AutoChem [®] *II 2920*

Calculations

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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):

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

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

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CROSS-SECTIONAL AREA

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

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. $\frac{l}{T_p}$ 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:

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

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

$V_{s_{STP}}$	=	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):

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

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METAL DENSITY

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

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)

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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

VAPOR GENERATOR

The partial pressure of the vapor is estimated using the Antoine equation:

$$\ln p_v = A - \frac{B}{T_R + C}$$

where

P_v	=	Partial pressure of vapor at reflux temperature in mmHg
A	=	Antoine coefficient A
B	=	Antoine coefficient B
C	=	Antoine coefficient C
T_R	=	Reflux temperature in Kelvin

The following references contain Antoine constants:

- R. Reid et.al., The Properties of Gases and Liquids, McGraw-Hill (1987)
- J. Dean, Lange's Handbook of Chemistry, McGraw-Hill (1999)

Use the appropriate format of the Antoine equation as given by R. Reid or J. Dean. Some authors prefer to use temperature in Celsius rather than Kelvin and, similarly, $\log_{10}(Pv)$ rather than $\ln(P_v)$.

The fraction of vapor can then be calculated using:

$$y_v = \frac{P_v}{P}$$

y_v	=	Fraction of vapor at the reflux temperature
P	=	Ambient pressure

The volume of vapor for each peak in the vapor calibration is determined from:

$$V_v = y_v \times V_1 \times \frac{273.15}{T_L}$$

V_v	=	Vapor volume (as a function of) reflux temperature
V_1	=	Loop volume at STP
T_L	=	Loop temperature in Kelvin (instrument default is 383.15K)

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).

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

V_{STP} = Volume at STP, cm^3

V_α = Volume at ambient temperature and pressure, cm^3

T_α = Ambient temperature, $^\circ$C

P_α = Ambient pressure, mmHg