Estimation of Monolayer Capacity for the BET Equation

Certain laboratories have used the surface area computed by fitting the BET (*1*) equation to N_2 adsorption data at liquid air temperatures to characterize various porous solids. The purpose of this note is to describe an experimental design criterion for determining the best settings of the relative pressures at which to run adsorption determinations in order that a good estimate of the monolayer capacity, and hence the surface area, will be obtained. Experiments are selected by maximizing a function of the partial derivatives of the equation at specific values of the parameters. The statistical considerations which lead to the experimental design criterion that is used here are discussed in the Appendix and elsewhere (*2*).

The case where two determinations are to be run will be treated in detail. The case where only a single determination is run will also be discussed. If more than two determinations are to be made, the procedure discussed here can be readily extended to such cases.

The BET equation is

$$v = \frac{v_m c p}{(p_0 - p)\{1 + (c - 1)p/p_0\}} \quad (1)$$

where v is the volume of gas adsorbed on the solid at the relative pressure p/p_0, c is a constant characteristic of the gas–solid pair, and v_m is the monolayer capacity. The equation may be written in the form

$$v = \frac{v_m c x}{(1 - x)\{1 + (c - 1)x\}} \quad (2)$$

by dividing numerator and denominator by p_0 and writing x for the relative pressure p/p_0.

Experimental Design Criterion

The two required partial derivatives are:

$$y_{1u} = \frac{\partial v_u}{\partial v_m} = \frac{c x_u}{(1 - x_u)\{1 + (c - 1)x_u\}} \qquad u = 1, 2, \ldots, n \quad (3)$$

$$y_{2u} = \frac{\partial v_u}{\partial c} = \frac{v_m\{x_u + x_u^2(2c - 1)\}}{(1 - x_u)\{1 + (c - 1)x_u\}^2} \qquad u = 1, 2, \ldots, n \quad (4)$$

where n is the number of determinations to be made. The function which is to be maximized is written in terms of these partial derivatives. Suppose two runs are to be made and that the errors in measuring v are independently and Normally distributed with constant variance. Then, if the object is to obtain a precise estimate of v_m, the function to be maximized with respect to x_1 and x_2 is:

$$\sum_{u=1}^{2} y_{1u}^2 - \left(\sum_{u=1}^{2} y_{1u}y_{2u}\right)^2 \Big/ \sum_{u=1}^{2} y_{2u}^2 \quad (5)$$

Note that the value of this function is independent of the magnitude of v_m. If more than two determinations are to be made (i.e., $n > 2$), the same criterion is used except the summations go to n and not 2. Intuitively, this criterion concentrates on v_m and more or less ignores c except that an estimate of c must be obtained.

Although the BET equation is capable of describing Type II or Type III isotherms (*3*), it has been used primarily for isotherms of Type II with the general range of validity between 0.05 and 0.30 relative pressure. Commonly, nitrogen adsorption at 90°K is used to determine the surface area of solids. When the surface area is expressed in square meters per gram and a molecular area of 16.2 square angströms is assumed for the adsorbed nitrogen molecule, surface areas from 5 to 5000 m^2/g approximately correspond to values of v_m of from 1 to 1000 cm^3 (at STP)/g adsorbent. The magnitude of c can range from 1 to more than 100. For the majority of adsorbents studied at liquid air temperatures, nitrogen exhibits high values of c, usually between 50 and 150.

Optimal Two-Point Designs

Using the design criterion presented above, one can calculate two optimal relative pressures at which adsorption should be determined so that the most precise estimate of the monolayer capacity will be obtained, thereby yielding the most precise estimate of the surface area of the solid. These values are given in Table 1. The best two experimental points are independent of the magnitude of v_m. An estimate of c can often be obtained from studies on similar adsorbents. The location of the best experimental points was determined (correct to the nearest hundredth) subject to the constraint that the relative pressures should lie between 0.05 and 0.30. If it is known or expected that the range of validity of the BET equation will be smaller that this, then in most cases the two adsorption experiments should be carried out at the endpoints of the range.

TABLE 1
LOCATION OF THE TWO BEST EXPERIMENTAL POINTS FOR THE MOST PRECISE ESTIMATE OF THE MONOLAYER CAPACITY IN THE BET EQUATION FOR x BETWEEN 0.05 AND 0.30

c	Determine adsorption at relative pressures x of:
2	0.13, 0.30
10	0.06, 0.30
40	0.05, 0.30
80	0.05, 0.30
100	0.05, 0.30
1000	0.05, 0.30

Optimal Single-Point Designs

In the original paper for situations in which only one determination was to be made, Brunauer *et al.* (*1*) proposed that one take a single nitrogen adsorption point at a relative pressure of 0.3, and, using a BET plot (Eq. (1) in a linearized form), connect the single point so plotted with the origin and then determine v_m from the slope. Values obtained in this single-point design for the monolayer capacity agreed within 5% of the value determined by the usual BET plot with additional data points. This single-point design is equivalent to taking $c \gg 1$.

Likewise, if we set c equal to some value much larger than unity in our design criterion (Eq. 5) with $0.05 \leq x \leq 0.30$, the result would be to determine a single adsorption at $x = 0.30$, which is what Brunauer *et al.* proposed. For some other region of validity for the BET equation, the criterion suggests taking a data point at the upper limit of this range. A danger exists in the Brunauer method, as well as in the present one, in that the upper point may be out of the region of validity for the BET equation. If this were true, biased estimates of v_m would be obtained. Another single-point method has been described by Halasz and Schay (*4*). Katz (*5*) has presented an equation for the surface area involving experimental quantities for a constant volume apparatus.

APPENDIX

For a nonlinear mathematical model $\eta = f(\boldsymbol{\theta},\boldsymbol{\xi})$ with $\boldsymbol{\theta}$ indicating the p parameters and $\boldsymbol{\xi}$ the independent variables, under suitable reasonable assumptions (see Box and Hunter (*A-1*)), the posterior distribution of $\boldsymbol{\theta}$ is

$$p(\boldsymbol{\theta}|\mathbf{y}) = \frac{|\boldsymbol{\Sigma}|^{-1/2}}{(\sqrt{2\pi}\,\sigma)^p} \times \exp\left\{-\frac{1}{2\sigma^2}(\boldsymbol{\theta}-\hat{\boldsymbol{\theta}})'\boldsymbol{\Sigma}^{-1}(\boldsymbol{\theta}-\hat{\boldsymbol{\theta}})\right\},$$

where

$$\boldsymbol{\Sigma}^{-1} = \mathbf{X}'\mathbf{X},\ \mathbf{X} = \begin{bmatrix} x_{11} & x_{21} & \cdots & x_{p1} \\ x_{12} & x_{22} & \cdots & x_{p2} \\ & & \vdots & \\ x_{1N} & x_{2N} & \cdots & x_{pN} \end{bmatrix},$$

$$x_{ij} = \left[\frac{\partial f(\boldsymbol{\theta},\boldsymbol{\xi})}{\partial \theta_i}\right]_{\boldsymbol{\theta}=\hat{\boldsymbol{\theta}}}$$

and

$$\boldsymbol{\theta} - \hat{\boldsymbol{\theta}} = \begin{bmatrix} \theta_1 - \hat{\theta}_1 \\ \theta_2 - \hat{\theta}_2 \\ \vdots \\ \theta_p - \hat{\theta}_p \end{bmatrix}.$$

It is reasonable to design a set of experiments at those conditions which give the maximum posterior density to the most probable values. Thus the posterior density is maximized with respect to both $\boldsymbol{\theta}$ and $\boldsymbol{\xi}$. The maximum probability density will be at the point $\boldsymbol{\theta} = \hat{\boldsymbol{\theta}}$ whatever the settings of $\boldsymbol{\xi}$, so that

$$\underset{\text{w.r.t. } \boldsymbol{\theta}}{\text{Max}}\ p(\boldsymbol{\theta}|\mathbf{y}) = \frac{|\boldsymbol{\Sigma}|^{-1/2}}{(\sqrt{2\pi}\,\sigma)^p};$$

where σ is a positive constant. Therefore it is necessary to minimize the determinant of $\boldsymbol{\Sigma}$ or, equivalently, to maximize the determinant of $\mathbf{X'X}$. This can be used as a design criterion when the goal is to obtain precise parameter estimates for *all the parameters in the model*. (See Box and Lucas (*A-2*) and Box and Hunter (*A-1*)). To obtain a design criterion for the case where the experimenter is interested only in *a subset of the parameters*, a procedure such as the following may be used.

Partition the $(\boldsymbol{\theta} - \hat{\boldsymbol{\theta}})$ vector,

$$(\boldsymbol{\theta} - \hat{\boldsymbol{\theta}}) = \begin{pmatrix} \boldsymbol{\theta}_1 - \hat{\boldsymbol{\theta}}_1 \\ \cdots\cdots \\ \boldsymbol{\theta}_2 - \hat{\boldsymbol{\theta}}_2 \end{pmatrix} = \begin{array}{c} \left[\begin{array}{c} \theta_1 - \hat{\theta}_1 \\ \theta_2 - \hat{\theta}_2 \\ \vdots \\ \theta_{p_1} - \hat{\theta}_{p_1} \\ \cdots\cdots\cdots \\ \theta_{p_1+1} - \hat{\theta}_{p_1+1} \\ \vdots \\ \theta_{p_1+p_2} - \hat{\theta}_{p_1+p_2} \end{array}\right] \end{array} \begin{array}{l} p_1 \\ \\ p_2 \end{array}$$

$$= \begin{pmatrix} \mathbf{a}_1 \\ \cdots \\ \mathbf{a}_2 \end{pmatrix} = \mathbf{A}$$

where $p = p_1 + p_2$.

We are interested in finding an expression for the marginal distribution,

$$p(\boldsymbol{\theta}_1|\mathbf{y}) = \int p(\boldsymbol{\theta}_1 \vdots \boldsymbol{\theta}_2|\mathbf{y})\, d\boldsymbol{\theta}_2$$

$$= \int \frac{|\boldsymbol{\Sigma}|^{-1/2}}{(\sqrt{2\pi}\,\sigma)^p} \times \exp\left\{-\frac{1}{2\sigma^2}\mathbf{A'}\boldsymbol{\Sigma}^{-1}\mathbf{A}\right\} d\boldsymbol{\theta}_2.$$

Letting

$$\underset{(p \times p)}{\boldsymbol{\Sigma}} = \begin{array}{c} \begin{array}{cc} p_1 & p_2 \end{array} \\ \left[\begin{array}{c:c} \boldsymbol{\Sigma}_{11} & \boldsymbol{\Sigma}_{12} \\ \hdashline \boldsymbol{\Sigma}'_{12} & \boldsymbol{\Sigma}_{22} \end{array}\right] \end{array} \begin{array}{l} \\ p_1 \\ p_2 \end{array}$$

we have

$$\mathbf{A'}\boldsymbol{\Sigma}^{-1}\mathbf{A} = (\mathbf{a'}_1 \vdots \mathbf{a'}_2)\begin{bmatrix} \mathbf{I} & -\boldsymbol{\Sigma}_{11}^{-1}\boldsymbol{\Sigma}_{12} \\ \mathbf{O} & \mathbf{I} \end{bmatrix}$$
$$\times \begin{bmatrix} \boldsymbol{\Sigma}_{11}^{-1} & \mathbf{O} \\ \mathbf{O} & (\boldsymbol{\Sigma}_{22} - \boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1}\boldsymbol{\Sigma}_{12})^{-1} \end{bmatrix}$$
$$\times \begin{bmatrix} \mathbf{I} & \mathbf{O} \\ -\boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1} & \mathbf{I} \end{bmatrix} \begin{pmatrix} \mathbf{a}_1 \\ \cdots \\ \mathbf{a}_2 \end{pmatrix}.$$

$Q_p = \mathbf{A'}\boldsymbol{\Sigma}^{-1}\mathbf{A}$ can always be written as a sum of two quadratic terms Q_{p_1} and Q_{p_2} containing p_1 and p_2 elements, respectively, where

$$Q_p = Q_{p_1} + Q_{p_2}$$
$$Q_{p_1} = \mathbf{a'}_1\boldsymbol{\Sigma}_{11}^{-1}\mathbf{a}_1$$

$Q_{p_2} = (\mathbf{a}_2 - \boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1}\mathbf{a}_1)'(\boldsymbol{\Sigma}_{22} - \boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1}\boldsymbol{\Sigma}_{12})^{-1}(\mathbf{a}_2 - \boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1}\mathbf{a}_1) = \mathbf{R'S}^{-1}\mathbf{R}$, say where $\mathbf{S}$ is $(p_2 \times p_2)$.

We now have

$$p(\boldsymbol{\theta}_1|\mathbf{y}) = \left[\frac{|\boldsymbol{\Sigma}|^{-1/2}}{(\sqrt{2\pi}\,\sigma)^p}\exp\left\{-\frac{1}{2\sigma^2}\mathbf{a'}_1\boldsymbol{\Sigma}_{11}^{-1}\mathbf{a}_1\right\}\right] \times \int \exp\left\{-\frac{1}{2\sigma^2}[\mathbf{R'S}^{-1}\mathbf{R}]\right\} d\mathbf{R}.$$

Using the well known integral

$$\int \exp\left\{-\frac{1}{2\sigma^2}\mathbf{y'By}\right\} d\mathbf{y} = \frac{(\sqrt{2\pi}\,\sigma)^q}{|\mathbf{B}|^{1/2}}$$

where B is $(q \times q)$,

$$p(\boldsymbol{\theta}_1|\mathbf{y}) = \left[\frac{|\boldsymbol{\Sigma}|^{-1/2}}{(\sqrt{2\pi}\,\sigma)^p}\exp\left\{-\frac{1}{2\sigma^2}\mathbf{a'}_1\boldsymbol{\Sigma}_{11}^{-1}\mathbf{a}_1\right\}\right] \times \frac{(\sqrt{2\pi}\,\sigma)^{p_2}}{|(\boldsymbol{\Sigma}_{22} - \boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1}\boldsymbol{\Sigma}_{12})^{-1}|^{1/2}}.$$

Since

$$|\boldsymbol{\Sigma}| = |\boldsymbol{\Sigma}_{22} - \boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1}\boldsymbol{\Sigma}_{12}| \cdot |\boldsymbol{\Sigma}_{11}|,$$

$$p(\boldsymbol{\theta}_1|\mathbf{y}) = \frac{|\boldsymbol{\Sigma}_{22} - \boldsymbol{\Sigma}'_{12}\boldsymbol{\Sigma}_{11}^{-1}\boldsymbol{\Sigma}_{12}|^{-1/2} \cdot |\boldsymbol{\Sigma}_{11}|^{-1/2}}{(\sqrt{2\pi}\,\sigma)^{p_1+p_2}}$$

$$\times \frac{(\sqrt{2\pi}\,\sigma)^{p_2}}{|\mathbf{\Sigma}_{22} - \mathbf{\Sigma}'_{12}\mathbf{\Sigma}_{11}^{-1}\mathbf{\Sigma}_{12}|^{-1/2}}$$

$$\times \exp\left\{-\frac{1}{2\sigma^2}\mathbf{a}'_1\mathbf{\Sigma}_{11}^{-1}\mathbf{a}_1\right\}$$

$$p(\boldsymbol{\theta}_1|\mathbf{y}) = \frac{|\mathbf{\Sigma}_{11}|^{-1/2}}{(\sqrt{2\pi}\,\sigma)^{p_1}} \exp\left\{-\frac{1}{2\sigma^2}\mathbf{a}'_1\mathbf{\Sigma}_{11}^{-1}\mathbf{a}_1\right\}.$$

$$\mathbf{\Sigma} = (\mathbf{X}'\mathbf{X})^{-1} = \mathbf{c}^{-1} = \begin{pmatrix} \mathbf{c}_{11} & \cdot & \mathbf{c}_{12} \\ \cdots & \cdot & \cdots \\ \mathbf{c}_{21} & \cdot & \mathbf{c}_{22} \end{pmatrix}^{-1}$$

$$= \frac{1}{\Delta}\begin{pmatrix} \mathbf{c}_{22} & -\mathbf{c}_{21} \\ -\mathbf{c}_{12} & \mathbf{c}_{11} \end{pmatrix}; \ \Delta = \mathbf{c}_{11}\mathbf{c}_{22} - \mathbf{c}_{12}\mathbf{c}_{21}$$

$$\mathbf{\Sigma} = \begin{pmatrix} \dfrac{1}{\mathbf{c}_{11} - \mathbf{c}_{12}\mathbf{c}_{22}^{-1}\mathbf{c}_{21}} & -\dfrac{\mathbf{c}_{21}}{\Delta} \\ -\dfrac{\mathbf{c}_{12}}{\Delta} & \dfrac{\mathbf{c}_{11}}{\Delta} \end{pmatrix}$$

$$\mathbf{\Sigma}_{11} = (\mathbf{c}_{11} - \mathbf{c}_{12}\mathbf{c}_{22}^{-1}\mathbf{c}_{21})^{-1}$$

$$|\mathbf{\Sigma}_{11}| = |\mathbf{c}_{11} - \mathbf{c}_{12}\mathbf{c}_{22}^{-1}\mathbf{c}_{21}|^{-1}$$

and

$$p(\boldsymbol{\theta}_1|\mathbf{y}) = \frac{|\mathbf{c}_{11} - \mathbf{c}_{12}\mathbf{c}_{22}^{-1}\mathbf{c}_{21}|^{+1/2}}{(\sqrt{2\pi}\,\sigma)^{p_1}} \times \exp\left\{-\frac{1}{2\sigma^2}(\boldsymbol{\theta} - \hat{\boldsymbol{\theta}}_1)'\mathbf{\Sigma}_{11}^{-1}(\boldsymbol{\theta} - \hat{\boldsymbol{\theta}}_1)\right\}.$$

The design criterion, then, for the case where only a subset of the parameters are of interest which is analogous to the criterion for the full parameter set would be to maximize the determinant of $(\mathbf{c}_{11} - \mathbf{c}_{12}\mathbf{c}_{22}^{-1}\mathbf{c}_{21})$ with respect to the independent variables $\boldsymbol{\xi}$. For $p = 2$

$$c_{ij} = \sum_{u=1}^{n} \left(\frac{\partial f_u}{\partial \theta_i}\right)\left(\frac{\partial f_u}{\partial \theta_j}\right)$$

so that

$$\underset{\text{w.r.t. } \boldsymbol{\xi}}{\text{Max}} |\mathbf{c}_{11} - \mathbf{c}_{12}\mathbf{c}_{22}^{-1}\mathbf{c}_{21}|$$

$$= \underset{\text{w.r.t. } \boldsymbol{\xi}}{\text{Max}} \left| \sum_{u=1}^{n} \left(\frac{\partial f_u}{\partial \theta_1}\right)^2 - \left\{\left[\sum_{u=1}^{n}\left(\frac{\partial f_u}{\partial \theta_1}\right)\left(\frac{\partial f_u}{\partial \theta_2}\right)\right]^2 \Big/ \sum_{u=1}^{n}\left(\frac{\partial f_u}{\partial \theta_2}\right)^2\right\}\right|.$$

For the case of the BET equation

$$f = v = \frac{v_m c x}{(1 - x)\{1 + (c - 1)x\}}; \ \xi = x$$

$$\frac{\partial f_u}{\partial \theta_1} = \frac{\partial v_u}{\partial v_m} = y_{1u} \quad \text{and} \quad \frac{\partial f_u}{\partial \theta_2} = \frac{\partial v_u}{\partial c} = y_{2u}$$

and the design criterion is

$$\underset{\text{w.r.t. } x}{\text{Max}} \left\{\sum_{u=1}^{n} y_{1u}^2 - \left(\sum_{u=1}^{n} y_{1u}y_{2u}\right)^2 \Big/ \sum_{u=1}^{n} y_{2u}^2\right\},$$

which is equation (5) when $n = 2$.

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Appendix References

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