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FROM ADSORPTION ISOTHERMS

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OPTIMAL SMOOTHING OF SITE-ENERGY DISTRIBUTIONS FROM ADSORPTION ISOTHERMS

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ABSTRACT

The equation for the adsorption isotherm on a heterogeneous surface is a Fredholm integral equation. In solving it for the site-energy distribution (SED), some sort of smoothing must be carried out. The optimal amount of smoothing will give the most information that is possible without introducing nonexistent structure into the SED. Recently, Butler, Reeds, and Dawson (1) proposed a criterion (the BRD criterion) for choosing the optimal smoothing parameter when using regularization to solve Fredholm equations. The BRD criterion is tested for its suitability in obtaining optimal SED's. This criterion is found to be too conservative. While using it never introduces nonexistent structure into the SED, significant information is often lost. At present, no simple criterion for choosing the optimal smoothing parameter exists, and a modeling approach is recommended.

INTRODUCTION

Single-energy adsorption isotherms, $\theta(p,q)$, such as the Langmuir and Hill-de Boer relationships, normally cannot model experimental isotherms adequately. This has been recognized from the earliest studies of adsorption, and so the heterogeneous nature of an adsorbent or catalytic surface long has been perceived as an important property. The usual equation for the nonuniform-surface adsorption isotherm, relating the amount adsorbed to the pressures and energies of adsorption, has embodied within it both a single-energy adsorption isotherm (local isotherm) and an energy distribution function $\eta(q)$:

$$\theta_{gr}(p) = \int_{q_{min}}^{q_{max}} \theta(p,q)\eta(q)dq \quad (1)$$

The function $\eta(q)dq$ is defined as the fraction of adsorption sites with energies between q and $q + dq$; $\eta(q)$ is called the site-energy distribution (SED) and has been the principal choice as a device to quantify the heterogeneity of an adsorbent's surface. Beginning with the work of Roginsky (2) almost forty years ago, studies in a continuing stream have examined means of extracting $\eta(q)$ from adsorption isotherms and analyzed the implications of the resulting distributions. Reviews of these efforts (3-5) show the extent of these investigations.

Equation (1) is a first-kind Fredholm integral equation. Because of properties inherent in this equation, some form of smoothing must be carried out before an acceptable solution is obtained (e.g., 6).

Sometimes the experimental isotherm data are smoothed, as when the data are approximated by an analytic function (e.g., 5,7). Other times the solution is smoothed, as in the regularization method for solving first-kind Fredholm equations (cf. 8). Sometimes both data and solution are smoothed (e.g., 3,9).

The smoothing is necessary to prevent nonexistent structure from being introduced into the solution of Eq. (1). An example is presented in Fig. 1. Here a unimodal, gaussian SED was postulated and used with a Langmuir local isotherm to generate an isotherm. Random errors with a standard deviation of 1% were imposed on the isotherm data, and regularization was used to extract the SED. A low amount of solution smoothing created the structured SED, while the best agreement between the postulated and

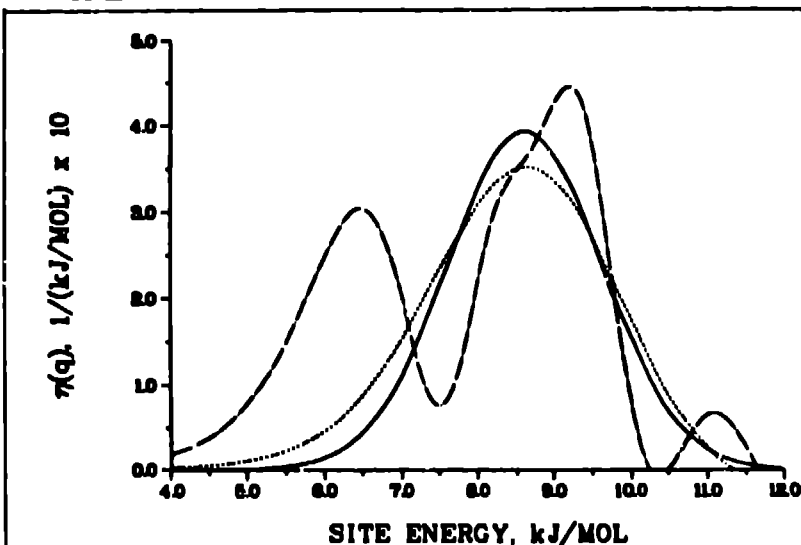


Figure 1. Creation of Nonexistent Structure by Inadequate Smoothing. 1% RMS Error in Isotherm Data.

- Postulated Distribution.
- - - $\alpha = \alpha_{LS}$. Calculated Distribution with Minimum Least-Squares-of-Differences between Original Isotherm and Isotherms from All Calc. Distributions.
- $\alpha_{opt} = 1000\alpha_{LS}$. Calculated Distribution Closest to Postulated Distrib.

calculated SED required a much greater amount of smoothing. This was true even though the least squares criterion, i.e., the minimum of the sums of the squared differences between the generated isotherm data and the isotherms calculated using the extracted SED's, said that the structured SED was the best possible. Thus such a least squares criterion can be a very poor guide to the optimal smoothing. Some other direction is needed to tell what amount of smoothing will give the maximum amount of information concerning the structure of the SED without introducing nonexistent components.

While significant smoothing is needed, too much smoothing obviously can destroy information in the original data. Our purpose is to examine quantitatively this aspect of obtaining SED's from isotherms, and to propose some guidelines for telling how much smoothing is optimal for a level of error in the isotherm data.

Another factor which has the potential of affecting the solution $\eta(q)$ is the choice of local isotherm $\theta(p,q)$ in Eq. (1). We do not examine this factor here. There has been work in this area (e.g., 9), and these efforts indicate that using different, though still reasonable, local isotherms results in qualitatively similar SED's.

Since the particular local isotherm $\theta(p,q)$ does not appear to be a crucial factor in the SED which results from solving Eq. (1), the Langmuir isotherm appears throughout this work; it is the simplest single-energy isotherm which also is physically reasonable.

PRELIMINARY CONSIDERATIONS

The technique of regularization, developed by Phillips (6), Twomey (10), and Tikhonov (8,11-12), is used throughout the present work. Papenhuijzen and Koopal (13) recently have shown that regularization is a superior method for extracting SED's from adsorption isotherms. We employ the formulation of Tikhonov, as it has been found to lead to a straightforward method for solving Eq. (1) numerically. In addition, work by Butler et al. (1) has built upon the Tikhonov formulation to incorporate a nonnegativity constraint upon $\pi(q)$. These latter investigators also proposed a criterion for an optimal value of the regularization smoothing parameter, α . We use the additions proposed by Butler and his coworkers, and the algorithm employed for this work is presented in Appendix A. As was mentioned above, either the data or the solution, or both, must be smoothed in the process of solving Eq. (1). The present work examines directly only the effects of smoothing the solution; it is felt, however, that some of the results may be applicable to situations where instead the data are smoothed.

In spite of the long-recognized need for smoothing of data or solution when obtaining SED's by solving Eq. (1), until very recently no quantitative guideline had been proposed for judging when the optimal amount of smoothing has been carried out. As mentioned above, Butler et al. (1) proposed such a criterion for use with regularization. Their optimal α was supposed to smooth the calculated distribution so as to give the most probable distribution for the existing level of error in the data. They pointed out that their guideline was probably a conservative one, in that it might give some degree of oversmoothing. Our algorithm for implementing the BRD (Butler, Reeds, and Dawson) criterion is included in Appendix A.

In a recent work (14), we calculated isotherms from postulated $\eta(q)$'s, then used regularization to determine the SED using Eq. (1) and the generated isotherm data. Good agreements between postulated and calculated unimodal and bimodal SED's were obtained, and our results suggested that the best agreement between postulated and calculated SED's could be found at an α -value one-tenth that generated by the BRD criterion. In this paper we investigate the optimal smoothing matter more extensively. Amount of error, characteristics of the peaks in the SED, and number and location of data points appear to be aspects which may affect the optimal smoothing.

APPROACH TO PROBLEM

To study the effects of different factors upon the optimal degree of smoothing, a numerical approach was taken. Different situations, each containing characteristics typical of experimental possibilities, were examined. In each situation an SED containing particular properties was postulated, a series of pressures chosen, and Eq. (1) used to generate a vector of accurate isotherm data. Seven significant figures were retained in each of the isotherm points. Random, normally

distributed errors, with a specified standard deviation, were then imposed upon the individual points of the generated isotherm. Using the modified isotherm containing the error, regularization was employed to extract a series of calculated SED's, each SED corresponding to a different value of the smoothing parameter α . The best value of α by the BRD criterion, α_{BRD} , was identified.

Trial and error found the optimal value of α . Visual comparison was used to identify the best α , as it was difficult to create analytical criteria which would be satisfactory. Usually, the optimal value of α occurred at the point just before nonexistent structure began to appear in the solution. Once the optimal value of α was found, it was compared with α_{BRD} to see if any consistency occurred. The comparison between α_{opt} and α_{BRD} was also used to see if information was lost using α_{BRD} which otherwise could be extracted without creating nonexistent structure.

RESULTS

The results are in Figs. 2-5, and the parameters used, distributions employed, and ranges covered are presented in Appendix B.

Figure 2 shows the results with a 2-peaked SED and a 1% RMS error. Here the α of the BRD criterion gives a solution with the two peaks, but the solution does not indicate the heights at all well. It is possible, however, to match the peaks quite well by using a more sensitive smoothing parameter. This indicates some loss of information if α_{BRD} is used.

It may be noted that the optimal value of α in the 2-peaked, 1% error situation is equal to $0.05\alpha_{BRD}$, while

in the 1-peaked, 1% error situation (Fig. 1) it is equal to $0.2\alpha_{BRD}$. This indicates that there may be little consistency between the optimal α and the BRD α , although the optimal α does appear to be always less than α_{BRD} .

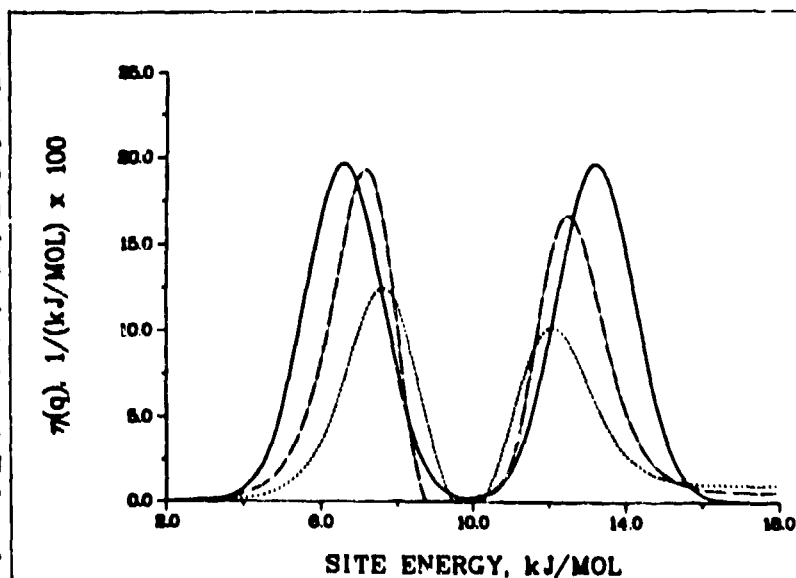


Figure 2. Comparison between Distributions from Optimal α and α_{BRD} . Two-Peaked SED, 1% RMS Error in 51-Point Isotherm.

————— Postulated Distribution.
 Calculated Distribution Using α_{BRD} .
 - · - · - · Calculated Optimal Distribution,
 $\alpha_{opt} = 0.05\alpha_{BRD}$.

In Fig. 3, error in the data is tripled over that in Fig. 2; other factors remain the same. With the higher level of error, use of α_{BRD} destroys the nature of the distribution. Only the approximate range of the distribution is maintained. The optimal calculated distribution does give a good representation of the original SED, although the height is attenuated significantly with the increased error. In this case, $\alpha_{opt} = 0.006\alpha_{BRD}$, confirming the inconsistencies between α_{opt} and α_{BRD} .

Figure 4 presents a 4-peaked distribution. This distribution was so sensitive to error in the data that an error level of 0.01% RMS deviation was necessary to obtain significant results; higher levels of error resulted in distributions that did not reflect the distribution with any realism whatsoever. Even at this level of error, though, important information is lost if α_{BRD} is used as the smoothing parameter. When

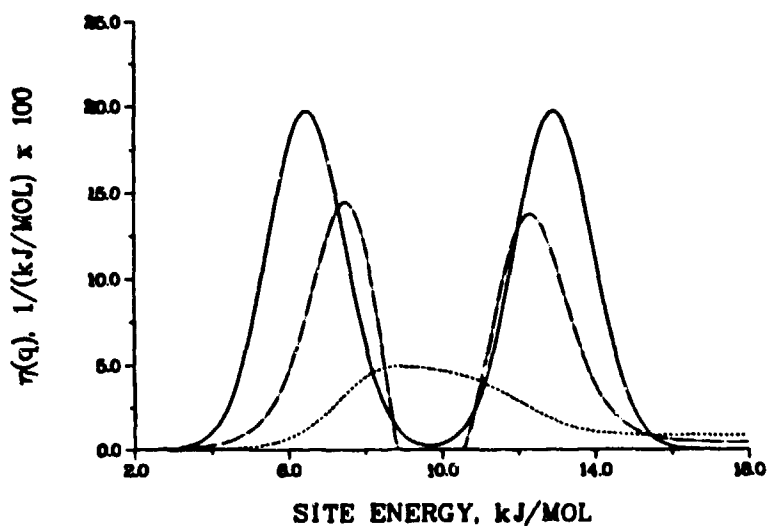


Figure 3. Comparison between Distributions from Optimal α and α_{BRD} . Two-Peaked SED, 3% RMS Error in 51-Point Isotherm.

— Postulated Distribution.
 - - - - - Calculated Distribution Using α_{BRD} .
 - · - · - · Calculated Optimal Distribution,
 $\alpha_{opt} = 0.006\alpha_{BRD}$.

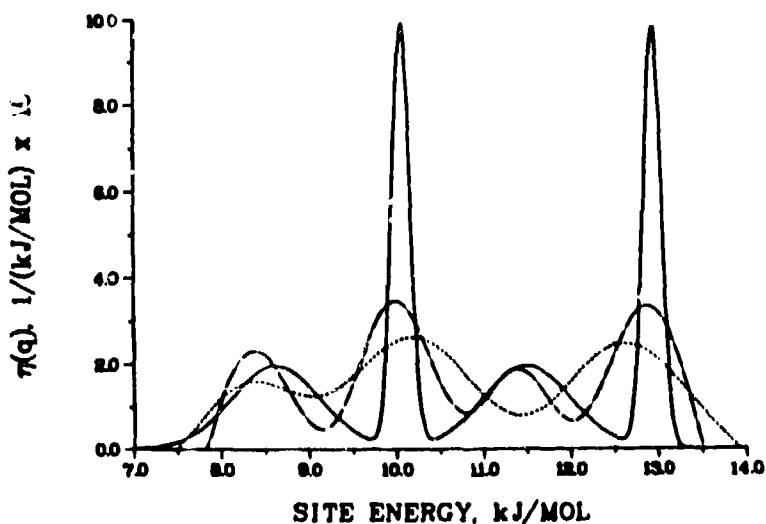


Figure 4. Comparison between Distributions from Optimal α and α_{BRD} . Four-Peaked SED, 0.01% RMS Error in 51-Point Isotherm.

— Postulated Distribution.
 - - - - - Calculated Distribution Using α_{BRD} .
 - · - · - · Calculated Optimal Distribution,
 $\alpha_{opt} = 0.006\alpha_{BRD}$.

this is done, only three peaks appear in the resulting distribution, while the optimal SED gives the four peaks. The results reflect the true situation only qualitatively; the true nature of the peaks remains obscured even by this low level of error. Again, the optimal value of the smoothing parameter is far removed from that resulting from the BRD criterion.

A comparison of Figs. 4 and 5 shows the importance of the number of points in the isotherm. Figure 5 results from using one-third the number of points that were used in Fig. 4. The points were spread over the same range, yet one of the peaks has been lost. Here there is little difference in the distributions from α_{BRD} and α_{opt} .

DISCUSSION AND CONCLUSIONS

Butler et al. said that their criterion was a conservative one. When extracting SED's from adsorption isotherms, it is too conservative. Nonexistent structure never appears when using α_{BRD} , but significant information loss occurs frequently.

No other simple criterion now exists for choosing the optimal value of the smoothing parameter. Nevertheless, it is important that a guide to optimum smoothing be available. Otherwise, nonexistent structure may be reported if too low an α is used. One way of approaching this difficulty is to carry out numerical calculations in conjunction with the experimental studies. SED's can be postulated with characteristics similar to that calculated, and isotherms generated with the level of error imposed on the data equal to that estimated for the experiments being carried out. The optimal α may then be found by trial and error, as was done for the synthetic situations analyzed here. This may give a reasonable estimate of α_{opt} for a particular situation, albeit with significant effort.

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The suggestions and comments of Professor John L. Falconer of the University of Colorado were very helpful.

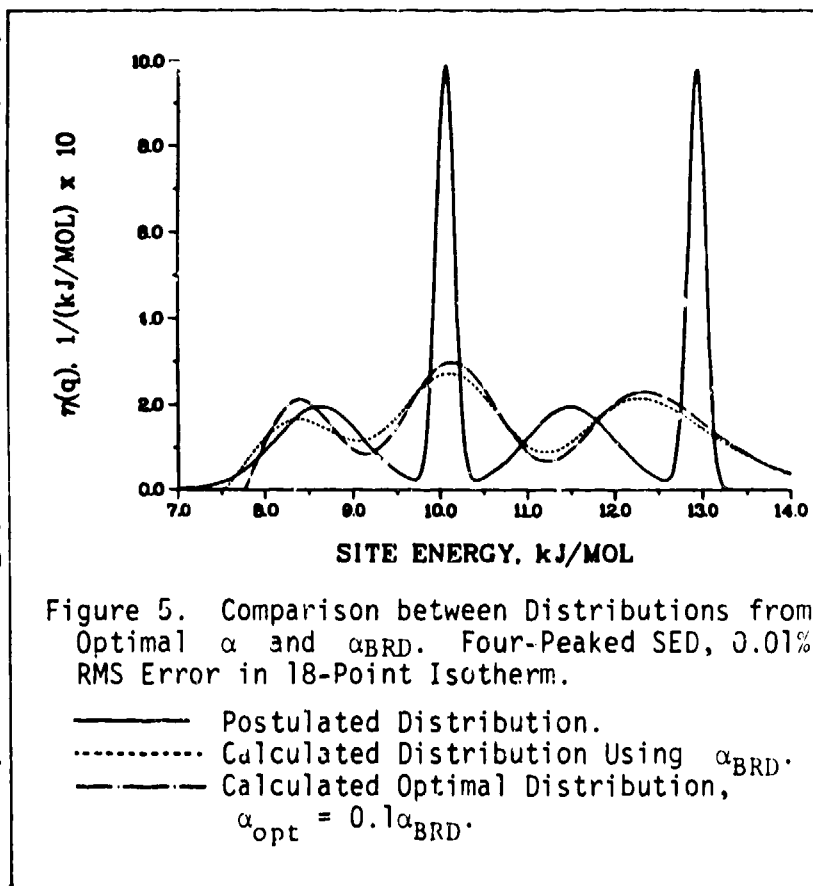


Figure 5. Comparison between Distributions from Optimal α and α_{BRD} . Four-Peaked SED, 0.01% RMS Error in 18-Point Isotherm.

— Postulated Distribution.
 Calculated Distribution Using α_{BRD} .
 - - - Calculated Optimal Distribution,
 $\alpha_{opt} = 0.1\alpha_{BRD}$.

NOTATION

- c Nonnegative components of g in the additive smoothing term of Eq. (A3), dimensionless.
- D Function of α defined by Eq. (A9).
- f Function of experimental variable, various units.
- f^e Experimental observations, various units.
- g^e Distribution function, various units.
- H Nonlinear differential operator.
- I An integral, various units.
- I The identity matrix
- K Kernel of integral equation, various units.
- M Matrix defined by Eq. (A6).
- N Number of experimental data points.
- p Pressure, Pa.
- q Energy of desorption, J/mol (negative of the enthalpy change upon adsorption).
- R Gas constant, J/(mol)(K).
- T Absolute temperature, K.
- T Matrix defined by Eq. (A7).
- t Variable over which distribution function g occurs, various units.
- w_i Weighting factor, inversely proportional to the variance in the data taken at point i .
- x Experimental variable, various units.
- α Adjustable smoothing parameter, dimensionless.
- η Site-energy distribution function, 1/J.
- $\theta(p,q)$ Fraction of sites of energy q covered at pressure p , dimensionless (the local isotherm).
- θ_{gr} Gross fractional surface coverage, dimensionless.

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APPENDIX A

ALGORITHM FOR EXTRACTING NONNEGATIVE DISTRIBUTION FUNCTIONS FROM FIRST-KIND FREDHOLM EQUATIONS

The general form of Eq. (1) in the text is

$$f(x) = \int_a^b K(x,t)g(t)dt \quad . \quad (A1)$$

K is representative of the experimental system and procedure. When observations $f(x)$ have been obtained from a system characterized by Eq. (A1), a solution for $g(t)$ would minimize locally the integral

$$I = \int_c^d [f_e(x) - \int_a^b K(x,t)g(t)dt]^2 dx \quad , \quad (A2)$$

in which $f_e(x)$ represents the experimental observations. In regularization, a smoothing term is added to the RHS of Eq. (A2), and the functional to be minimized is altered so that

$$I = \int_c^d [f_e(x) - \int_a^b K(x,t)g(t)dt]^2 dx + \alpha \int_a^b [H(g)]dt \quad , \quad (A3)$$

where $H(g)$ is a nonlinear differential operator on g with nonnegative coefficients, and α is a parameter. In the simplest formulation, $H(g) = g^2$, which is what we have used throughout this work. Applying variational calculus gives the necessary condition for a minimum with $H(g) = g^2$ (e.g., 14):

$$\alpha g(t) + \int_a^b \left\{ \int_c^d K(x,z)K(x,t)dx \right\} g(z)dz = \int_c^d K(x,t)f_e(x)dx \quad . \quad (A4)$$

Equation (A4) can be put into finite-difference form:

$$(\underline{K}^{tr} \underline{\delta x} \underline{K} \underline{\delta t} + \alpha \underline{I})g = \underline{K}^{tr} \underline{\delta x} \underline{f}_e \quad , \quad (A5)$$

in which \underline{K}^{tr} is the transpose of \underline{K} , and $\underline{\delta x}$ and $\underline{\delta t}$ are diagonal matrices whose elements are the weighting factors for the intervals $[c,d]$ and $[a,b]$. Butler et al. (1) suggested a means by which $g(t)$ can be restricted to nonnegative values, and we have followed their proposal. Equation (A4), using a given α , is solved for g . The points at which g is negative are recorded, and the evaluation of the quantity $(\underline{K}^{tr} \underline{\delta x} \underline{K} \underline{\delta t} + \alpha \underline{I})$ is not performed at these points. A new g is obtained, and the process is repeated. The iteration is continued until no change in g is seen. The entire process is then repeated for all subsequent values of α .

To provide resolution of narrow peaks and near-discontinuities, a variable integration mesh is included in the computer code. For each value of α , the integration mesh is altered to allow finer zoning in regions where the emerging distribution has large gradients.

Butler et al. also offered a criterion for choosing an optimal value of α , based on the estimated error in the calculated $g(t)$ over t between a and b . This in turn depends on the error in the data. To express their criterion, some terms are defined:

$$\underline{M} \equiv \underline{K}^{tr} \underline{\Delta x} \underline{K} \underline{\Delta t} \quad (A6)$$

$$\underline{I} \equiv (\underline{M} + \alpha \underline{I})^{-1} \quad (A7)$$

$$\underline{c} \equiv \text{a vector which satisfies } (\underline{M} + \alpha \underline{I})\underline{c} = \underline{f}_e \text{ in which } \quad (A8)$$

\underline{M} is evaluated only for points in t where $g(t) > 0$.

A function of α is then defined:

$$D(\alpha) \equiv (\underline{f}_e^{tr} \underline{I} \underline{M} \underline{I} \underline{f}_e) - (2 \underline{f}_e^{tr} \underline{I} \underline{f}_e) + [2\alpha(N \underline{c}^{tr} \underline{c})^{1/2}] \quad (A9)$$

The criterion of Butler, Reeds, and Dawson states that the optimal value of α (α_{BRD}) is attained when $D(\alpha)$ is a minimum.

When the levels of error in the various data points are not equal, elements in the \underline{K} matrix and \underline{f}_e vector must be weighted. Let the weights w_i^2 be inversely proportional to the variances in the data points f_i . The weights are scaled so that $\sum_{i=1}^N w_i^2 = N$. The elements in the \underline{K} matrix are then weighted so that k_{ij} becomes $w_i k_{ij}$ and those in the \underline{f}_e vector are weighted so that f_{ei} becomes $w_i f_{ei}$.

APPENDIX B

FACTORS AND PARAMETERS USED IN GENERATION OF FIGURES

Figure 1:

$$\theta(p, q) = (4.464 \cdot 10^{-6})(p)(e^{q/RT}) / [1 + (4.464 \cdot 10^{-6})(p)(e^{q/RT})]$$

(p in torr, q in joules)

$$\eta(q) = (3.931 \cdot 10^{-4}) [e^{-(4.856 \cdot 10^{-7})(q-8619)^2}] \quad (q \text{ in joules})$$

Range of p: $0 < p < 3$ torr. $N = 51$

Range of q: $0 < q < 3.5 \cdot 10^4$ joules. $T = 77.5$

Accuracy of isotherm data: Random, normally distributed errors with a standard deviation of 1% were imposed on the isotherm data.

Smoothing parameters: $\alpha = \alpha_{LS}$ (Minimizes $\sum_{i=1}^N [f_e(x_i) - \int_a^b K(x_i, t)g(t)]^2$)

$\alpha = 0.2\alpha_{BRD}$ ($\alpha = 1000\alpha_{LS}$)

Figure 2:

$\theta(p, q)$: Same as for Fig. 1.

$$\eta(q) = (1.965 \cdot 10^{-4}) [e^{-(4.856 \cdot 10^{-7})(q-6600)^2} + e^{-(4.856 \cdot 10^{-7})(q-13200)^2}]$$

(q in joules)

Range of p: 0 < p < 0.01 torr: 15 points N = 51
 0.01 < p < 2 : 25
 2 < p < 3 : 11

Range of q: 0 < q < 4·10⁴ joules. T: Same as for Fig. 1.

Accuracy of isotherm data: Same as for Fig. 1.

Smoothing parameters: $\alpha_{opt} = 0.05\alpha_{BRD}$

Figure 3:

$\theta(p,q)$: Same as for Figs. 1 and 2. $\eta(q)$: Same as for Fig. 2.

Range of p: Same as for Fig. 3. N = 51

Range of q: 0 < q < 6·10⁴ joules. T: Same as for Figs. 1 and 2.

Accuracy of isotherm data: Random, normally distributed errors with a standard deviation of 3% were imposed on the isotherm data.

Smoothing parameters: $\alpha_{opt} = 0.006\alpha_{BRD}$

Figure 4:

$\theta(p,q)$: Same as for Figs. 1-3.

$$\eta(q) = (1.965 \cdot 10^{-4}) [e^{-(1.942 \cdot 10^{-6})(q-8619)^2} + e^{-(1.942 \cdot 10^{-6})(q-11492)^2}] \\ + (9.826 \cdot 10^{-4}) [e^{-(4.854 \cdot 10^{-5})(q-10056)^2} + e^{-(4.854 \cdot 10^{-5})(q-12929)^2}]$$

(q in joules)

Range of p: 0 < p < 0.01 torr: 15 points N = 51
 0.01 < p < 1 : 30
 1 < p < 3 : 6

Range of q: 0 < q < 8·10⁴ joules. T: Same as for Figs. 1-3.

Accuracy of isotherm data: Random, normally distributed errors with a standard deviation of 0.01% were imposed on the isotherm data.

Smoothing parameters: $\alpha_{opt} = 0.006\alpha_{BRD}$

Figure 5:

$\theta(p,q)$: Same as for Figs. 1-4. $\eta(q)$: Same as for Fig. 4.

Range of p: 0 < p < 0.01 torr: 5 points N = 18
 0.01 < p < 1 : 10
 1 < p < 3 : 3

Range of q: Same as for Fig. 4. T: Same as for Figs. 1-4.

Accuracy of isotherm data. Same as for Fig. 4.

Smoothing parameters: $\alpha_{opt} = 0.1\alpha_{BRD}$