AUTOCHEM® III 2930

AUTOMATED CATALYST CHARACTERIZATION SYSTEM

CALCULATIONS

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(Rev -)

CORPORATE PROFILE

Micromeritics Instrument Corporation is the world's leading supplier of high-performance systems to characterize particles, powders and porous materials with a focus on physical properties, chemical activity, and flow properties. Our technology portfolio includes: pycnometry, adsorption, dynamic chemisorption, particle size, intrusion porosimetry, powder rheology, and activity testing of catalysts. The company has R&D and manufacturing sites in the USA, UK, and Spain, and direct sales and service operations throughout the Americas, Europe, and Asia. Micromeritics systems are the instruments-of-choice in more than 10,000 laboratories of the world's most innovative companies and prestigious government and academic institutions. Our world-class scientists and responsive support teams enable customer success by applying Micromeritics technology to the most demanding applications. For more information, please visit www.Micromeritics.com.

PATENTS

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CONSTANTS

Symbol	Values and Units	Description
V_{ideal}	$22414\,\mathrm{cm}^3\,\mathrm{at\ STP}$	Ideal gas molar volume at STP
N_A	$6.02214076 \times 10^{23}\ \mathrm{mol}^{-1}$	Avogadro constant
R	$8.31446\,\mathrm{J} \cdot \mathrm{K}^{-1}\,\mathrm{mol}^{-1}$	Ideal gas constant
T_{std}	$0\,^{\circ}\mathrm{C} = 273.15\,\mathrm{K}$	Standard temperature
P_{std}	$1\,\mathrm{atm} = 760\,\mathrm{mmHg}$	Standard pressure

ACTIVE METAL SURFACE AREA

This equation calculates the effective surface area per gram of metal.

$$A_{\text{metallic}} = \frac{Q \cdot S_{\text{calc}} \cdot N_A \cdot A_{\text{calc}}}{m \cdot V_{\text{ideal}}}$$

Parameter	Description	Units
A_{metallic}	Specific metal surface area	m^2/g
Q	Quantity adsorbed	cm^3 at STP
S_{calc}	Calculated stoichiometry factor	
A_{calc}	Cross-sectional area	m^2
m	Sample mass	g

BET SURFACE AREA

For a blend of inert and active gases, we take P to be the fraction of the pressure attributed to the active gas, found by taking the product of the active gas concentration and the measured pressure. For a given experiment, the active gas concentration varies with time as more active gas is adsorbed onto the surface. By holding the pressure constant over the duration of the experiment and measuring the total active gas concentration at the center time for a given peak i, the active gas pressure P_i can be determined by multiplying by the total pressure measured at the start of the experiment. The relative pressure is then written as P_i/P_0.[1]

Parameter	Description
P_i	Fraction of the pressure from the active gas
P_0	Saturation pressure of the adsorbate
i	Peak index

The specific quantity adsorbed for a single peak Q_i is determined from the sum of individual peak volumes V_j of those that preceded it and the sample mass m.

$$Q_i = \sum_{j=1}^{i} V_j/m$$

Then the BET transformation B is given by:

$$B_i = \frac{P_i/P_0}{(1-P_i/P_0)\,Q_i}$$

Parameter	Description	Units
B_i	BET transformation	$\mathrm{g/cm^3}$ at STP
Q_i	Quantity adsorbed	$\mathrm{cm^3/g}$ at STP
i	Peak index	

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[1] P.A. Webb, C. Orr, Analytical Methods in Fine Particle Technology [60-63], Micromeritics Instrument Corporation (1997)

A linear least squares fit is performed on the $(B_i, P_i/P_0)$ pairs where B_i is the dependent variable and P_i/P_0 is the independent variable, from which we obtain the following:

Parameter	**Description**	**Units**
S	Slope	$\mathrm{g/cm^3}$ at STP
Y	Y intercept	$\mathrm{g/cm^3}$ at STP
σ_S	Error of the slope	$\mathrm{g/cm^3}$ at STP
σ_Y	Error of the y-intercept	$\mathrm{g/cm^3}$ at STP
	Correlation coefficient	

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

BET SPECIFIC SURFACE AREA

$$A_{\mathrm{BET}} = \frac{A_c N_A}{\alpha V_{\mathrm{ideal}} (S + Y)}$$

Parameter	**Description**	**Units**
A_{BET}	BET specific surface area	$\mathrm{m^2/g}$
A_c	Adsorbate molecular cross-sectional area	$\mathrm{nm^2}$
$\alpha = 10^{18}$	Unit conversion factor	$\mathrm{nm^2/m^2}$

BET C VALUE

$$C = \frac{S+Y}{Y}$$

VOLUME OF MONOLAYER PER GRAM

$$V_m = \frac{1}{CY} = \frac{1}{S+Y}$$

Parameter	**Description**	**Units**
V_m	Volume of monolayer per gram	$\mathrm{cm^3/g}$ at STP

SINGLE EXPERIMENT

The calculation for a single experiment is obtained by linearly interpolating a line that passes through the collected data point and the origin. Setting the y-intercept to zero we obtain:

$$V_m = \frac{1}{S} = \frac{P_i/P_0}{B_i} = Q_i(1 - P_i/P_0)$$

ERROR OF THE BET SURFACE AREA PER GRAM:

$$\sigma_{\mathrm{BET}} = \frac{A_{\mathrm{BET}} \cdot \sqrt{\sigma_S^2 + \sigma_Y^2}}{Y + S}$$

Parameter	Description	Units
σ_{BET}	Error of the BET specific surface area	m^2/g

CALIBRATION ERROR (GOODNESS OF FIT)

Let μ be the mean value of the measured quantities:

$$\mu = \frac{1}{N} \sum_{i=0}^{N-1} Q_{m_i}$$

Then, the goodness of fit is given by r^2:

$$r^2 = 1 - \frac{\sum_{i=0}^{N-1} (Q_{m_i} - Q_{c_i})^2}{\sum_{i=0}^{N-1} (Q_{m_i} - \mu)^2}$$

Parameter	Description
r^2	Coefficient of determination
Q_{m_i}	Quantity measured for measurement i
Q_{c_i}	Quantity calculated for measurement i
i	Measurement index
N	Total number of measurements

CROSS-SECTIONAL AREA

$$A_{\text{calc}} = G_{\text{calc}} \sum_{i=0}^{N-1} \frac{F_i \cdot A_i}{W_i}$$

Parameter	Description	Units
A_{calc}	Calculated cross-sectional area	m^2
F_i	Fraction of sample weight for metal i	
A_i	Cross-sectional area for metal i	m^2
W_i	Gram molecular weight for metal i	$\mathrm{g/mol}$
i	Metal index	
N	Total number of metals	
G_{calc}	Calculated gram molecular weight	$\mathrm{g/mol}$

CRYSTALLITE SIZE

This equation calculates the crystal size.

$$d = \frac{k}{\rho A}, \quad \text{where} \quad k = \begin{cases} 6 & \text{hemispheric} \\ 5 & \text{cubic} \end{cases}$$

Parameter	**Description**	**Units**
d	Crystallite size	m
ρ	Calculated metal density	$\mathrm{g/m^3}$
A	Active specific surface area per gram of metal	$\mathrm{m^2/g}$
k	Shape factor	

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 three experiments are run. The ramp rate must be different for each run. The data are plotted and the slope determined.

The general equation is:

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

Determine the slope S by plotting:

$2\ln(T_p) - \ln(\beta)$ vs $1/T_p$

Then determine E_d using:

$$E_d = S \times R$$

Parameter	Description	Units
β	Ramp rate	$\mathrm{K/min}$
E_d	Heat of desorption	$\mathrm{K \cdot J/mol}$
T_p	Temperature at peak max	K
S	Slope	K
Q	The quantity adsorbed at saturation	$\mathrm{cm^3\ at\ STP}$
C	A constant related to the desorption rate	

FIT PEAKS CURVE SHAPES

Parameter	Description
a	Peak height at maximum amplitude
$x > 0$	Position
x_0	Peak position at maximum amplitude
$\sigma > 0$	Width parameter for peak functions
$\gamma > 0$	Log-normal shape factor
m	Pearson VII exponent
f	Blend fraction for pseudo-Voigt
x_L	Left x location of peak at half peak maximum
x_R	Right x location of peak at half peak maximum
$t(x) = \frac{x-x_0}{\sigma}$	Transform function
$\omega = x_R - x_L$	Full peak width at half peak maximum height $(a/2)$

GAUSSIAN

$$y = a\,\mathrm{e}^{-t^2\,\ln(2)}$$

LORENTZIAN

$$y = \frac{a}{1+t^2}$$

PEARSON VII

$$y = \frac{a}{[1+t^2(2^{1/m}-1)]^m}$$

PSEUDO-VOIGT

$$y = a[(1-f)\,\mathrm{e}^{-t^2\,\ln(2)} + \frac{f}{1+t^2}]$$

LOG-NORMAL WITH THREE PARAMETERS

$$y = a\,\mathrm{e}^{-\frac{1}{2}\beta^2}\ \text{, where}\ \beta = \frac{\ln(x/x_0)}{\sigma}$$

LOG-NORMAL WITH FOUR PARAMETERS

Let:

$$f = \frac{(x-x_0)(\gamma^2-1)}{\omega\,\gamma}$$

$$g = \frac{\ln(2)\ \ln(f+1)^2}{\ln(\gamma)^2}$$

Then:

$$y = \begin{cases} a\,\mathrm{e}^{-g}, & \gamma \neq 1 \\ a\,2^{-4t^2} & \gamma = 1 \text{ and } \sigma = \gamma \end{cases}$$

GRAM MOLECULAR WEIGHT

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

$$G_{\text{calc}} = \frac{1}{\sum_{i=0}^{N-1} F_i / W_i}$$

Parameter	**Description**	**Units**
G_{calc}	Calculated gram molecular weight	g/mol
F_i	Fraction of sample weight for metal i	
W_i	Gram molecular weight of metal i	g/mol
i	Metal index	
N	Total number of metals	

INJECTION LOOP CALIBRATION

These equations are used during a loop calibration to determine the gas capacity of the loop.

For each syringe injection:

$$Q_s = \frac{V_s}{Z} \times \left(\frac{P_a}{T_a}\right)\left(\frac{T_{\text{std}}}{P_{\text{std}}}\right)$$

Parameter	**Description**	**Units**
Q_s	Syringe quantity	cm^3 at STP
V_s	Physical injection volume	cm^3
T_a	Ambient temperature	K
P_a	Ambient pressure	mmHg
Z	Compressibility (of the loop gas)	

For loop injections, we take that the peak area of each injection will be linear with respect to the injection volume. Taking the slope of the line to be S, and the y-intercept to be Y, we obtain the loop quantity for each injection:

$$Q_l = SA_l + Y$$

We compute the average loop quantity $\bar{Q}_l$ from these values. The loop volume is then given by:

$$V_l = \bar{Q}_l Z \left(\frac{T_a \cdot P_{\text{std}}}{T_{\text{std}} \cdot P_a}\right)$$

Parameter	**Description**	**Units**
V_l	Effective loop volume (at loop temperature)	cm^3

METAL DENSITY

$$\rho = G_{\text{calc}} \sum_{i=0}^{N-1} \frac{F_i \cdot \rho_i}{W_i}$$

Parameter	Description	Units
ρ	Calculated metal density	$\mathrm{g/cm^3}$
F_i	Fraction of sample weight for metal i	
ρ_i	Density of metal i	$\mathrm{g/cm^3}$
W_i	Gram molecular weight for metal i	$\mathrm{g/mol}$
i	Metal index	
N	Total number of metals	

PEAK AREA TO QUANTITY OF GAS

The quantity of gas for a given peak area and calibration is determined by:

$$Q_p = \sum_{i=0}^{M-1} A_p^i \omega_i$$

Parameter	Description	Units
Q_p	Quantity of gas	cm^3 at STP
A_p	Peak area	cm^3
M	Calibration polynomial degree	
i	Calibration polynomial coefficient index	
ω_i	Calibration polynomial coefficient	

INTEGRATED PEAK AREA

To compensate for the slope of the baseline ascribed to a given peak (S_{base}), we derive the equation for the baseline and subtract it from the measured TCD signal.

Since signal measurements are taken at constant intervals (Δt), let k and j represent the indices (in the signal's domain) of the first and last points for the baseline (respectively).

Then, the height of the baseline for an arbitrary data point n is given by:

$$b_n = S_{\text{base}}(n-k) + b_k, \quad \text{where} \quad S_{\text{base}} = \frac{b_j - b_k}{j-k}$$

The peak area is then found by numerical integration:

$$A_p = \sum_{n=k}^{j} (Y_n - b_n) \cdot \Delta t$$

Parameter	Description
Δt	Number of minutes per data point (inverse of sampling rate)
Y_n	TCD signal at point n
b_n	Baseline height at point n
n	Data point index

PERCENT DISPERSION

The fractional coverage F_D used in reporting is derived as:

$$F_D = \left(\frac{Q_s \cdot S_{\text{calc}}}{V_{\text{ideal}}}\right) G_{\text{calc}}$$

From this the percent dispersion P_D can be calculated by:

$$P_D = 100\% \times F_D$$

Parameter	**Description**	**Units**
P_D	Percent dispersion	$\%$
F_D	Fractional coverage	
Q_s	Specific quantity adsorbed	$\text{cm}^3/\text{g at STP}$
S_{calc}	Calculated stoichiometry factor	

QUANTITY AT STP

Gas quantity at standard temperature and pressure (STP) conditions.

$$Q_{\mathrm{STP}} = Q \frac{T_{\mathrm{std}}}{T} \frac{P}{P_{\mathrm{std}}}$$

Parameter	**Description**	**Units**
Q_{STP}	Quantity at standard temperature and pressure	cm^3 at STP
Q	Quantity at measured temperature and pressure	cm^3
T	Measured temperature of the gas	K
P	Measured pressure of the gas	mmHg

QUANTITY ADSORBED

These equations are used for loop or syringe injections to calculate volume removed from the injections by the sample.

The general equation for the Quantity Sorbed Q_S is:

$$Q_s = \left(\sum_{i=0}^{N-1} Q_i\right) - Q_{na}$$

Assuming the same quantities are used for each injection, we obtain:

$$Q_s = NQ_i - Q_{na}$$

This is often represented in calculations as Volume Sorbed V_S:

$$V_s = Q_s \times m$$

Parameter	Description	Units
Q_s	Quantity sorbed	cm^3/g at STP
V_s	Volume sorbed	cm^3
i	Injection index	
N	Number of injections	
Q_i	Quantity per injection	cm^3/g at STP
Q_{na}	Total quantity not sorbed	cm^3/g at STP
m	Mass of sample	g

STOICHIOMETRY FACTOR FOR CHEMICAL ADSORPTION

$$S_{\text{calc}} = G_{\text{calc}} \sum_{i=0}^{N-1} \frac{F_i \cdot S_i}{W_i}$$

Parameter	Description	Units
S_{calc}	Calculated stoichiometry factor	
S_i	Stoichiometry factor for metal i	
F_i	Fraction of sample mass for metal i	
W_i	Gram molecular weight for metal i	g/mol
i	Metal index	
N	Total number of metals	

VAPOR GENERATOR

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

$$\log_{10}(P_v) = A - \frac{B}{T_R + C}$$

Parameter	**Description**	**Units**
P_v	Partial pressure of vapor at reflux temperature	bar
A	Antoine coefficient A	bar
B	Antoine coefficient B	$\mathrm{K \cdot bar}$
C	Antoine coefficient C	K
T_R	Reflux temperature	K

Pressures determined from the calculation above are converted internally, such that displayed units are in mmHg.

Use the appropriate format of the Antoine equation as given by R. Reid[1] or J. Dean.[2] Some authors prefer to use temperature in Celsius rather than Kelvin and, similarly, $\ln(P_v)$ rather than $\log_{10}(P_v)$.

The fraction of vapor can then be calculated using:

$$y_v = \frac{P_v}{P_{\mathrm{std}}}$$

Parameter	**Description**
y_v	Fraction of vapor at reflux temperature

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[1] R. Reid et.al., The Properties of Gases and Liquids, McGraw-Hill (1987)

[2] J. Dean, Lange's Handbook of Chemistry, McGraw-Hill (1999)

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

$$V_v = y_v \cdot V_l \cdot \frac{T_{\text{std}}}{T_l}$$

Parameter	Description	Units
V_v	Vapor volume as a function of reflux temperature	cm^3
V_l	Loop volume	cm^3 at STP
T_l	Loop temperature (instrument default $383.15K$)	K

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