

Determination of Adsorption Energy Distribution by Regularization and a Characterization of Certain Adsorption Isotherms

PAUL H. MERZ

Chevron Research Company, P.O. Box 1627, Richmond, California 94802

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The determination of the distribution of adsorption energies from an adsorption isotherm experiment is an ill-posed problem. The numerical technique of regularization with generalized cross-validation is recommended and outlined for solving this problem. An example demonstrates the techniques. Data for the adsorption of pyridine on silica-alumina at 150°C are presented. A concavity criterion is proven for adsorption isotherms when the unisorptic isotherm is Langmuir or BET. Although the pyridine data appear Langmuir-like, the adsorption data cannot be described by using the Langmuir or BET unisorptic isotherms as kernel in the integral equation model since the data do not conform to the concavity criterion.

1. INTRODUCTION

Early models of gas adsorption on solid surfaces postulated uniform and homogeneous surfaces. The first quantitative discussion is generally attributed to Langmuir [20], who derived an expression for the adsorption isotherm which relates the fraction of sites covered at equilibrium to pressure and the energy of adsorption which characterizes the adsorbate–adsorbent interaction. The Langmuir isotherm is a model for monolayer coverage. Brunauer, Emmett, and Teller [3] derived an isotherm (BET isotherm) which models multilayer coverage. Both the Langmuir and BET isotherms are based on kinetic mechanisms and assume fixed sites (an immobile film) with no lateral interaction between adsorbed molecules. If the methods of statistical mechanics are used, the assumptions of fixed sites and no lateral interaction may be dropped. The Hill–de Boer isotherm [6] describes the coverage of a surface by a mobile film with lateral interaction. An isotherm which assumes an immobile film but permits interaction is due to Fowler and Guggenheim [8].

These isotherms share the idealistic assumption that the surface is uniform, i.e., that the surface is characterized by exactly one energy of adsorption. But, it has long been recognized that solid surfaces are energetically heterogeneous due to different surface species, crystal faces, contaminations, and other effects. Adsorption is more properly envisioned as occurring on patches or regions which individually are energetically homogeneous. Such patches have been called homotactic by Sanford and Ross [28]. Let the number of sites which have energy of adsorption between q and

$q + dq$ be $f(q) dq$. Let $\theta(p, q)$ be a function (isotherm) which relates the fraction of sites covered θ at equilibrium to pressure p and the energy of adsorption q . Then the number of molecules $\bar{\theta}$ adsorbed on the surface is obtained by integration as

$$\bar{\theta}(p) = \int_0^{\infty} \theta(p, q) f(q) dq. \quad (1)$$

Equation (1) is justified if adsorption on one homotactic patch proceeds independently of that on other patches.

The problem associated with (1) is this: given experimental adsorption isotherm data $\bar{\theta}_i$ as approximations to $\bar{\theta}$ at pressures p_i , and assuming that all homotactic patches obey the rule θ , solve for the density function f which satisfies (1). Knowledge of f would elucidate the surface structure and assist understanding of surface reactions and catalytic mechanisms.

Equation (1) is a linear Fredholm integral equation of the first kind with kernel θ . Solution methods and solutions have been proposed assuming different functions as kernel and using different methods of solution. The Langmuir isotherm has been used as a kernel in (1) in several studies [1, 4, 18, 19, 25, 29, 30]. The BET isotherm has been used as a kernel also [7, 14]. House and Jaycock [15] developed a computer program HILDA which attempts to solve (1) using any of the Langmuir, Hill-de Boer, or Fowler-Guggenheim isotherms as kernel. Morrison [23] and Ross and Morrison [26] attempt to solve the integral equation using a two-dimensional virial equation of state and the Gibbs adsorption theorem to define an isotherm; they use a computer program called CAEDMON. More recently, Sacher and Morrison [27] discuss an improvement of CAEDMON in which the density function is constrained to be nonnegative.

These attempts to solve (1) use or counsel various techniques. Methods based on transforms and complex analysis have been used. Graphing techniques and ad hoc methods have been tried as well. But usually investigators have ignored the mathematical character of inverting the integral equation and also, sometimes, have strayed too far from the data.

The integral equation (1) is ill-posed; that is, the solution f is not a continuous function of the data. A simple argument demonstrates the ill-posedness. For any integrable kernel K we have (according to the Riemann-Lebesgue lemma)

$$\lim_{m \rightarrow \infty} \int K(p, q) \sin(mq) dq = 0. \quad (2)$$

Consequently, a small change in the data (as produced, for instance, by experimental error) will produce a large change in the solution. Indeed, for some large m , let the small change in the data $\delta\bar{\theta}(p)$ be given by the integral in (2). Then the corresponding large change in the answer is $\delta f(q) = \sin(mq)$. It is not possible mathematically to circumvent the ill-posedness of inverting the integral equation (1). Methods which purport to solve (1) analytically assume that the left-hand side $\bar{\theta}$ is an analytic function; but, of course, the data do not qualify as such.

None of the above-mentioned investigations addresses the problem of ill-posedness. A method of solution which does address the ill-posed character of inverting linear operator equations is Tikhonov regularization [31, 32], and there are related methods. One application which confronts the difficulty has been performed by Hanson [11], who worked with the hapten binding equation of immunology, which is identical to the Langmuir isotherm. Recently, House [16] has also recognized this aspect of the problem.

A more insidious error is to assume that (1) has any solution at all. If the left-hand side is not in the range of the linear operator on the right-hand side, it is impossible to invert the equation. For instance, suppose the kernel $\theta(p, q)$ is chosen as the Langmuir isotherm. For any fixed energy of adsorption q , coverage θ as a function of pressure p has the familiar Langmuir profile, viz., strictly monotonic increasing, concave down, and asymptotically constant corresponding to full coverage. Suppose there is adsorption data $\bar{\theta}$, whose profile also exhibits this character but for which no individual $\theta(p, q)$ provides an adequate fit. The tacit assumption in all of the above investigations is that the lack of fit is due to surface heterogeneity and that the data can be explained by integrating (or summing) over a distribution of adsorption energies. This assumption is, in general, incorrect, as shown by presenting pyridine adsorption data as a counterexample.

Data for the adsorption of pyridine on silica-alumina are tabulated in Table I and plotted in Fig. 1. The shape is Langmuirian. Tikhonov regularization was applied to solve for the density function of energies of adsorption. The numerical implementation of regularization will be outlined in this paper. However, the approach did not succeed—the resulting solution f always assumed unacceptably large negative values. Subsequently, a criterion was found which demonstrates that the pyridine adsorption data cannot be described by (1) using a Langmuir kernel. The criterion is obtained by observing the concavity of $p/\bar{\theta}$ versus p . It constitutes a necessary condition on $\bar{\theta}$ for the kernel to be Langmuirian; this condition is violated by the data. Similarly, the pyridine data cannot be explained using a BET isotherm as kernel. Numerical simulations indicate that the Fowler–Guggenheim and Hill–de Boer isotherms are also unacceptable.

While this concavity criterion is a necessary condition on the adsorption data $\bar{\theta}$ (for some kernels θ) in order for the model (1) to be correct, it is not a sufficient condition. It is recommended that before trying to solve (1), the investigator should confirm the validity of the unisorptic isotherm θ which will be used as kernel. Furthermore, given the ill-posed character of this integral equation, an appropriate numerical algorithm should be used—regularization is recommended.

2. EXPERIMENTAL

The importance of acid-type catalysts in petroleum processes has stimulated interest in the adsorptive and acid properties of solid surfaces. My involvement in this activity was initiated by P. R. Ryason, who was interested in Lewis and Bronsted

acid site distribution functions. Early data (1972) gathered by P. R. Ryason, J. M. Hubert, and H. F. Harnsberger already indicated that a unisorptic isotherm model was inadequate. Consequently, we began looking at the model (1) in order to explain our data. Subsequent efforts focused on obtaining very reliable, accurate data, and in-

TABLE I
Pyridine Adsorption on 50% Silica, 50% Alumina at 150°C^a

Pressure (mTorr)	Adsorption ($\mu\text{mole g}^{-1}$)	Pressure (mTorr)	Adsorption ($\mu\text{mole g}^{-1}$)
2.42	23.05	123.13	414.22
4.10	35.57	129.42	417.87
5.88	47.96	135.90	421.25
7.74	59.46	142.43	424.77
9.57	70.82	148.85	427.74
11.15	81.71	155.16	430.72
12.97	92.50	161.58	433.42
14.77	103.20	168.5	436.26
16.50	113.65	174.3	438.43
18.38	123.90	180.7	440.73
20.12	133.90	187.5	442.76
23.69	153.59	194.5	444.92
25.42	163.30	201.6	446.68
27.28	172.88	208.6	448.98
29.01	182.17	215.2	451.28
30.84	191.45	229.0	456.01
32.60	200.31	236.4	457.77
34.58	209.19	243.5	459.66
36.27	218.43	250.8	461.56
38.28	227.44	258.2	463.45
40.19	236.50	266.0	465.34
42.40	246.64	273.6	467.37
44.76	257.73	281.6	469.26
47.25	269.09	289.0	471.70
49.94	281.27	297.0	473.73
52.90	293.85	305.1	475.76
55.83	306.69	313.8	477.78
59.10	319.54	322.9	479.68
62.39	332.39	332.3	481.84
66.14	344.56	342.2	483.87
70.20	356.20	352.0	486.04
79.61	375.94	362.7	488.20
85.33	383.65	373.1	490.50
91.05	390.53	384.4	492.66
97.15	396.36	396.1	494.96
103.50	401.50	408.0	497.13
110.01	406.10	420.0	499.56
116.53	410.57		

^a Data of Hubert and Harnsberger [17].

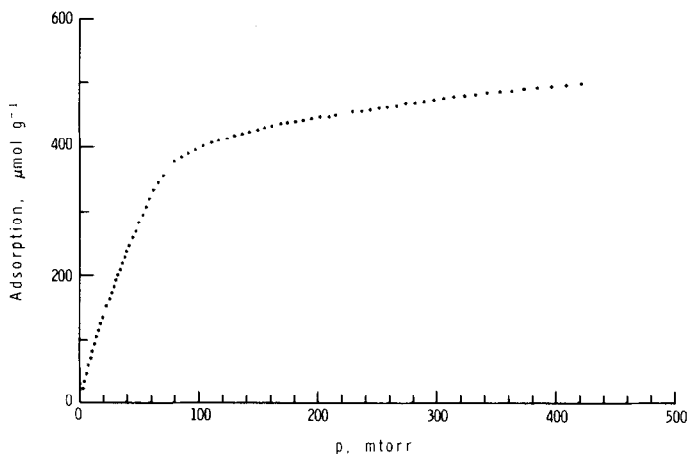


FIG. 1. Pyridine adsorption data on 50% silica, 50% alumina at 150°C; Hubert and Harnsberger [17].

volved J. A. Schwarz also. Data for pyridine adsorption on silica-alumina, however, exhibited characteristics not in accordance with (1) using a Langmuir unisorptic isotherm as kernel. One such data set is now presented.

Gravimetric data for the adsorption of pyridine on 50% silica, 50% alumina at 150°C were gathered by Hubert and Harnsberger [17]. These data are listed in Table I and plotted in Fig. 1. Equipment included a Cahn Model RG torsion electromicrobalance (capacity 1 g) for obtaining sample weight and amount of vapor adsorbed, a Texas Instruments spiral manometer (0–760 Torr), and an MKS Baratron capacitance manometer (0–1 Torr). This apparatus is described in detail by Beavers and Hubert [2]. The general shape of the curve in Fig. 1 is Langmuirian—monotonic increasing, concave down, and (perhaps) asymptotically constant.

3. REGULARIZATION

3.1. Method

Using these data, an attempt was made to determine the density f of energies of adsorption assuming Eq. (1) as model and a Langmuir isotherm as kernel θ , which seemed to be a natural choice. The method used was Tikhonov regularization, a description of which follows in general outline.

A sensible way of spacing values of q is logarithmically. Under the transformation $r = \ln q$, Eq. (1) becomes

$$\bar{\theta}(p) = \int_{-\infty}^{\infty} \alpha(p, r) x(r) dr, \quad (3)$$

where $\alpha(p, r) = \theta(p, e^r)$ and $x(r) = e^r f(e^r)$. Denote the observed coverages by $b_i = \bar{\theta}(p_i)$ for pressures p_i ($i = 1, 2, \dots, n$). Suppose it is known (or guessed) that almost all of the energies of adsorption belong to the interval $[q, \bar{q}]$. Equation (3) can be discretized in the following manner. Define nodes r_j by

$$r_j = \ln q + (j - 1)h \quad (j = 1, 2, \dots, m),$$

where

$$h = (m - 1)^{-1} \ln(\bar{q}/q).$$

We seek approximations x_j to $x(r_j)$. It is necessary to choose m sufficiently large in order for the x_j to adequately describe the density. Approximate (3) using some quadrature such as the trapezoidal rule or Simpson's rule. Let $a_{ij} = w_j \alpha(p_i, r_j)$, where the w_j are weights determined by the quadrature chosen. For example, when m is odd and Simpson's rule is used

$$\begin{aligned} w_j &= h/3 & (j = 1, m), \\ &= 4h/3 & (j = 2, 4, \dots, m - 1), \\ &= 2h/3 & (j = 3, 5, \dots, m - 2). \end{aligned}$$

The discretized version of (3) takes the form

$$A\mathbf{x} = \mathbf{b} + \boldsymbol{\varepsilon}, \tag{4}$$

where $A = (a_{ij})$, $\mathbf{x} = (x_j)$, $\mathbf{b} = (b_i)$, and $\boldsymbol{\varepsilon} = (\varepsilon_i)$ is error. The magnitude of the error depends on experimental error, the quadrature chosen, the size of m , and the size of the interval $[q, \bar{q}]$. Collocation might improve on the error introduced by this simple quadrature, but this representation is adequate.

Suppose that the error $\boldsymbol{\varepsilon}$ in (4) were strictly experimental (stochastic) error. Then, if the distribution is Gaussian, $\boldsymbol{\varepsilon} \sim \mathbf{N}(\mathbf{0}, \Sigma)$, the maximum likelihood solution $\hat{\mathbf{x}}$ to (4) would be obtained by minimizing the sum of squared, scaled residuals

$$\text{Min}_{\mathbf{x}} (\mathbf{Ax} - \mathbf{b})^T \Sigma^{-1} (\mathbf{Ax} - \mathbf{b}).$$

When $m \leq n$ and $A^T \Sigma^{-1} A$ is nonsingular, the solution is given by

$$\hat{\mathbf{x}} = (A^T \Sigma^{-1} A)^{-1} A^T \Sigma^{-1} \mathbf{b}. \tag{5}$$

But such a solution is doomed to failure. For, if one plots \hat{x}_j versus r_j , the plot will almost certainly oscillate wildly between large negative and positive values. This is due to the fact that the matrix A is ill-conditioned. Recall that for different values of q , the pressure profiles $\theta(p, q)$ are similar. Consequently, the columns of A are nearly linearly dependent and $A^T \Sigma^{-1} A$ is very nearly singular. The ill-conditioned character of the algebraic problem (4) reflects the ill-posed character of the physical problem (1).

An improvement on solution (5) can be obtained by constraining the solution to be nonnegative. In this case, the formulation is

$$\text{Min}_x (Ax - b)^T \Sigma^{-1} (Ax - b) \quad \text{such that } x \geq 0.$$

This is an approach advocated by Sacher and Morrison [27]. The solution to the constrained problem, however, is still likely to be fraught with oscillations—in this case between zero and large positive values. Such oscillations are artifacts and again reflect the ill-posedness of the problem of inverting (1). A solution with nonnegative constraints using simulated data appears in Fig. 2; artificial oscillations are present. The solution was calculated using the algorithm NNLS as presented by Lawson and Hanson [21]. The simulated data are described in a subsequent section of this paper.

A survey of numerical methods for linear, discrete ill-posed problems has recently been given by Varah [35]. Regularization as introduced by Tikhonov [31, 32] applies to the inversion of general operator equations and addresses ill-posedness. There are varying implementations of regularization. Hanson [10, 11] and Varah [34] discussed several examples and use the singular value decomposition. In the context of numerical differentiation, the procedure has been discussed by Cullum [5]. Other general discussions include Phillips [24] and Twomey [33]. Application of regularization to adsorption isotherm data was performed by Merz [22]; a summary of this particular implementation follows.

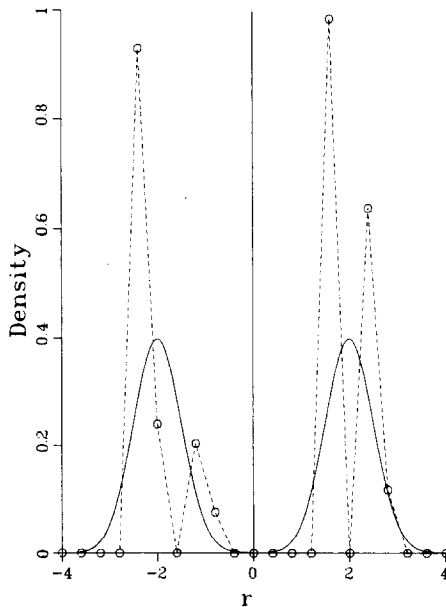


FIG. 2. Comparison of the density computed using the nonnegative least squares algorithm NNLS (dashed line) of Lawson and Hanson [21] with the correct density (solid line) for the simulated data. The oscillations between zero and large positive values are artifacts.

The failure of the least squares solution $\hat{\mathbf{x}}$ given by (5) is that in minimizing the sum of squared residuals, the data are fitted more closely than is warranted. Consequently, $\hat{\mathbf{x}}$ undergoes marked excursions in order to follow the experimental error. The correct \mathbf{x} does not fit the data so closely. Consider the set of candidate solutions which miss the data by a prescribed amount. How does one select a solution from the members of such a set? The final solution should be smooth. Consequently, one chooses the smoothest candidate solution which misses the data by the prescribed amount. A measure of smoothness is provided by the magnitude of the second derivative. More precisely, define a set of vectors X_s by

$$X_s = \{\mathbf{x} \mid A\mathbf{x} = \mathbf{b} + \mathbf{e} \text{ and } \mathbf{e}^T D^{-2} \mathbf{e} = S\},$$

where S is prescribed, $D = \text{diag}(\delta_1, \delta_2, \dots, \delta_n)$, and δ_i is a guess at the standard deviation σ_i of experimental error in measuring $\bar{\theta}(p_i)$. (This tacitly introduces the simplifying assumption that the errors ϵ_i are statistically independent.) The quantity S represents the sum of squared, scaled residual differences. Define a measure of roughness $\|\mathbf{x}\|_2$ for any vector \mathbf{x} by

$$\|\mathbf{x}\|_2^2 = \sum_{j=1}^m (x_{j-1} - 2x_j + x_{j+1})^2,$$

where $x_0 = x_{m+1} = 0$. Then $\|\cdot\|_2$ is a norm on the space R^m . The quantity $\|\mathbf{x}\|_2^2$ is approximately proportional to the sum of squared second derivatives since a typical divided second difference is $(x_{j-1} - 2x_j + x_{j+1})/h^2$. The choice $x_0 = x_{m+1} = 0$ is reasonable since we anticipate that f will be small outside the interval $[q, \bar{q}]$.

A regularized solution to (4) is given by the solution to the constrained minimization problem

$$\text{Min}_{\mathbf{x} \in X_s} \|\mathbf{x}\|_2$$

or

$$\text{Min}_{\mathbf{x}} \|\mathbf{x}\|_2 \quad \text{such that} \quad (\mathbf{b} - A\mathbf{x})^T D^{-2} (\mathbf{b} - A\mathbf{x}) = S. \quad (6)$$

In order to solve problem (6), it suffices to be able to solve the problem

$$\text{Min}_{\mathbf{z}} \mathbf{z}^T \mathbf{z} \quad \text{such that} \quad (\mathbf{c} - B\mathbf{z})^T (\mathbf{c} - B\mathbf{z}) = S. \quad (7)$$

Indeed, if H , B , and \mathbf{c} are defined by

$$H\mathbf{x} = (-2x_1 + x_2, x_1 - 2x_2 + x_3, \dots, x_{m-2} - 2x_{m-1} + x_m, x_{m-1} - 2x_m)^T,$$

$$B = D^{-1}AH^{-1},$$

$$\mathbf{c} = D^{-1}\mathbf{b},$$

then problems (6) and (7) have solutions related by $\mathbf{z} = H\mathbf{x}$.

Different norms can be used. The one chosen above $\|\cdot\|_2$ measures the sum of squared second differences. There are many other possible choices; for instance, the sum of squared first differences or simply the sum of squares (in which case $H = I$). If one minimizes the sum of squared second differences, then for a given S the variation in the slope of the solution \mathbf{x} is minimized. Similarly, if one minimizes the sum of squared first differences, the variation of \mathbf{x} from a constant is minimized; and if one minimizes the sum of squares, the variation of \mathbf{x} from $\mathbf{0}$ is minimized. My experience has indicated that working with second differences is preferable to these other two alternatives on this particular problem.

The formulation of problem (7) using a Lagrange multiplier λ^{-1} is

$$\text{Min}_{\mathbf{z}, \lambda} \mathbf{z}^T \mathbf{z} + \lambda^{-1} [(\mathbf{c} - \mathbf{Bz})^T (\mathbf{c} - \mathbf{Bz}) - S].$$

A necessary condition for a minimum is that the first derivatives vanish, that is,

$$(\mathbf{B}^T \mathbf{B} + \lambda \mathbf{I}) \mathbf{z} = \mathbf{B}^T \mathbf{c} \quad (8)$$

and

$$(\mathbf{c} - \mathbf{Bz})^T (\mathbf{c} - \mathbf{Bz}) = S. \quad (9)$$

The regularized solution is obtained by the simultaneous solution of (8) and (9) for prescribed S . In order to solve this problem, one could generate solutions \mathbf{z} to (8) for various trial values of λ , and then modify λ iteratively until (9) is satisfied.

The solution defined by (8) and (9) depends on S and δ_i . If one knows the standard deviation σ_i of the experimental error, then let $\delta_i = \sigma_i$. If the errors are independent with zero mean, then the expected value of S is n . But one rarely has a good estimate of σ_i . And, even if one does know σ_i exactly, $S = n$ is not always a good choice, since the solution is not robust to changes in S which will assume its expected value with probability zero. What is required is a method to estimate S (or equivalently λ) from the data.

Given this perspective on the problem, one omits (9) and considers the solution to (8) for various values of λ . This approach will not use approximations to σ_i . For example, if uniform weighting of the residuals is deemed appropriate, one can set $\delta_i = 1$. The use of (8) (especially with $H = I$) is also known as ridge regression [12, 13] in statistics; thus, ridge regression can be viewed as a special case of regularization. The literature on ridge regression provides another interpretation to the difficulty inherent in solving (1). The least squares solution to the problem (4) is given by (5). Let \mathcal{E} denote the expected value operator. The Gauss–Markov estimate (5) is well known to be the minimum variance, unbiased estimate when $\mathcal{E}\boldsymbol{\varepsilon} = \mathbf{0}$ and $\mathcal{E}\boldsymbol{\varepsilon}\boldsymbol{\varepsilon}^T = \boldsymbol{\Sigma} = \sigma^2 \mathbf{I}$. The least squares estimation procedure is good when $A^T A$ is nearly a scalar multiple of I . However, if the columns of A are nearly linearly dependent, as they are when A is a discrete, numerical approximation to the operator in (1), then $A^T A$ is badly conditioned and the least squares estimates are unstable. In particular, if $\hat{\mathbf{x}}$ is the estimate of \mathbf{x} as given by (5), $\boldsymbol{\Sigma} = \sigma^2 \mathbf{I}$, and $\mathbf{L} = \mathbf{x} - \hat{\mathbf{x}}$, then it has been shown

[12] that $\mathcal{E}\mathbf{L}^T\mathbf{L} > \sigma^2/\mu$, where μ is the smallest positive eigenvalue of $A^T A$. As the columns of A becomes more nearly linearly dependent, μ becomes smaller and $\hat{\mathbf{x}}$ can be expected to be farther from \mathbf{x} . The regularized or ridge regression solution (8) introduces a bias but may reduce the variance tremendously.

There are two limiting cases of (8), namely, $\lambda = 0$ and $\lambda = \infty$. The case $\lambda = 0$ corresponds to the least squares solution (5) with $\Sigma = D^2$. This solution, when λ is zero or very small, will likely oscillate between large negative and positive values. The limiting case $\lambda = \infty$ has the solution $\mathbf{x} = \mathbf{z} = 0$. What is required is the estimation of the optimum value of λ between these two extremes.

This last obstacle is overcome by the recent technique of generalized cross-validation (GCV) due to Wahba [36], a brief description of which follows. For a given λ , Eq. (8) defines a regularized solution \mathbf{z}_λ which depends on all n data points. Let \mathbf{z}_λ^i denote the regularized solution similarly obtained, but deleting the data point c_i . Then the i th coordinate of the fitted data $(B\mathbf{z}_\lambda^i)_i$ may be used as a predictor of c_i . The mean squared prediction error is given by

$$P(\lambda) = n^{-1} \sum_{i=1}^n ((B\mathbf{z}_\lambda^i)_i - c_i)^2.$$

An ordinary cross-validation solution is the \mathbf{z} satisfying (8) for the λ which minimizes $P(\lambda)$. After some algebraic manipulation, $P(\lambda)$ may be rewritten as

$$P(\lambda) = n^{-1} \|E(M - I)\mathbf{c}\|^2, \tag{10}$$

where

$$M(\lambda) = B(B^T B + \lambda I)^{-1} B^T, \\ E(\lambda) = \text{diag}(1/(1 - M_{ii})),$$

and $\|\cdot\|$ is the Euclidean norm so that $\|\mathbf{a}\|^2 = \mathbf{a}^T \mathbf{a}$ for any $\mathbf{a} \in R^n$. Note that for any λ , the fit to the data is given by $\hat{\mathbf{c}} = M\mathbf{c}$. Thus, the representation (10) exhibits $P(\lambda)$ as a weighted sum of squared residuals, with weights given by $E(\lambda)$. Wahba has shown that there is a rotation of the data coordinate system such that these weights are equal. In the rotated system, $P(\lambda)$ becomes $V(\lambda)$, given by

$$V(\lambda) = \frac{n \|(M - I)\mathbf{c}\|^2}{[\text{Trace}(M - I)]^2}. \tag{11}$$

The GCV solution is the \mathbf{z} which satisfies (8) for the λ which minimizes $V(\lambda)$ in (11).

It would appear from the form of (11) that evaluation of $V(\lambda)$ is prohibitively expensive since for each value of λ it seems necessary to compute $M(\lambda)$. However, the singular value decomposition proves to be an effective means of reducing the complexity of (11). The singular value decomposition of the $n \times m$ matrix B may be written

$$B = U\Delta V^T,$$

where U is an $n \times n$ orthogonal matrix, Δ is an $n \times m$ diagonal matrix whose entries are the square roots of the eigenvalues of $B^T B$, and V is an $m \times m$ orthogonal matrix. Some algebraic manipulation reveals that $V(\lambda)$ in (11) can be rewritten as

$$V(\lambda) = n \sum_{i=1}^n [\lambda d_{ii}/(\lambda + \Delta_{ii}^2)]^2 / \left[\sum_{i=1}^n \lambda/(\lambda + \Delta_{ii}^2) \right]^2,$$

where $\mathbf{d} = (d_1, d_2, \dots, d_n)^T = U^T \mathbf{c}$ and $\Delta_{ii} = 0$ if $i > m$.

Regularization directly confronts the ill-posed character of the integral equation (1). Some technique which deals with the ill-posedness must be used. Otherwise, solutions to (1) will likely include artifacts in the form of excess wiggleness in the estimated density f . Even with regularization, the problem is difficult.

3.2. Numerical Example

A numerical example will be presented to demonstrate the use of regularization. The Langmuir isotherm may be written in the form

$$\theta(p, k) = kp/(1 + kp), \quad (12)$$

$$\alpha(p, r) = p/(p + e^{-r})$$

in the manner of (3). An adsorption isotherm experiment was numerically simulated by generating $n = 41$ values of $\bar{\theta}$ satisfying

$$\bar{\theta}(p_i) = \int_{-\infty}^{\infty} \alpha(p, r) x(r) dr + \varepsilon_i$$

where $\boldsymbol{\varepsilon} = (\varepsilon_i) \sim \mathbf{N}(\mathbf{0}, \sigma^2 I)$ with $\sigma = 0.001$ and

$$x(r) = (2\pi)^{-1/2} [\exp(-2(r+2)^2) + \exp(-2(r-2)^2)]. \quad (13)$$

The pressure values p_i were logarithmically uniformly spaced from $p_1 = 0.01$ to $p_{41} = 100$. It was then attempted to recover the correct density x of Eq. (13) by using regularization and GCV.

Values of r_j were chosen on the interval $[-4, 4]$ with $r_j = -4 + 0.4(j-1)$ ($j = 1, 2, \dots, m = 21$). Then the regularized solution $\mathbf{x} = H^{-1} \mathbf{z}$ satisfying (8) was computed for several values of λ using $\delta_i = 0.001$. (In an actual problem, one might set $\delta_i = 1$. In this case, the choice $\delta_i = \sigma = 0.001$ will enable us to compare $S(\lambda)$ in (9) with n .) A measure of the deviation of the regularized solution from the true density is given by

$$T(\lambda) = \sum_{j=1}^m (x(r_j) - x_j)^2.$$

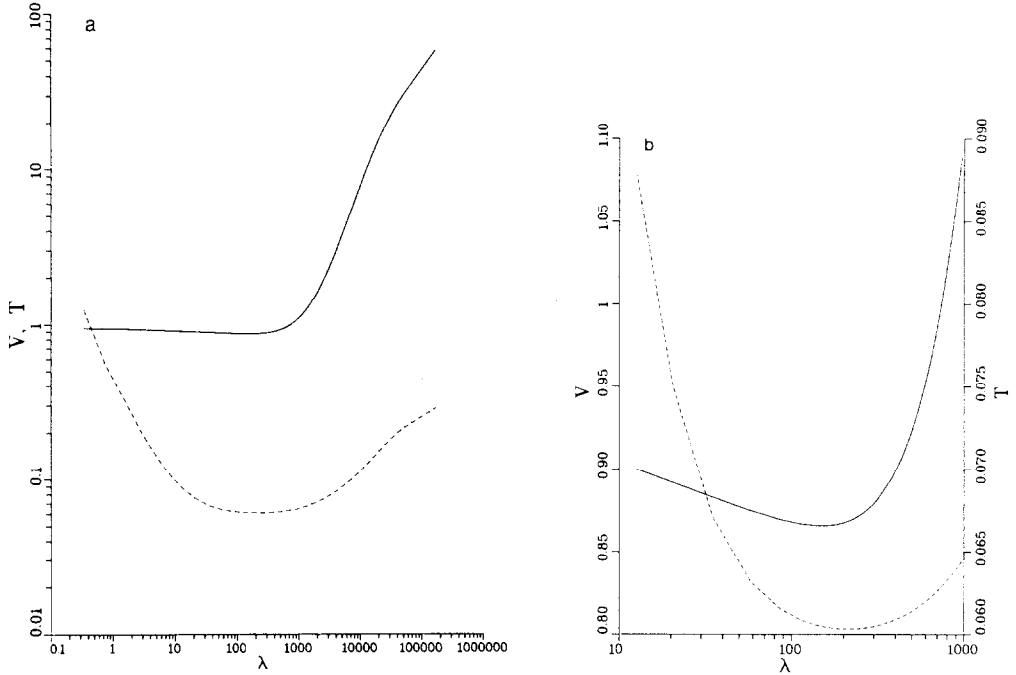


FIG. 3. Comparison of the GCV function $V(\lambda)$ (solid line) with the “true” sum of squared deviations $T(\lambda)$ (dashed line) for the simulated data. (b) λ is restricted to the interval $[10, 1000]$ in order to magnify the behavior in a neighborhood of the minima.

One hopes that the minimizer of $V(\lambda)$ of Eq. (11) also nearly minimizes $T(\lambda)$. In Figs. 3a, b appear plots of both $V(\lambda)$ and $T(\lambda)$. Figure 3b magnifies the portion of Fig. 3a in the neighborhood of the minima of $T(\lambda)$ and $V(\lambda)$. The value of λ which minimizes $T(\lambda)$ occurs at $\lambda_1 \approx 200$ ($S = 25.5$). The value of λ which minimizes $V(\lambda)$ occurs at $\lambda_2 \approx 140$ ($S = 25.0$). The excess of the ratio $T(\lambda_2)/T(\lambda_1)$ over unity is a measure of the inefficiency of GCV as an estimate of the optimum value for the parameter λ . For these particular data, $T(\lambda_2)/T(\lambda_1) = 1.004$, which is quite good. The value of λ corresponding to $S = n = 41$ is $\lambda_3 \approx 1500$. Since $T(\lambda_3)/T(\lambda_1) = 1.12$, this estimate λ_3 of λ is inferior to the GCV estimate λ_2 .

In Figs. 4a–c are plots of regularized solutions of (8) for selected values of λ . These figures demonstrate that a proper choice of λ is critical. Figure 4a illustrates the regularized solution for $\lambda = 0.0029$ ($S = 18$); it bears no resemblance to the correct solution. The solution of (8) for $\lambda = 0$ is the solution (5) (the least squares solution) with $\Sigma = D^2$; it is, of course, even worse than the solution depicted in Fig. 4a. Figure 4b illustrates the GCV solution for $\lambda = 140$ ($S = 25$). Finally, Fig. 4c illustrates the regularized solution for the extreme value $\lambda = 50,000$ ($S = 1000$); in this case, the smoothing is too great.

Occasionally, the GCV method does not locate a proper value for λ . Extensive simulations have been performed by Wahba [37], by Golub *et al.* [9], and by Merz;

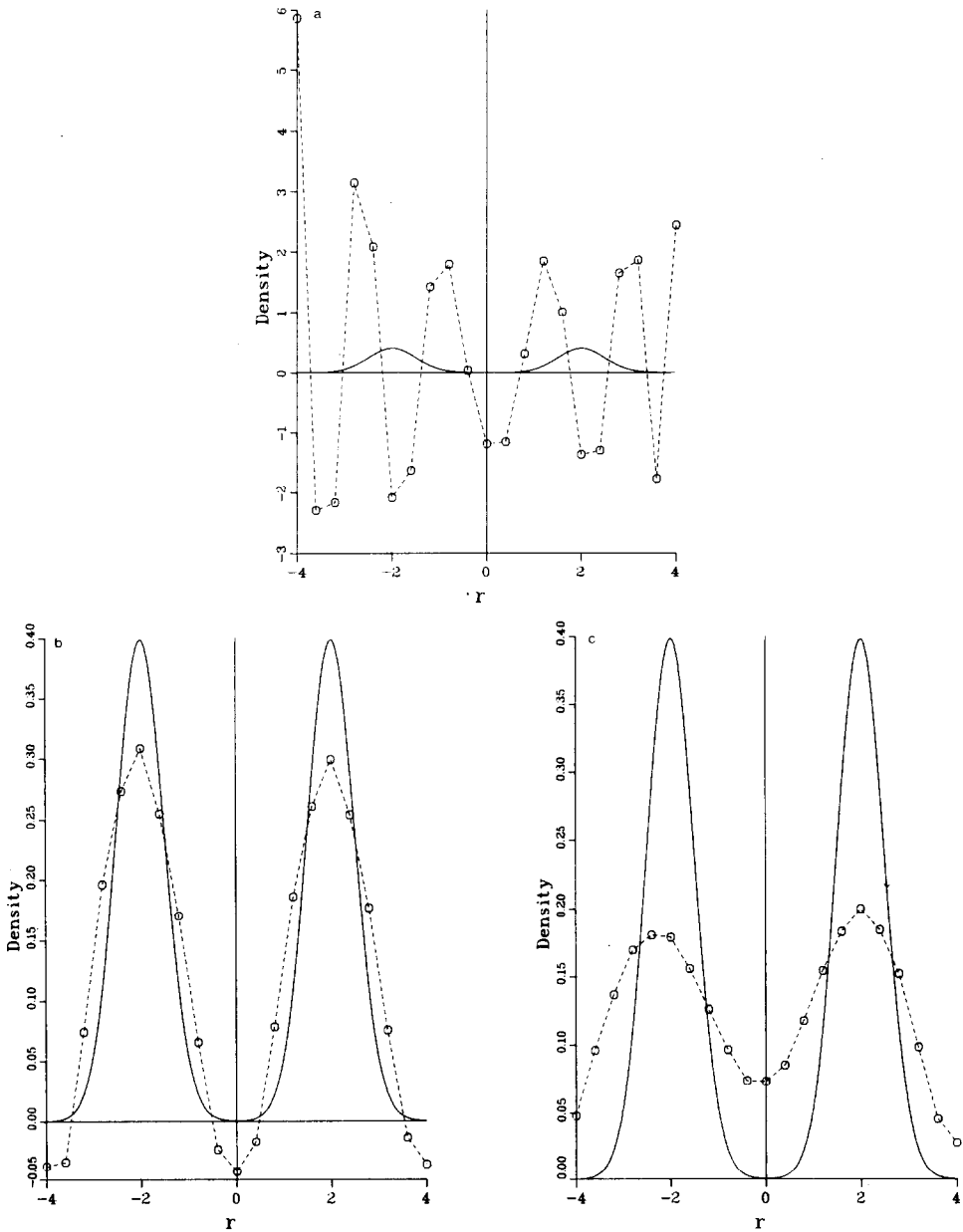


FIG. 4. Comparison of the density computed using regularization (dashed line) with the correct density (solid line) for the simulated data. (a) Regularized solution for $\lambda \approx 2.9 \times 10^{-3}$ ($S = 18$); this value of λ is too small, and is manifested as excessive oscillations. (b) Regularized solution for $\lambda \approx 140$ ($S = 25$); this is the value of λ determined by the GCV criterion of minimizing $V(\lambda)$. (c) Regularized solution for $\lambda \approx 5.0 \times 10^4$ ($S = 1000$); this value of λ is too large, and is manifested as excessive smoothness. These plots demonstrate that the choice of λ is critical, and that GCV is an effective means for a proper choice.

the results indicate that the method is, on the whole, reliable. On occasion, but infrequently, the GCV function $V(\lambda)$ has multiple local minima. Then there is again uncertainty over which value of λ to choose; indeed, in simulations which I have performed, the choice of the global minimizer of $V(\lambda)$ is sometimes an inferior choice.

One would anticipate, looking at Fig. 4b, that further improvement could be made by incorporating nonnegativity constraints with regularization and GCV. To my knowledge, such a procedure is not currently available.

An important characterization of catalysts is the total number of adsorbing sites, i.e., $\int_0^\infty f(q) dq$. In the event that this cumulative number is all which it is desired to estimate, then the most sophisticated estimate of f is probably not required. Clearly, of the four estimates of the density x given by Figs. 2 and 4a-c, by pointwise measure the estimate given by Fig. 4b is substantially better than the others. The density x was constructed such that $\int_{-\infty}^\infty x(r) dr = 1$. The areas calculated under the fitted curves in Figs. 2 and 4a-c using a simple quadrature (Simpson's rule) are 1.00, 1.02, 1.00, and 1.02, respectively. Thus, for the simulated data set, any of these estimates of the cumulative number of sites would be approximately correct.

4. CONCAVITY CRITERION

Regularization was applied to solve (1) using a Langmuir isotherm as kernel for the pyridine adsorption data of Table I. Regardless of the value of λ (or S) used, the density f so estimated would assume unacceptably large negative values. It will be shown that although the data profile in Fig. 1 appears Langmuir-like, this cannot be the correct model. A concavity criterion will be stated which is a necessary condition if the model is Langmuirian; but the data of Fig. 1 violate this condition.

The concavity criterion is stated as follows: if a plot of p/θ versus p is concave down at some pressure and for all heats of adsorption (i.e., $\partial^2(p/\theta)/\partial p^2 \leq 0$), then $p/\bar{\theta}$ versus p is concave down at that pressure (i.e., $d^2(p/\bar{\theta})/dp^2 \leq 0$). The criterion is proved in the Appendix.

For the Langmuir isotherm of (12), we have that $p/\theta = p + 1/k$ and $\partial^2(p/\theta)/\partial p^2 = 0$. Consequently, if the Langmuir model is correct for the pyridine adsorption data, it must be that $d^2(p/\bar{\theta})/dp^2 \leq 0$. A plot of $p/\bar{\theta}$ versus p for the pyridine data appears in Fig. 5. Clearly, the criterion is violated. Furthermore, the departure from the model occurs in the mid-pressure range; the departure is not a low pressure or high pressure model error. Therefore, the operator in (1) with Langmuir kernel and restricted domain of nonnegative functions f does not have the pyridine data in its range.

The pyridine data only slowly approach constant (full) coverage; perhaps multilayer coverage is required to explain these data. One model which allows for multiple layers is the BET isotherm [3] which can be written in the form

$$\theta(p, q) = \theta_0 \frac{cp}{(p_0 - p)[1 + (c - 1)p/p_0]}, \quad (14)$$

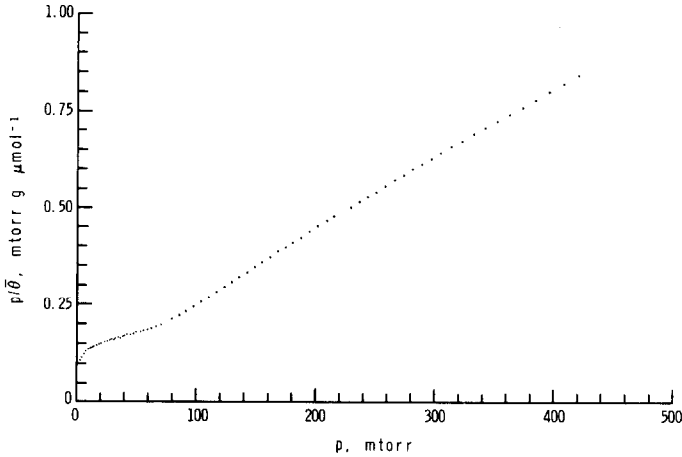


FIG. 5. Plot of $p/\bar{\theta}$ for the pyridine adsorption data. Note the concavity: for small p , concave down; for intermediate p , concave up; for large p , concave down. It follows from the concavity criterion that the unisorptic isotherm for this data cannot be either Langmuir or BET since a portion of the curve is concave up.

where p_0 is the adsorbate saturation pressure, θ_0 is the number of adsorbing sites, and $c = c(q) = \tau_1(q)/\tau_2$, where τ_1 is the mean time of adsorption of molecules bound directly to the surface and τ_2 is the mean time of adsorption of molecules not in the first layer. It is plausible that molecules which are directly bound to the surface are bound more strongly than molecules in higher layers. Consequently, one expects $\tau_1 \geq \tau_2$ and $c \geq 1$. The BET isotherm (14) can be rewritten as

$$p/\theta = [p_0 + p(c - 2) - p^2(c - 1)/p_0]/\theta_0 c.$$

Differentiation gives

$$\partial^2(p/\theta)/\partial p^2 = -2(c - 1)/\theta_0 p_0 c.$$

If $f(q) = 0$ for $c < 1$, the criterion applies. Thus, the BET isotherm is also inappropriate for the pyridine data.

At this juncture, it is obvious that the concavity criterion is only a necessary condition for the kernel in (1) to be Langmuirian. The criterion is not also a sufficient condition, i.e., the criterion does not uniquely characterize a particular kernel; indeed, if the data satisfy $d^2(p/\bar{\theta})/dp^2 \leq 0$ and (1) is the correct model for some θ , then (on the basis of the criterion) both the Langmuir and BET isotherms qualify as θ . Furthermore, if there are data such that $d^2(p/\bar{\theta})/dp^2 \leq 0$ for all $p > 0$, it does not even follow that $f \geq 0$. A counterexample is given by

$$\bar{\theta} = \sum_{i=1}^3 f_i k_i p / (1 + k_i p), \quad (15)$$

where

$$\begin{aligned}
 f_1 &= 10/19, & f_2 &= -1/19, & f_3 &= 10/19, \\
 k_1 &= 0.1, & k_2 &= 1, & k_3 &= 10.
 \end{aligned}$$

Plots of this function appear in Figs. 6a–c.

Both the Langmuir and BET isotherms assume fixed adsorption sites (immobile film) and no interaction between adsorbed molecules on different sites. The Fowler–Guggenheim isotherm [8] assumes an immobile film but allows for interaction between adsorbed molecules; it can be written in the form

$$k(q)p = \frac{\theta}{1 - \theta} e^{-\alpha\theta}, \tag{16}$$

where α is a parameter which is independent of the heat of adsorption. The

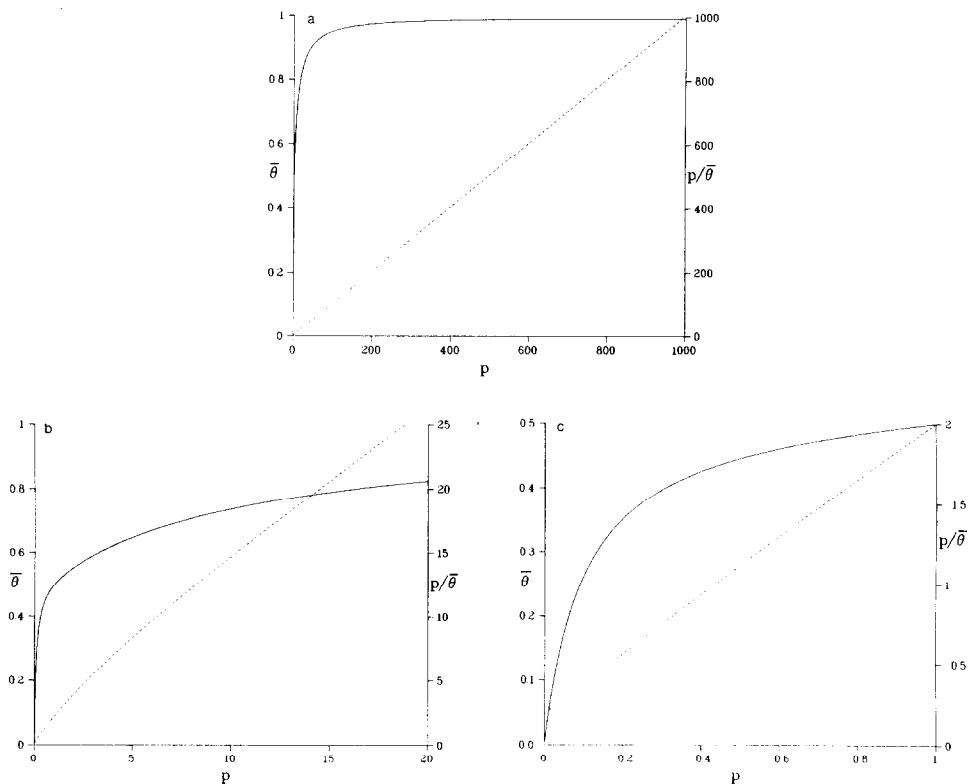


FIG. 6. Plots of $\bar{\theta}$ (solid line) and $p/\bar{\theta}$ (dashed line) for $\bar{\theta}$ of Eq. (15). In (b) and (c), p is restricted to smaller intervals in order to magnify the behavior of $p/\bar{\theta}$. Note that $d^2(p/\bar{\theta})/dp^2 \leq 0$ for all $p > 0$. This function $\bar{\theta}$ in (15) was constructed in order to demonstrate that data can satisfy the concavity criterion and yet not be in the range of the integral operator (1) with (say) Langmuir kernel and domain of nonnegative densities f .

Hill-de Boer isotherm [6] permits the film to be mobile and also allows for interaction between adsorbed molecules; it can be written as

$$k(q)p = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \beta\theta\right), \quad (17)$$

where β is independent of q . Each of these two isotherms models monolayer coverage.

The function $\theta(p, q)$ in each of (16) and (17) is defined implicitly. Differentiation reveals that $\partial^2(p/\theta)/\partial p^2$ can be negative or positive depending on q (for given α or β). The theorem does not apply, but the concavity idea is still useful. Extensive numerical simulations were performed using these two isotherms (16) and (17) as kernels and various trial density functions $f(q)$. In no case did the result mimic the behavior of Fig. 5: when $p/\bar{\theta}$ versus p is plotted, for small p the curve should be concave down, for intermediate p concave up, and for large p concave down again. In all simulations performed, at most one inflection point was found in a plot of $p/\bar{\theta}$ versus p . It does not appear that either the Fowler-Guggenheim or Hill-de Boer isotherms apply to the pyridine data.

Although our original intention (1972) was to fit adsorption isotherm data, the purpose of exhibiting this pyridine adsorption data is to focus attention on the nonconformance of the data with particular isotherms (Langmuir and BET) despite ostensible conformance and despite plausible arguments that the models should be correct. One can use a Langmuir or BET unisorptic isotherm as kernel in the integral equation (1) and solve for the distribution of adsorption energies. But the result will be a function which assumes unacceptably large negative values since the concavity criterion stated in the theorem is violated. One might then reason that the kernel is almost correct (which is not true if one is to judge from Fig. 5); and, therefore, a nearly correct solution is obtainable by performing the fit while constraining the distribution function to be nonnegative. However, that almost certainly will not result in a close approximation to the correct distribution function but rather one which is markedly wrong. Because, recall that the inversion of the integral equation (1) is an ill-posed problem. Consequently, a small error in the data (or, equivalently, a small error in the model) will result in a large error in the determined distribution function. If the model (kernel) is incorrect, then forcing the density function to be nonnegative will result in a density function which is alternately large and zero, in the manner of Fig. 2, but worse. In fact, if the kernel is incorrect, then even the least squares estimate \hat{x} given by (5) is biased. Furthermore, if a data set does conform with the concavity criterion, that alone does not constitute proof that the correct unisorptic isotherm is Langmuir or BET. The criterion is a necessary condition, not a sufficient condition.

5. CONCLUSIONS

Emphasis in this paper has been placed on two distinct aspects of the determination of adsorption energy distributions from adsorption isotherm experiments. The

first aspect is ill-posedness; the second aspect concerns the errors which result if the model is inadequate and the difficulty of determining whether or not the model is adequate.

The mathematical problem of inverting the integral equation (1) is ill-posed; that is, the solution is not a continuous function of the data. Consequently, a small perturbation in the data $\bar{\theta}$ (or small perturbation in the kernel θ) will almost certainly result in a substantial alteration in the solution f . Solutions to (1) which do not account for ill-posedness typically are spiky and not smooth in the manner of Figs. 2 and 4a. It is necessary to solve the problem (1) with a technique which confronts the ill-posedness; Tikhonov regularization is such a technique. Regularization introduces a parameter λ and provides a one-parameter family of solutions which vary from being spiky for small λ to excessively smooth for large λ . A good selection for the value of λ can be made using the technique of generalized cross-validation (GCV). Regularization in conjunction with GCV has shown to be an effective method of solving the integral equation (1). Presumably, a further improvement would result if regularization with GCV were combined with nonnegativity constraints.

More insidious than ill-posedness is model inadequacy. It seems that some of the kernels used in (1) in modeling efforts in the literature have been developed by postulation without testing. The pyridine adsorption data and concavity criterion exemplify the difficulty of determining model validity. The pyridine data cannot be explained by the model (1) with a Langmuir kernel, despite ostensible conformance with that model, since the concavity criterion is violated. That the integral equation model (1) is correct for particular sets of data is equivalent to the statement that the data $\bar{\theta}$ lie in the range of the operator equation (1) with kernel θ and domain of nonnegative, integrable functions f . But whether or not the data are in the range of the operator equation is, in general, very difficult to ascertain. The concavity criterion is a necessary condition, not a sufficient condition. If a set of adsorption data does conform with the concavity criterion, that does not demonstrate model validity using, say, a Langmuir unisorptic isotherm.

Potential and obscured model inadequacy combined with ill-posedness constitute severe obstacles to the determination of adsorption energy distributions from adsorption isotherm experiments. Research is required on two fronts: (1) experimental work to characterize the mechanism of adsorption and hence the correct kernel θ , and (2) mathematical work to enable the inference of the kernel θ from data sets $\bar{\theta}$.

APPENDIX

The following theorem establishes that if $\partial^2(1/\theta)/\partial(1/p)^2 \leq 0$, then $d^2(1/\bar{\theta})/d(1/p)^2 \leq 0$. The concavity criterion stated previously is that if $\partial^2(p/\theta)/\partial p^2 \leq 0$, then $d^2(p/\bar{\theta})/dp^2 \leq 0$. Equivalence between the theorem and criterion follows immediately from the observation that for any function $y (= 1/\theta)$, differentiation gives

$$p^{-3} d^2y/d(1/p)^2 = 2dy/dp + p d^2y/dp^2 = d^2(py)/dp^2.$$

Thus, the two second derivatives, $d^2y/d(1/p)^2$ and $d^2(py)/dp^2$, have the same sign for all $p > 0$.

THEOREM. For $p > 0$, $q > 0$, let

$$f(q) \geq 0$$

be a density for q ,

$$\theta(p, q) \geq 0,$$

$$\bar{\theta}(p) = \int_0^{\infty} \theta(p, q) f(q) dq,$$

$$\psi(s) = \theta(1/s, q),$$

$$\bar{\psi}(s) = \int_0^{\infty} \psi(s, q) f(q) dq,$$

$$\phi(s, q) = 1/\psi(s, q),$$

$$\bar{\phi}(s) = 1/\bar{\psi}(s).$$

If

$$\frac{\partial^2 \phi}{\partial s^2} \leq 0 \tag{18}$$

for all q such that $f(q) > 0$, then

$$\frac{d^2 \bar{\phi}}{ds^2} \leq 0 \tag{19}$$

whenever

$$\frac{d\bar{\psi}}{ds} = \int_0^{\infty} \frac{\partial \psi}{\partial s} f(q) dq$$

and

$$\frac{d^2 \bar{\psi}}{ds^2} = \int_0^{\infty} \frac{\partial^2 \psi}{\partial s^2} f(q) dq,$$

i.e., whenever differentiation under the integral sign is permitted.

Remarks. The proof of the theorem will be given after the following remarks. If there is a finite number of energies of adsorption, the integrals may be replaced by sums and the qualifications regarding differentiation under the integral sign are automatically satisfied. Also, if the energies of adsorption range only over a finite interval $[q, \bar{q}]$, then $f(q) = 0$ for $q \notin [q, \bar{q}]$. In either case, there is no loss of generality. Henceforth, the limits of integration are deleted.

The Langmuir isotherm of (12) in the notation of the theorem becomes $\phi(s, k(q)) = 1 + s/k$; that is, reciprocal coverage ϕ plots as a straight line against reciprocal pressure s with intercept 1 and slope $1/k$. Hypothesis (17) of the theorem is satisfied since $\partial^2\phi/\partial s^2 = 0$. The result that $d^2\bar{\phi}/ds^2 \leq 0$ is plausible. If there is only one k , then the slope $d\bar{\phi}/ds$ is a constant $1/k$. For a heterogeneous surface, $d\bar{\phi}/ds$ conveys averaged information regarding which sites are adsorbing at pressure $1/s$. At higher pressures (smaller s), the weaker sites (larger $1/k$) are adsorbing more than at lower pressures. Thus, one expects $d\bar{\phi}/ds$, like $1/k$, to increase with decreasing s ; that is, $d^2\bar{\phi}/ds^2 \leq 0$.

Proof of Theorem. Since $\phi = 1/\psi$, we have that

$$\partial^2\phi/\partial s^2 = -[\psi \partial^2\psi/\partial s^2 - 2(\partial\psi/\partial s)^2]/\psi^3 \leq 0. \tag{20}$$

Consequently, the numerator is nonnegative,

$$\psi \partial^2\psi/\partial s^2 - 2(\partial\psi/\partial s)^2 \geq 0. \tag{21}$$

In order to prove (19), evaluate $d^2\bar{\phi}/ds^2$. The resultant expression parallels (20) with each “ ψ ” replaced by “ $\bar{\psi}$ ”. So it suffices to prove that

$$I = \bar{\psi} d^2\bar{\psi}/ds^2 - 2(d\bar{\psi}/ds)^2 \geq 0. \tag{22}$$

Adopt the abbreviated notation

$$\begin{aligned} \psi_i &= \psi(s, q_i), \\ f_i &= f(q_i), \\ \psi'_i &= \partial\psi_i/\partial s, \\ \psi''_i &= \partial^2\psi_i/\partial s^2, \end{aligned} \tag{i = 1, 2}$$

where q_1 and q_2 are any two variables. Then

$$I = \int \psi_1 f_1 dq_1 \int \psi''_2 f_2 dq_2 - 2 \int \psi'_1 f_1 dq_1 \int \psi'_2 f_2 dq_2$$

or

$$I = \iint (\psi_1\psi''_2 - 2\psi'_1\psi'_2) f_1 f_2 dq_1 dq_2. \tag{23}$$

Interchanging the subscripts on the dummy variables q_1 and q_2 results in an expression similar to (23) for I ; adding them gives

$$2I = \iint (\psi_1\psi''_2 + \psi_2\psi''_1 - 4\psi'_1\psi'_2) f_1 f_2 dq_1 dq_2. \tag{24}$$

It suffices to show that the quantity in parentheses is nonnegative, i.e.,

$$\psi_1\psi_2'' + \psi_2\psi_1'' - 4\psi_1'\psi_2' \geq 0, \quad (25)$$

whenever $f'(q_1) > 0$ and $f'(q_2) > 0$. From (21) it follows that

$$\left(\frac{\psi_i'}{\psi_i}\right)^2 \leq \frac{1}{2} \frac{\psi_i''}{\psi_i} \quad (i = 1, 2). \quad (26)$$

Then

$$\begin{aligned} \frac{\psi_1'}{\psi_1} \frac{\psi_2'}{\psi_2} &= \left[\left(\frac{\psi_1'}{\psi_1}\right)^2 \left(\frac{\psi_2'}{\psi_2}\right)^2 \right]^{1/2} \\ &\leq \frac{1}{2} \left[\left(\frac{\psi_1'}{\psi_1}\right)^2 + \left(\frac{\psi_2'}{\psi_2}\right)^2 \right] \\ &\leq \frac{1}{4} \left[\frac{\psi_1''}{\psi_1} + \frac{\psi_2''}{\psi_2} \right] \end{aligned} \quad (27)$$

since the geometric mean is not greater than the arithmetic mean and by the use of (26). Multiplying (27) through by $4\psi_1\psi_2$ yields inequality (25) and completes the proof.

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