Desorption). At least two experiments must be run — commonly 3 experiments are run. The ramp rate must be different for each run. The data are plotted and the slope determined.

The general equation is:

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

Determine the slope *s* by plotting 2 ln T_p - ln β vs. $\frac{1}{T_p}$ then determine E_d using:

$$E_d = s \times R$$

β	=	Ramp rate, degrees/min
E_d	=	Heat of desorption, K joules/(mole K)
R	=	Gas constant
T_p	=	Temperature at peak max
s	=	Slope
A	=	The quantity adsorbed at saturation
C	=	A constant related to the desorption rate

GRAM MOLECULAR WEIGHT

The calculated Gram Molecular Weight is a weighted average of the number of moles of each active metal.

$$GMW_{calc} = \frac{1}{\left(\frac{F_1}{W_{atomic1}}\right) + \left(\frac{F_2}{W_{atomic2}}\right) + \cdots + \frac{F_N}{W_{atomicN}}}$$

GMW_{calc}	=	Gram molecular weight (g/g-mole)
F_N	=	Fraction of sample weight for metal N
$W_{atomicN}$	=	Gram Molecular Weight of first metal (g/g-mole)

INJECTION LOOP CALIBRATION

These equations are used during calibration of a dose loop:

$$V_{s_{STP}} = V_s \left(\frac{273.15}{23.15 + T_\alpha} \right) \times \left(\frac{P_\alpha}{760 mmHg} \right)$$

$$V_l = \left(\frac{A_l \times V_{s_{STP}}}{A_s} \right)$$

$V_{s_{STP}}$	=	Volume of syringe at STP, cm^3
V_S	=	Physical volume of syringe, cm^3
T_α	=	Ambient temperature, °C
P_α	=	Ambient pressure, mmHg
V_l	=	Effective loop volume (at loop temperature), cm^3
A_l	=	Average peak area of loop injections
A_S	=	Average peak area of syringe injections

INJECTION LOOP VOLUME - TEMPERATURE CHANGE

Used to correct the apparent loop volume when the temperature of the loop heat zone is changed.

$$V_n = V_o \left(\frac{T_o + 273.15}{T_n + 273.15} \right)$$

V_n = New Effective Loop Volume, cm^3
V_o = Old Loop Volume, cm^3
T_o = Old Loop Temperature, °C
T_n = New Loop Temperature, °C

LANGMUIR SURFACE AREA

For each included point $_i$, pressure P_i and specific volume adsorbed $VSTP_i$ are calculated as for a single point BET. Then the Langmuir transformation L_i is calculated:

$$L_i = \frac{P_i}{V_{STP_i}}$$

where L_i is in units of g/cm3 STP.

A linear least squares fit is performed on the (L_i, P) pairs where L_i is the dependent variable and P is the independent 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:

Langmuir Surface Area (SA_{LAN} m^2/g):

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

Volume of monolayer (cm^3/g STP):

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

Langmuir b value:

$$b = (Y_{INT}) V_M$$

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

$$LAN_{ERR} = \frac{SA_{LAN} \times S_{ERR}}{S}$$

METAL DENSITY

$$D_{calc} = \left[\left(\frac{F_1 \times D_1}{W_{atomic1}}\right) + \left(\frac{F_2 \times D_2}{W_{atomic2}}\right) + \cdots + \left(\frac{F_N \times D_N}{W_{atomicN}}\right)\right] \cdot GMW_{\text{calc}}$$

D_{calc}	=	Calculated density
F_N	=	Fraction of sample weight for metal N
D_N	=	Density of metal N
$W_{atomicN}$	=	Gram Molecular Weight of first metal (g/g-mole)

METALLIC SURFACE AREA

This equation calculates the effective metallic surface area per gram of sample.

$$SA_{Metallic} = \left(\frac{V_s}{SW \times 22414}\right) \times (SF_{calc}) \times (6.123 \times 10^{23}) \times (SA_{calc})$$

$SA_{Metallic}$	=	Metallic surface area (m^2/g of metal)
V_s	=	Volume sorbed (cm^3 at STP)
SF_{calc}	=	Calculated stoichiometry factor
SA_{calc}	=	Calculated specific surface area
SW	=	Sample weight (g)

PEAK AREA VOLUME

This is the basic data reduction equation. It converts the area under a peak to cm^3 of gas.

$$V_{p\alpha} = A_p \times F_c$$

$V_{p\alpha}$	=	Peak area volume, cm^3
A_p	=	Peak area
F_c	=	Calibration factor

PERCENT DISPERSION

This equation is used in a Pulse Chemisorption analysis to calculate the percent dispersion. Some understanding of the chemistry is required to select the proper stoichiometric factor and gram molecular weight.

$$PD = 100\left(\frac{V_S \times SF_{calc}}{SW \times 22414}\right) GMW_{calc}$$

PD	=	Percent dispersion
V_s	=	Volume sorbed (cm^3 at STP)
SF_{calc}	=	Calculated stoichiometry factor
SW	=	Sample weight (g)
GMW_{calc}		Gram Molecular Weight (g/g-mole)

STOICHIOMETRY FACTOR

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

$$SF_{calc} = \left[\left(\frac{F_1 \times SF_1}{W_{atomic1}}\right) + \left(\frac{F_2 \times SF_2}{W_{atomic2}}\right) + \cdots + \left(\frac{F_N \times SF_N}{W_{atomicN}}\right)\right] \cdot (GMW_{calc})$$

SF_{CALC}	=	Calculated stoichiometry factor
SF_N	=	Stoichiometry factor for metal N
F_1	=	Fraction of sample weight for metal N
$W_{atomic1}$	=	Gram molecular weight of first metal (g/g-mole)
GMW_{calc}	=	Gram molecular weight (g/g-mole)

TOTAL PORE VOLUME

Total pore volume V_{POR} at a selected physisorption point is calculated:

$$V_{POR} = (V_{STP})(DCF)$$

DCF = Adsorbate density conversion factor

VOLUME SORBED

This equation is for loop or syringe injections to calculate volume removed from the injections by the sample.

$$V_S = NV_i - V_{na}$$

V_S	=	Volume sorbed, cm^3
N	=	Number of injections
V_i	=	Volume per injection, cm^3
V_{na}	=	Total volume not sorbed, cm^3

VOLUME AT STP

Volume at standard reduction of gas data to Standard Temperature Pressure (STP) conditions (273.13K and 760 mmHg).

$$V_{STP} = V_a \left(\frac{273.15}{273.15 + T_a} \right) \times \left(\frac{P_a}{760 mmHg} \right)$$

V_{STP}	=	Volume at STP, cm^3
V_α	=	Volume at ambient temperature and pressure, cm^3
T_α	=	Ambient temperature, °C
P_α	=	Ambient pressure, mmHg