

The Solution of Adsorption Integral Equations by Means of the Regularization Method

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An overall adsorption quantity for a heterogeneous solid is usually expressed by an integral equation, which contains a distribution function that describes heterogeneous properties of this solid. The calculation of this distribution function is an ill-posed problem. The current article shows that the difficulties arising from the ill-posed nature of an adsorption equation can be overcome with the regularization method. This work presents general principles of regularization for solving the ill-posed problems without detailed mathematical considerations. The application of the regularization method to calculate a distribution function from any overall adsorption functions is illustrated with both simulated and experimental adsorption isotherms.

INTRODUCTION

The theoretical description of physical and chemical adsorption on heterogeneous adsorbents is based almost exclusively on the adsorption integral equations.¹ This concept consists in the use of a local adsorption function (e.g., local adsorption isotherm θ_l on a homotactic patch of the solid surface) as the kernel in an integral equation for the overall (total) function (e.g., overall adsorption isotherm θ_t). There are many overall adsorption quantities expressed by integral equations; for instance, in the homotactic-patch approximation of the Fowler-Guggenheim (FG) equation²

$$pk_0 \exp(-U/RT) = \frac{\theta_{FG}}{1 - \theta_{FG}} \exp(-zw\theta_{FG}/kT) \quad (1)$$

leads to the following integral representation of the overall adsorption isotherm³

$$\theta_t(T, p) = \int_0^\infty \theta_{FG}(T, p, U) f(U) dU, \quad (2)$$

with the distribution function $f(U)$ of the adsorption energy; this distribution characterizes the energetic heterogeneity of a solid. Similarly, the extension of the Dubinin-Radushkevich equation⁴ to adsorption

on heterogeneous microporous solids gives⁵

$$\theta_t(T, p) = \int_0^\infty \exp(-B[RT/\beta \ln(p_s/p)]^2) f(B) dB \quad (3)$$

with the distribution function $f(B)$ of the structural parameter B , which can be related to the sizes of the micropores in an adsorbent.⁶ Also, the integral equation can be derived for the overall thermodesorption rate $r(T)$ ^{7,8}

$$r(T) = -A/\beta^* \int_{E_{\min}}^{E_{\max}} [\theta(T, E)]^v \exp(-E/RT) f(E) dE \quad (4)$$

where

$$\frac{\partial \theta(T, E)}{\partial T} = -A/\beta^* [\theta(T, E)]^v \exp(-E/RT) \quad (5)$$

with the distribution function $f(E)$ of the desorption activation energy E ; for the definitions of other quantities in equations (1)–(5), see references related to these equations.^{2,8}

Further examples of the adsorption integral equations can be written for the gas solid virial coefficients,⁹ the chromatographic retention volume,¹⁰ the kinetic adsorption isotherm,¹¹ the adsorption and desorption rates, the liquid-solid excess adsorption isotherms,¹² and so on.

All these adsorption integral equations have formally the same mathematical construction

$$\theta_t(y) = \int_\Delta \theta_l(x, y) f(x) dx. \quad (6)$$

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The measured global function $\theta_i(y)$ is expressed by an integral over a certain integration range with the product of a local function $\theta_i(x, y)$ and distribution function $f(x)$. As measured values $\theta_i(y)$ the following quantities are often used: in gas adsorption, the adsorbed amount as a function of the equilibrium pressure; in adsorption from binary mixtures, the adsorption excess as a function of the mole fraction of a component; in thermodesorption, the desorption rate as a function of temperature or time.

The parameter x describes the adsorbent heterogeneity appropriate to the adsorption model $\theta_i(x, y)$; e.g., it can be the adsorption energy U , the structural parameter B , the micropore radius r , and so on. Thus, the function $f(x)$ describes the distribution of adsorption species (adsorption sites, homogeneous patches, meso or micropores or others) with that adsorbent property; which is expressed by the parameter x . Frequently, x is a property of the adsorbent-adsorbate system, e.g., adsorption energy U .

The distribution function $f(x)$ is of great importance for both energetic and structural characterization of solid adsorbents. Therefore, the calculation of this distribution function by solving an adsorption integral equation is one of the most important practical tasks in the field of physical adsorption.

FREDHOLM INTEGRAL EQUATIONS OF THE FIRST KIND

From the mathematical point of view, eq. (6) is a linear Fredholm integral equation of the first kind, which can be written in the following general form

$$g(y) = \int_a^b K(x, y)f(x) dx \quad (7)$$

The kernel $K(x, y)$ represents the adsorption model, $g(y)$ denotes the experimental function, and $f(x)$ is the unknown function. The variable x covers commonly the whole physically realistic range (mostly $[0, \infty]$). The development of the theory of physical adsorption during the last 30 years was closely connected with the development of methods for solving adsorption integral equations. This fact is caused by the following numerical problems appearing in solution of Fredholm integral equations of the first kind:

1. The analytical inversion of adsorption integral equations; an inverse operator for the integral equation exists only in a few cases. Because the majority of analytical solutions have a form of an infinite series expansions,¹³ numerical solutions of the integral equation are recommended very often.
2. The numerical solution of Fredholm integral equations of the first kind requires a discretization by a suitable quadrature.¹⁴ Then, the integral eq. (7)

is transformed to a system of linear equations solvable by linear algebra methods

$$g(y_i) = \int_a^b K(x, y_i)f(x) dx \approx \sum_{j=1}^n w_j K_{ij}f_j, \quad (8)$$

where

n is the number of the integration intervals,

$\mathbf{x} = (x_j)_{1..n}$ are the interpolation nodes of the quadrature in the integration range $[a, b]$,

$\mathbf{w} = (w_j)_{1..n}$ are the corresponding quadrature weights,

$K_{ij} = K(x_j, y_i)$ and

$f_j = f(x_j)$.

Introducing the definitions

$$\mathbf{W} = \text{diag}(\mathbf{w}), \quad (9)$$

$$\mathbf{K} = (K_{ij})_{i=1..m, j=1..n}, \quad (10)$$

$$\mathbf{A} = \mathbf{KW}, \quad (11)$$

$$\mathbf{g} = (g_i)_{1..m}; g_i = g(y_i); \mathbf{y} = (y_i)_{1..m}, \quad (12)$$

with m as the number of data points $(y_i, g(y_i))$ and

$$\mathbf{f} = (f_i)_{1..n}, \quad (13)$$

one obtains from eq. (7) a linear system of m equations with n unknowns

$$\mathbf{g} = \mathbf{Af}. \quad (14)$$

Such a linear system of equations can commonly be solved by minimizing the residual introduced by Gauss already in the last century

$$\text{Minimize } \|\mathbf{Af} - \mathbf{g}\|^2 \text{ with respect to } \mathbf{f}^* \quad (15)$$

In this case we get the solution (index ls stands for least squares solution)

$$\mathbf{f}_{ls} = (\mathbf{A}^T \mathbf{A})^{-1} \mathbf{A}^T \mathbf{g}. \quad (16)$$

3. Fredholm integral equations are numerically ill-posed nature. The peculiar behavior of the ill-posed problems consists in a possible transmission of experimental errors to the unknown result in such a way that the result can be completely distorted. The exclusive use of the minimizing least squares method for solving ill-posed problems leads almost always to strong oscillations in the solution \mathbf{f} ; consequently, any amount of physical information contained in this solution is almost impossible to extract. An explanation for the occurrence of such oscillations in the solution of such integral equations is given by Phillips.¹⁵ Therefore, the solution of the ill-posed problems always requires special numerical methods. The

*The norms $\|\cdot\|$ used by the authors in this article for mathematical descriptions are *always* understood as the Euclidean vector norm, which is defined as: $\|\mathbf{x}\|_2 = \sqrt{\mathbf{x}^T \mathbf{x}}$. The usual indication of the Euclidean norm by a lower index 2 is here omitted for reasons of simplicity.

ill-posedness of a problem is first of all a numerical question and is not due to any incorrect formulation of a physicochemical phenomenon.

Because of difficulties in solution of the adsorption integral equations, several indirect methods for their solution were established during the last few years. An actual summary of these methods is given elsewhere.¹ Most of them are based on the following principles:

1. Postulate an analytical form for the unknown function $f(x)$, the parameters of which are calculated by a least squares fitting. The Gauss or Gamma functions or superpositions of them are often assumed.
2. Postulate an analytical description of the experimental data, $g(y)$ which gives an analytical solution of the integral equation. The parameter fitting is performed by least squares methods.
3. Simplification of the integral kernel in such a way that a solution of the integral equation can be done by simple algebraic equations. The most popular method of this kind is the CA method (CA means condensation approximation) introduced by Roginskij¹⁶ and later reformulated by Harris¹⁷ and Cerofolini.⁴ In this method, the integral kernel is replaced by a one-step function. The step position is determined by minimizing the square of the deviation between the true integral kernel and the step function. The CA method is identical to a Taylor series expansion of the Stieltjes transformation of the integral kernel truncated after the first-order term. Therefore, from the point of view of an objective determination of the function $f(x)$ the CA method is preferred over other indirect methods with a subjective assumption of analytical forms for $f(x)$ or $g(y)$.

Most indirect methods for solving the adsorption integral equations are very easy to program and perform necessary calculations. Unfortunately, this fact does not mean an apparent simplicity in solution of Fredholm integral equations of the first kind. The ill-posedness of the above problem leads almost always to distorted results, although the description of the experimental data is acceptable in the range of their errors. In the case of ill-posed problems the use of the minimization of the squared deviations alone is never a sure criterion for an adequate solution.^{18,19}

REGULARIZATION METHOD

To the authors' knowledge, House deserves the credit for the introduction of regularization method for solving the adsorption integral equations.²⁰ Already, in the above quoted article, the smoothness of the distribution function was used as an additional minimizing condition for stabilizing the solution. But the solution of the linear equations system was carried

out by the Gauss algorithm, which is too unstable for ill-posed problems.

The next stage in use of regularization was done by Merz.²¹ He initiated the use of the Singular Value Decomposition (SVD) for the solution of the linear equations system. The SVD is well suited for such numerically unstable tasks because of its use of orthogonal transformations. Also, the use of SVD makes it possible to greatly diminish the expenditure for the calculation. Merz also gave suggestions for data weighting and for the choice of an optimal regularization parameter and he inspired the use of non-negative constraints with the regularization method. Another important article on the regularization method was published in 1982 by Provencher.²² This article presents a numerical algorithm for inverting noisy linear operator equations. According to this algorithm, the regularization parameter can be automatically chosen on the basis of an F-test and confidence region. The years 1983–1985 brought articles by Britten and Travis^{8,23} as well as by Koopal et al.^{24–26} The first group dealt particularly with the search of an optimal regularization parameter. Starting with a proposal for an optimal regularization parameter for nonnegative solutions made by Butler et al.,²⁷ they investigated its applicability to solution of the adsorption integral equations. These articles showed thoroughly the problems associated with finding a regularization parameter, which is sensible and appropriate to the experimental data. The Koopal's group also turned its attention to the calculation of non-negative solutions of the adsorption integral equations. Their work is based on the algorithm described by Lawson and Hanson²⁸ for nonnegative solution of a system of linear equations (NNLS method), which was first used in adsorption in 1978 by Sacher and Morrison.²⁹ Independently, Koopal et al. combined this method with regularization and proposed the CAESAR algorithm. By use of the discrete regularization method the difficulty in selecting the regularization parameter could be reduced to a rank determination of the kernel matrix. This is done in a similar way to a proposal by Hanson,³⁰ utilizing the postulated errors for the experimental data.

Since this time, the use of regularization methods has been sporadic^{7,31} and indirect methods were frequently applied. This fact is very surprising because today even personal computers are sufficient to deal with these numerical problems. Therefore, the authors believe that there is still a certain deficit in information about utility of the regularization method. Moreover, the availability of subroutines for regularization in the best known program libraries does not seem to exist up to now.

Ill-Posed Problems

The regularization as a method for solution of ill-posed problems was first introduced in 1943 by the

mathematician and geophysicist Tikhonov.³² Simply, the fact that the regularization method was found by an applied mathematician suggests an importance of regularization in solution of many practical problems.

The above statement becomes clear if one first realizes what is an ill-posed problem. Let us suppose that the experimental data \mathbf{g} from eq. (14) can be divided into a true part \mathbf{g}_{true} and the random errors ξ being inherent in all experiments

$$\mathbf{g} = \mathbf{g}_{\text{true}} + \xi. \quad (17)$$

Then, from eq. (14) and (15) by the formal use of the generalized inverse $\mathbf{A}^+ = \{\mathbf{A}^T \mathbf{A}\}^{-1} \mathbf{A}^T$ (also called pseudoinverse of \mathbf{A}) we have

$$\mathbf{f} = \mathbf{A}^+ \mathbf{g} + \mathbf{A}^+ \xi, \quad (18)$$

$$\mathbf{f} = \mathbf{f}_{\text{true}} + \mathbf{A}^+ \xi, \quad (19)$$

where \mathbf{f} is the resulting solution and \mathbf{f}_{true} is the actually unknown but true information. In case of $\xi = \mathbf{0}$ we have a well-posed problem, e.g., a one-to-one mapping between \mathbf{f}_{true} and \mathbf{g} ($\mathbf{f}_{\text{true}} = \mathbf{A}^+ \mathbf{g}$) exists.

In the common case, because of existence of experimental errors there is no unambiguous mapping between \mathbf{f}_{true} and \mathbf{g} . This means that an infinite set of solutions $\{\mathbf{f}_{\text{true}}\}$ will fit the data \mathbf{g} within the range of experimental errors. Thus, an optimal solution method has to ensure that deviations between \mathbf{f} and \mathbf{f}_{true} are minimal in the presence of ξ .

It can be pointed out, that the existence of experimental errors is not yet a sufficient condition for ill-posedness of a problem. Moreover, from the numerical point of view the boundary between well- and ill-posedness of the problem is not exactly definable. Therefore, from a practical point of view it is useful to understand as ill-posed all the problems, which are not consistent with the least squares solution principle.

From this definition follows immediately the necessity of using a modified solution principle for ill-posed problems, which is able to stabilize the solution. Commonly two principal methods are employed

1. Replacement of the least squares principle given by eq. (15), which is completely sufficient for well-posed problems, by special solution principles for ill-posed problems. The regularization, as the best known method of such a kind, expands the minimizing condition (15) by an additional term for stabilizing the solution:

$$\text{Minimize } \|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2 + \gamma \|\mathbf{C}\mathbf{f}\|^2 \text{ with respect to } \mathbf{f}. \quad (20)$$

The regularization parameter fixes here the mutual weighting of both terms in eq. (20). The term $\gamma \|\mathbf{C}\mathbf{f}\|^2$ can be evaluated to $\gamma \sum_i (\sum_j C_{ij} f_j)^2$.²¹ In this

completely equivalent form the regularization was introduced by House.²⁰

The quadratic matrix \mathbf{C} , which should stabilize the solution, must be positive definite. The solution of problem (20) can be carried out further with elementary methods of the linear algebra. Other methods similar to regularization, as a rule, minimize single functionals like $\|\mathbf{C}\mathbf{f}\|$ or $(\mathbf{f}, \mathbf{C}\mathbf{f})$ with regard to \mathbf{f} .

2. Restriction of the solution range for \mathbf{f} on the base of known a-priori information about the solution \mathbf{f} . The most common case is here the incorporation of the non-negative constraint: $\mathbf{f} \geq \mathbf{0}$.

The solution of a constrained problem (15) is by itself a nonlinear optimization problem and can normally not carry out by standard methods of the linear algebra. In practice these methods require iterative solution algorithms, are very time consuming and especially very sensitive to different sets of data than the methods mentioned above.

Nowadays, the solution methods which employ both principles are widely used.

From a formal viewpoint, the regularization and methods similar to it provide more stable solutions than least squares fitting. But such a view is only partial. In our opinion, the essence consists more in the choice of a more advantageous solution principle for the ill-posed problems. In light of this reflection, we can speak only about an ill-posed problem in relation with a concrete selected solution principle. It follows from it that the ill-posedness of a problem is first of all a numerical problem, namely the question of selecting a suitable solution principle.

Base Equations

Let

$$\Phi(\mathbf{f}) = \|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2 + \gamma \|\mathbf{C}\mathbf{f}\|^2 \quad (21)$$

be the minimizing functional of the regularization principle with the still unspecified quadratic matrix \mathbf{C} . The minimization of $\Phi(\mathbf{f})$ with respect to \mathbf{f} is equal to the condition

$$\mathbf{0} = \frac{\partial \Phi(\mathbf{f})}{\partial \mathbf{f}} \quad (22)$$

By putting in eq. (21) we get

$$\mathbf{0} = \mathbf{A}^T (\mathbf{A}\mathbf{f} - \mathbf{g}) + \gamma \mathbf{C}^T \mathbf{C} \mathbf{f}, \quad (23)$$

$$\mathbf{A}^T \mathbf{g} = \{\mathbf{A}^T \mathbf{A} + \gamma \mathbf{C}^T \mathbf{C}\} \mathbf{f}, \quad (24)$$

$$\mathbf{f} = \{\mathbf{A}^T \mathbf{A} + \gamma \mathbf{C}^T \mathbf{C}\}^{-1} \mathbf{A}^T \mathbf{g}. \quad (25)$$

The regularized solution (25) differs from least squares minimization alone (eq. (16)) by the additional term $\gamma \mathbf{C}^T \mathbf{C}$ in matrix $\mathbf{A}^T \mathbf{A}$ being inverted. As is well known, the numerical instability of least squares solutions is caused by the quasi-singularity of the matrix \mathbf{A}

and thus also of $\mathbf{A}^T\mathbf{A}$. Because the matrix \mathbf{C} was forced to be positive definite, the term $\gamma\mathbf{C}^T\mathbf{C}$ will always prevent the quasi-singularity of the inverted matrix $\{\mathbf{A}^T\mathbf{A} + \gamma\mathbf{C}^T\mathbf{C}\}$ by selecting a sufficiently high regularization parameter. This explains the stabilizing effect of the additional term $\gamma\|\mathbf{Cf}\|^2$ in the solution principle of the regularization method.

The solution given by eq. (25) still requires a new calculation of the inverse matrix for each value of the regularization parameter γ . Using the Singular Value Decomposition³³

$$\mathbf{P} = \mathbf{U}\mathbf{\Sigma}\mathbf{V}^T \quad (26)$$

it minimizes the calculation expenditure of the solution in case of different regularization parameters. The matrices \mathbf{U} and \mathbf{V} are orthogonal, $\mathbf{\Sigma}$ is the diagonal matrix of the singular values σ_i of the matrix \mathbf{P} . Moreover, the use of orthogonal matrices with their known good numerical properties is a further advantage.

By setting

$$\mathbf{P} = \mathbf{A}\mathbf{C}^{-1}, \quad (27)$$

from eq. (25) we get

$$\mathbf{f} = \{\mathbf{C}^T\mathbf{P}^T\mathbf{P}\mathbf{C} + \gamma\mathbf{C}^T\mathbf{C}\}^{-1}\mathbf{C}^T\mathbf{P}^T\mathbf{g}. \quad (28)$$

After putting eq. (26) into eq. (28) we have

$$\mathbf{f} = \{\mathbf{C}^T\mathbf{V}\mathbf{\Sigma}^2\mathbf{V}^T\mathbf{C} + \gamma\mathbf{C}^T\mathbf{V}\mathbf{V}^T\mathbf{C}\}^{-1}\mathbf{C}^T\mathbf{V}\mathbf{\Sigma}\mathbf{U}^T\mathbf{g}. \quad (29)$$

$$\mathbf{f} = \{\mathbf{C}^T\mathbf{V}(\mathbf{\Sigma}^2 + \gamma\mathbf{I})\mathbf{V}^T\mathbf{C}\}^{-1}\mathbf{C}^T\mathbf{V}\mathbf{\Sigma}\mathbf{U}^T\mathbf{g}. \quad (30)$$

$$\mathbf{f} = \mathbf{C}^{-1}\mathbf{V}(\mathbf{\Sigma}^2 + \gamma\mathbf{I})^{-1}\mathbf{\Sigma}\mathbf{U}^T\mathbf{g}. \quad (31)$$

After calculation of the matrix \mathbf{C}^{-1} and the singular value decomposition for \mathbf{P} , the solution for any values of the regularization parameter can be determined by simple matrix multiplications. By additional calculations of

$$(\mathbf{C}^{-1}\mathbf{V})_{ij} = l_{ij} \quad (32)$$

and

$$(\mathbf{U}^T\mathbf{g})_i = s_i, \quad (33)$$

the elements of the solution vector are readily calculated by the summation

$$f_i = \sum_{j=1}^n \frac{\sigma_j}{\sigma_j^2 + \gamma} s_j l_{ij} \quad (34)$$

Besides this kind of regularization introduced by Tikhonov³² and often called continuous one, further varieties of regularization were established in the past. At this point we enter briefly into the discrete regularization. The discrete regularization is only feasible when the singular value decomposition is used. In this case the decomposition must be realized in such a way that the relation

$$\sigma_1 \geq \sigma_2 \geq \dots \geq \sigma_n \geq 0 \quad (35)$$

is fulfilled. By means of a cutting value τ for the singular values, which are not taken into account in

the condition

$$\sigma_1 \geq \dots \geq \sigma_q > \tau > \sigma_{q+1} \geq \dots \geq \sigma_n \geq 0 \quad (36)$$

an index q is determined, which can be regarded as the pseudo rank of the matrix \mathbf{P} . In calculation of the solution only the first q singular values are used. Thus, the summation

$$f_i = \sum_{j=1}^q \frac{\sigma_j}{\sigma_j^2 + \gamma} s_j l_{ij} \quad (37)$$

is only over $q \leq n$ terms. Therefore, the discrete regularization is often called q regularization. Moreover, we want also to show two further generalizations of the regularization principle. The first one is an extension by a diagonal weighting matrix $\mathbf{\Lambda}$ to the experimental errors of \mathbf{g} . From eq. (15) we get

$$\text{Minimize } \|\mathbf{\Lambda}^{1/2}(\mathbf{A}\mathbf{f} - \mathbf{g})\|^2 + \gamma \|\mathbf{Cf}\|^2 \quad \text{with respect to } \mathbf{f}. \quad (38)$$

Another expansion of the general principle is obtained by the use of a priori information about the solution in form of the vector \mathbf{f}_0

$$\text{Minimize } \|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2 + \gamma \|\mathbf{C}(\mathbf{f} - \mathbf{f}_0)\|^2 \quad \text{with respect to } \mathbf{f}. \quad (39)$$

The effect of the vector \mathbf{f}_0 consists in narrowing the solution quantity $\{\mathbf{f}\}$ to a closer domain for different values of the regularization parameter. The solution with the principle (39) is as follows

$$\mathbf{f} = \mathbf{C}^{-1}\mathbf{V}(\mathbf{\Sigma}^2 + \gamma\mathbf{I})^{-1}(\mathbf{\Sigma}\mathbf{U}^T\mathbf{g} - \gamma\mathbf{V}\mathbf{C}\mathbf{f}_0) \quad (40)$$

$$\mathbf{f} = \mathbf{f}_0 + \mathbf{C}^{-1}\mathbf{V}(\mathbf{\Sigma}^2 + \gamma\mathbf{I})^{-1}\mathbf{\Sigma}(\mathbf{U}^T\mathbf{g} - \mathbf{\Sigma}\mathbf{V}\mathbf{C}\mathbf{f}_0) \quad (41)$$

and requires only slightly more time than the solution of eq. (31). It is also possible to combine the solution principles (38) and (39).

The regularization method can be improved next by an additional restriction of the solution quantity for \mathbf{f}

$$\text{Minimize } \|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2 + \gamma \|\mathbf{Cf}\|^2 \quad \text{with respect to } \mathbf{f} \in D \quad (42)$$

to a convex domain D . The best known constraint is the restriction for a nonnegative solution \mathbf{f}

$$\text{Minimize } \|\mathbf{A}\mathbf{f} - \mathbf{g}\|^2 + \gamma \|\mathbf{Cf}\|^2 \quad \text{with respect to } \mathbf{f} \geq \mathbf{0}, \quad (43)$$

which is called the NNLS method in the literature.²⁸ The calculation of the nonnegative regularized solutions is not possible with linear algebra methods only. This results in a considerable increasing in the calculation time.

All the above considerations on the regularization method are based on the use of the functional $\|\mathbf{Cf}\|^2$ to stabilize the solution. Below, we look in detail at the concrete form of the quadratic and positive definite matrix \mathbf{C} .

The most popular choice for \mathbf{C} is the unit matrix applied already by Tikhonov.³²

$$\|\mathbf{C}\mathbf{f}\|^2 = \|\mathbf{f}\|^2 = \int_a^b f(x)^2 dx. \quad (44)$$

With regard to the solution of the integral equation, the assumption $\mathbf{C} = \mathbf{I}$ minimizes additionally the residual of the integral over the square of the unknown solution $f(x)$ through the regularization principle.* It is easy to understand that this results in a suppression of oscillations of the solution, because these oscillations would increase the value of the minimizing functional $\|\mathbf{f}\|^2$. The assumption that \mathbf{C} is the unit matrix makes it possible to simplify the base equations formulated in this paragraph. The matrices \mathbf{C} and \mathbf{C}^{-1} can then be canceled in all equations without any replacement.

A further widely used class of matrices are the discretized differential matrixes of the n th order

$$\|\mathbf{C}\mathbf{f}\|^2 = \|\mathbf{W}^{1/2}\mathbf{D}_n\mathbf{f}\|^2 = \int_a^b \left[\frac{\partial^n f(x)}{\partial x^n} \right]^2 dx. \quad (45)$$

The matrixes \mathbf{D}_n minimize with respect to the integral equation, the integral over the squares of the n th derivatives of the desired solution $f(x)$. Here, the most interesting is the case $n = 2$, originating to Phillips and Twomey.^{15,34} In this case, the square over the curvature of the unknown solution is minimized from which the preference for smooth functions $f(x)$ becomes clear immediately. Therefore, the assumption $\mathbf{C} = \mathbf{W}^{1/2}\mathbf{D}_n$ is more able to stabilize the solution than the principle (44). The concrete form of the matrix \mathbf{C} depends on the quadrature nodes \mathbf{x} and weights \mathbf{w} of the selected quadrature as well as on the boundary conditions for the desired solution at the bounds a and b . For the most used case of equidistant nodes ($\Delta x_i = h$) and with the assumption of disappearance of the solution out of the integration region ($f(x) = 0$ and $f'(x) = 0$ for $x < a$ and $x > b$), one obtains

$$\mathbf{C} = -\frac{1}{h^2} \begin{pmatrix} 2 & -1 & & & & \\ -1 & 2 & & & & \\ & & \ddots & & & \\ & & & \ddots & & \\ & & & & \ddots & \\ & & 0 & & & 2 & -1 \\ & & & & & -1 & 2 \end{pmatrix} \quad (46)$$

In this case, the inverse of \mathbf{C} can be stated analytically as well,³⁵ which avoids a time-consuming numerical calculation of \mathbf{C}^{-1}

$$\mathbf{C}^{-1} = \mathbf{D}_2^{-1}\mathbf{W}^{-1/2}, \quad (47)$$

*Exactly, we have to set $\mathbf{C} = \mathbf{W}^{1/2}$, but very often \mathbf{W} differs from \mathbf{I} only by a scalar factor.

$$\mathbf{W}^{-1/2} = \text{diag}(\sqrt{w_i}), \quad (48)$$

$$(\mathbf{D}_2^{-1})_{ij} = -h^2 \frac{i(n+1-j)}{n+1}. \quad (49)$$

The Choice of the Regularization Parameter

It follows from the above considerations that the regularization parameter describes the weighting of both the residual and stabilizing term $\|\mathbf{C}\mathbf{f}\|^2$ in eq. (20). Thus the choice of the regularization parameter plays a central role in finding the solution.

At the limits of a positive regularization parameter the following relations can be proven.³⁶⁻³⁹

$$\lim_{\gamma \rightarrow 0} \mathbf{f} = \mathbf{f}_{ls}, \quad (50)$$

$$\lim_{\gamma \rightarrow \infty} \mathbf{f} = \begin{cases} \mathbf{0} & \text{for } \|\mathbf{C}\mathbf{f}\|^2 \\ \mathbf{f}_0 & \text{for } \|\mathbf{C}(\mathbf{f} - \mathbf{f}_0)\|^2 \end{cases}, \quad (51)$$

$$\lim_{\gamma \rightarrow 0} \|\mathbf{f}\| = \|\mathbf{f}_{ls}\| \leq \|\mathbf{f}\| \leq \begin{cases} 0 & \text{for } \|\mathbf{C}\mathbf{f}\|^2 \\ \|\mathbf{f}_0\| & \text{for } \|\mathbf{C}(\mathbf{f} - \mathbf{f}_0)\|^2 \end{cases} \\ = \lim_{\gamma \rightarrow \infty} \|\mathbf{f}\| \quad (52)$$

and

$$\lim_{\gamma \rightarrow 0} \|\mathbf{A}\mathbf{f} - \mathbf{g}\| = \|\mathbf{A}\mathbf{f}_{ls} - \mathbf{g}\| \leq \|\mathbf{A}\mathbf{f} - \mathbf{g}\| \\ \leq \begin{cases} \|\mathbf{g}\| & \text{for } \|\mathbf{C}\mathbf{f}\|^2 \\ \|\mathbf{A}\mathbf{f}_0 - \mathbf{g}\| & \text{for } \|\mathbf{C}(\mathbf{f} - \mathbf{f}_0)\|^2 \end{cases} \\ = \lim_{\gamma \rightarrow \infty} \|\mathbf{A}\mathbf{f} - \mathbf{g}\|. \quad (53)$$

In the range from 0 to ∞ for the regularization parameter, the norms $\|\mathbf{A}\mathbf{f} - \mathbf{g}\|$ and $\|\mathbf{f}\|$ are strictly monotonic (Fig. 1). The residual $\|\mathbf{A}\mathbf{f} - \mathbf{g}\|$ has its minimum always at $\gamma = 0$ and is monotonically increasing. Thus the solution \mathbf{f}_{ls} is always the minimal solution concerning the residual. The norm $\|\mathbf{f}\|$ has its maximum at $\gamma = 0$ and is monotonically decreasing (if $\|\mathbf{f}_{ls}\| \neq 0$).

There exist two principally different ways for the choice of the regularization parameter

- manual choice by interactive judgment of the solution on a graphic display for several values for γ
- postulation of an aim function for the appropriate optimal regularization parameter γ_{opt} , the choice of which can be automated by suitable search algorithms.

The manual choice of the regularization parameter is done in such a way that the user offers several values for the regularization parameter and judges the solution on a graphic display. The solution is evaluated subjectively by means of known as well as expected a priori properties (smoothness, number, and position of some peaks, monotony, positivity, and others) with simultaneous avoidance of oscillations, especially on the bounds of the integration region due to a regularization parameter selected too

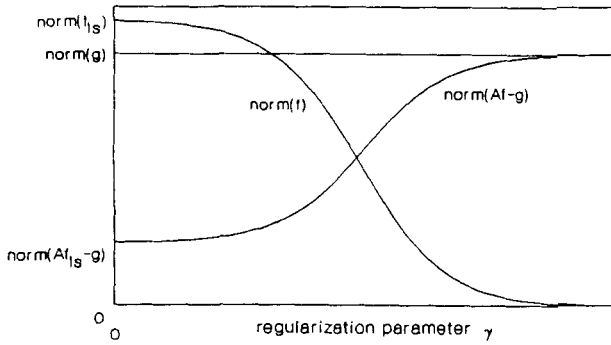


Figure 1. Change of the norm $\|f\|$ and the residual $\|Af - g\|$ with the regularization parameter.

small. Moreover, some numerically quantifiable properties of the solution like the residual $\|Af - g\|$, the norm over the solution $\|f\|$, the integral over $f(x)$ or others can be used for judging the solution.

The assumption of an aim function for calculation of the optimal regularization parameter γ_{opt} is an alternative way. One can distinguish between two principal ways of consideration. In the first one, the regularization parameter is understood as a Lagrange multiplier and in practice a new solution principle is formulated

$$\text{Minimize } \varphi(f, \gamma) \text{ with respect to } f \text{ and } \gamma, \quad (54)$$

where

$$\varphi(f, \gamma) = (\|Af - g\|^2 - S) + \gamma \|Cf\|^2. \quad (55)$$

The value of S is a lower limit for the residual to be fixed. Minimizing conditions

$$0 = \frac{\partial \varphi(f, \gamma)}{\partial f} \quad (56)$$

and

$$0 = \frac{\partial \varphi(f, \gamma)}{\partial \gamma} \quad (57)$$

yields the two simultaneous equations:

$$f = \{A^T A + \gamma C^T C\}^{-1} A^T g. \quad (58)$$

and

$$S = \|Af - g\|^2. \quad (59)$$

In comparison to the solution (25) for the common principle of regularization we have additionally the second condition (59) for our solution. But because the residual $\|Af - g\|$ is strictly monotonic with increasing regularization parameter, the solution can be found unproblematic in such a way that the regularization parameter started from 0 is increased as long that eq. (59) is fulfilled. This can be taken manually or with the help of a simple search algorithm. Due to this monotonic behavior, the problem of formulating the regularization parameter as a La-

grange multiplier can be attributed to the common regularization principle. The value for the error limit S must be found by the user.

A second way for the determination of an optimal regularization parameter consists of postulating of a functional for calculating γ_{opt}

$$\text{Minimize } \Omega(f(\gamma), \gamma) \text{ with respect to } \gamma, \quad (60)$$

where f is taken from eq. (25). The known proposals for γ_{opt} in the adsorption literature originated from Merz²¹ and Butler et al.,²⁷ and others, can be used. The problems associated with this determination of the optimal regularization parameter are due to the fact that instead of the true error functional

$$\Omega(f(\gamma), \gamma) = \|f_{\text{true}} - f(\gamma)\| \quad (61)$$

and because of the ignorance of f_{true} , one is forced to formulate a replaced problem (60). Therefore the statistical knowledge about the errors in the experimental data is utilized to solve this problem. For the applicability of a determination method for the optimal regularization parameter, it is finally important to know up to what extent the assumptions are correct in a given case. It can happen that the minimizing functional (60) in the range from 0 to 1 of the regularization parameter has no minimum or has more than one minima.²¹ Also it is possible that the found values for γ_{opt} can be too small or too large.²⁷

Up to now, a commonly applicable criterion for determination of the optimal regularization parameter is not known so that one is forced to the manual determination of the regularization parameter. But this way is reproached very often as a subjective one. In our opinion, this seems to be unjustified because in the case of use of a criterion for the optimal regularization parameter the subjectivity consists in the choice of such a criterion as well as in the validity of the contained statistics or other assumptions.

According to the authors's experience, the manual choice of the regularization parameter offers the utmost reliability to eliminate a subjectively falsified solution of the adsorption integral equations when simultaneously the known a priori information concerning the solution as well as the experimental errors of the data are taken into account.

At this point the description of the regularization method should be finished. The several variants of this method described, illustrate the complexity of solving Fredholm integral equations of the first kind by means of the regularization method. Nevertheless, such questions as the quadrature of integral equation (14), the use of iterative or adaptive regularization⁴¹⁻⁴³ and others were not considered here.

The application of the regularization method for solving the adsorption integral equations demands from the user a certain experience in dealing with such problems. The determination of the numerical

and physicochemical parameters, e.g.,

- Choice of the stabilizing term $\|Cf\|$,
- Choice of the regularization parameter,
- Choice of the used measurement points,
- Choice of the adsorption model and the appropriate parameters or
- Number of result points and the integration range

offer a very broad spectrum of possibilities. This fact makes a wide use of the regularization method in solution of the adsorption integral equations more difficult. However, due to the use of linear algebra methods, the regularization methods are much faster than most indirect solution methods, which are normally based on the solution of a nonlinear system of equations. Furthermore the regularization method, in comparison to the indirect methods, has some advantages because it does not make any assumptions of analytical forms for the desired solution and is applicable for any kind of adsorption model, even if there is no analytical or explicit form of the model.

In addition, the regularization method is the sole method, which takes into account the ill-posedness of the problem at all. Thus, it offers a maximum of objectivity concerning the desired information.

THE INTEG METHOD

The INTEG program was written for calculation of the distribution functions from the adsorption integral equations by one of the authors (M.v.Sz.). It uses the regularization principles (20), (38), (39), and (43) as well as the proposals (44) and (45) for selecting the matrix C . The regularization parameter can be chosen both manually and by means of search algorithms taken from the literature.^{8,21,36-40} In addition to the previous program developments known in the literature,^{24,26,31} the following improvements were carried out

1. The use of the positive definite matrix C for the stabilization of the solution by the regularization method fixes the rank of the matrix $\{A^T A + \gamma C^T C\}$ to the value $\min(m, n)$. This allows one to select the dimension $(m * n)$ as follows

$$m \stackrel{<}{>} n. \quad (62)$$

With respect to the evaluation of the experimental data this means that it is possible to calculate more points (n) than the number of experimental points (m) available. This is especially important for measurements with only a small number of the data points because the use of such small amount of the result points causes a very crude quadrature of the integral equation. An improvement of the quadrature by integration formulas of a higher degree like Simpson is not possible since the oscillations in the weights of these quadra-

tures are transferred to the result.¹⁴ For the quadrature of integral equations of the first kind, only the simple trapezoid or middle points rule and the piecewise use of the Tshebyshev approximation are suitable practically.

In contrast to the previous methods there are only a few changes if $m < n$. One has only to take care of a proper work of the singular value decomposition. Golub and Reinsch³³ already gave some suggestions in this matter. Besides this, it is noteworthy that the rank of the system is now only $\min(m, n)$.

Therefore, all summations, in which the singular values σ_i appear, can be carry out in the general case (62) only up to $\min(m, n)$. Thus the general solution has the form

$$f_i = \sum_{j=1}^{\min(m,n)} \frac{\sigma_j}{\sigma_j^2 + \gamma} s_{ji} l_{ij} \quad (63)$$

2. A connection of the regularization method with the NNLS method²⁸ was realized as well. In the iterative algorithm proposed by Lawson and Hanson, the linear problem for the positively fixed values of the solution f_p always has to be solved by

$$\text{Minimize } \|A_p f_p - g\| \text{ with respect to } f_p. \quad (64)$$

Replacing this step by the appropriate regularization problem

$$\text{Minimize } \|A_p f_p - g\|^2 + \gamma \|C_p f_p\|^2 \text{ with respect to } f_p. \quad (65)$$

one is able to get the best possible nonnegative solution of the regularization problem. The matrix C_p is constructed in the same way as A_p .^{28,29}

3. Up to this point the SVD of the matrix AC^{-1} always was used for calculating the solution f by selecting several regularization parameters. Moreover, there exists still another decomposition of this matrix to a bidiagonal form⁴⁴

$$P = AC^{-1} = U_1 \begin{bmatrix} B \\ 0 \end{bmatrix} V_1^T, \quad (66)$$

which is applicable to the regularization method very efficiently. The matrixes U_1 and V_1 represent orthogonal matrixes analogously with the SVD. The matrix B is a quadratic and bidiagonal matrix. The first step in the calculation of the SVD after Golub and Reinsch³³ consists even of this decomposition to a bidiagonal form. For that reason, this way to calculate the solution f can be regarded as an incomplete SVD.

The regularization problem (20) is transformed by putting in eq. (66) to the following form

$$\text{Minimize } \left\| \begin{bmatrix} U_1^T g \\ 0 \end{bmatrix} - \begin{bmatrix} B \\ \sqrt{\gamma} I \end{bmatrix} V_1^T f \right\| \text{ with respect to } f. \quad (67)$$

For the calculation of the solution \mathbf{f} for a certain value of an orthogonal matrix \mathbf{Q} constructed from $2n - 1$ Givens rotations⁴⁴ is determined so that

$$\mathbf{Q}^T \begin{bmatrix} \mathbf{B} \\ \sqrt{\gamma} \mathbf{I} \end{bmatrix} = \begin{bmatrix} \mathbf{B}_q \\ \mathbf{0} \end{bmatrix} \quad (68)$$

results with the bidiagonal matrix \mathbf{B}_q . By putting \mathbf{Q}^T in eq. (67) we get the solution*

$$\mathbf{f} = \mathbf{V}_1 \mathbf{B}_q^{-1} \mathbf{Q}^T \mathbf{U}_1^T \mathbf{g}. \quad (69)$$

The determination of a regularized solution after calculation of the matrixes \mathbf{U}_1 , \mathbf{V}_1 , and \mathbf{B} requires only a little more effort in comparison to the SVD. But on the other side, we have the advantage that the calculation time for the matrixes \mathbf{U}_1 , \mathbf{V}_1 , and \mathbf{B} takes only a fraction of the time that is needed to calculate the singular values σ_i of SVD. Therefore, if the singular values σ_i are not needed or the discrete regularization is not used, then the calculation of a regularized solution \mathbf{f} by means of the bidiagonal form is preferred as the obviously faster method.

4. In order to save programming expense some algorithmic simplifications were carried out. By means of the definition

$$\mathbf{z} = \mathbf{C}\mathbf{f} \quad (70)$$

and eq. (27) the regularization problem (20) can be changed to the uniform and equivalent form

$$\text{Minimize } \|\mathbf{P}\mathbf{z} - \mathbf{g}\|^2 + \gamma \|\mathbf{z}\|^2 \text{ with respect to } \mathbf{z}. \quad (71)$$

Because now \mathbf{f} is

$$\mathbf{f} = \mathbf{C}^{-1}\mathbf{z} \quad (72)$$

the matrix \mathbf{C} no longer appears explicitly. In the case of an analytic form of \mathbf{C}^{-1} the memory for this matrix can be saved too.

Furthermore the calculation of the SVD or bidiagonal form occurs in situ, and therefore occupies the same memory as the matrix \mathbf{P} . The matrix \mathbf{U} appears always only in the term $\mathbf{U}^T \mathbf{g}$. Therefore, it is no longer calculated separately but it is directly multiplied by $\mathbf{U}^T \mathbf{g}$ to save time. The matrix \mathbf{V} is calculated at the memory place of \mathbf{P} destroying it. Then, the calculation of the residual has to occur over the corresponding decompositions

$$\|\mathbf{A}\mathbf{f} - \mathbf{g}\| = \|(\Sigma^2(\Sigma^2 + \gamma \mathbf{I})^{-1} - \mathbf{I})\mathbf{U}^T \mathbf{g}\| \quad (73)$$

or

$$\|\mathbf{A}\mathbf{f} - \mathbf{g}\| = \|(\mathbf{B}\mathbf{B}_p^{-1}\mathbf{B} - \mathbf{I})\mathbf{U}_1^T \mathbf{g}\|. \quad (74)$$

The elaborated program INTEG is an algorithm for solution of adsorption integral equations. It pre-

sents a consequent application of the actual knowledge about the regularization method directed to the solution of Fredholm integral equations of the first kind. The best known adsorption models for describing the energetic or structural heterogeneities of adsorbents are already taken into account. Its extension to further adsorption models or to any other integral kernels is also possible because an appropriate interface is included.

For a further distribution of the regularization method, the authors are ready to place the elaborated program at disposal of the interested persons.* A publication of the part of the program concerning the regularization method is planned later.

INTEG runs on IBM PC® compatible computers under MS-DOS® or OS/2 and is written in the programmer's language C. The available base memory, as well as the number of the used measured points, determine the maximal possible number of result points. Using MS-DOS for about 30 measured points, the maximum number of the result points comes to about 150–200. The calculation time for one evaluation of 30 measurement points with 60 result points amounts to about 40 s for calculation of the singular value decomposition or only 15 s for the bidiagonal form and in both cases less than 1 s for calculating the solution by variation of the regularization parameter inclusive of its graphic presentation.† For the calculation of nonnegative solutions the needed calculation time for SVD as well as for the bidiagonal form has to be multiplied by the half of the number of result points in average.

APPLICATION TO ADSORPTION ISOTHERM DATA

The examples shown at this section illustrate only partially all possibilities of application of the regularization method for solving adsorption integral equations. The demonstration of the influence of some factors like the errors of the experimental data or the value of the regularization parameter on the solution is discussed extensively.

Simulated Isotherm Data

The use of the simulated isotherm data is a common procedure for verifying and testing numerical methods for solving the adsorption integral equations.^{8,13,21,23,24,26} The starting point for the use of simulated isotherm data is always the assumption of one or more distribution functions. This distribution

*In case of interest in the program INTEG contact the first specified author.

†All information about calculation time are referred to the speed of a standard IBM PC/AT running with 12 MHz and numerical coprocessor.

*Norms are invariant to the multiplication with orthogonal matrixes.

function is used to generate the theoretical isotherm on the basis of eq. (6) with an a priori assumption of an adsorption model to represent the local isotherm $\theta_i(x, y)$. The simulation of the experimental isotherms consists now in a disturbance of the theoretically calculated isotherm by distributed normally random errors. Thus, for a reproduction of the postulated distribution function the adsorption model and the expected distribution function are known a priori.

Figure 2(a) shows the postulated distribution function consisting of three Gaussian peaks used to calculate the simulated adsorption isotherms. This distribution function was already used (see Appendix A, eq. (A2) and Table I, type c of reference 13). The Langmuir equation was chosen for representing the local adsorption isotherm. On this basis analogously, as in the article (Appendix A, eq. (A8)–(A16) with (A5)), the theoretical isotherm for N_2 at $T = 140$ K was calculated for 25 pressure points. The calculated values are listed in Table I. The 25 data points are distributed nearly logarithmic over the pressure range from 10^{-4} to 10^4 Torr, which can be covered by most experiments. Then, this theoretical isotherm was disturbed by normally distributed random errors with the fixed average values (0.1, 1.0, 10.0%). Figure 2(b) shows the theoretical isotherm

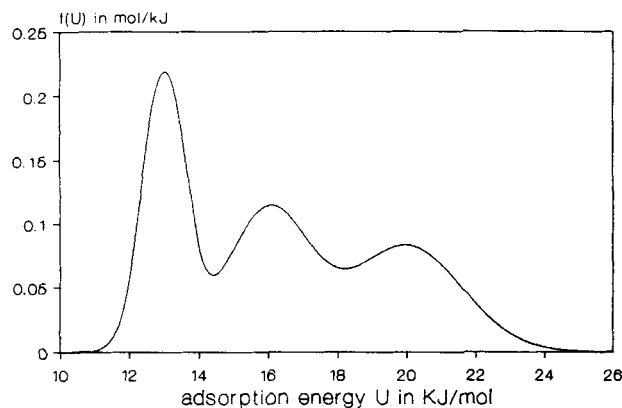


Figure 2(a). Postulated adsorption energy distribution.

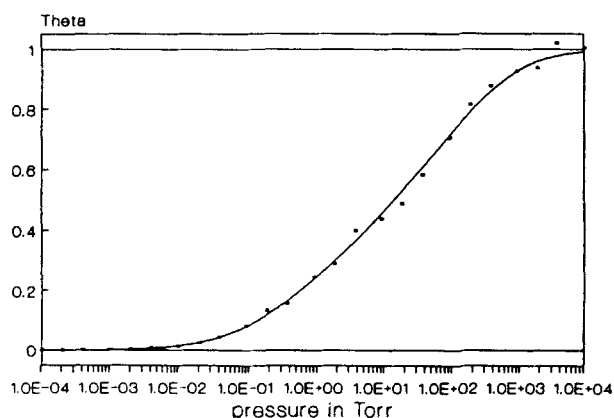


Figure 2(b). Theoretical adsorption isotherm calculated from the postulated adsorption energy distribution.

as a line and the simulated points with an average error of 10%. As is often observed in practice, the theoretical isotherm does not show any steps, which could suggest the existence of some peaks in the adsorption energy distribution. In Figure 3(a) and 3(b) the reproduced distribution functions from the theoretical isotherm (without simulated experimental errors) obtained by the use of the common least squares method are presented without (Fig. 3(a)) and with (Fig. 3(b)) restrictions to nonnegative values of the distribution functions. The dotted curve in Figure 3(b) shows the postulated distribution function. These figures prove convincingly that the sole use of the least squares methods is insufficient for solving the adsorption integral equations.

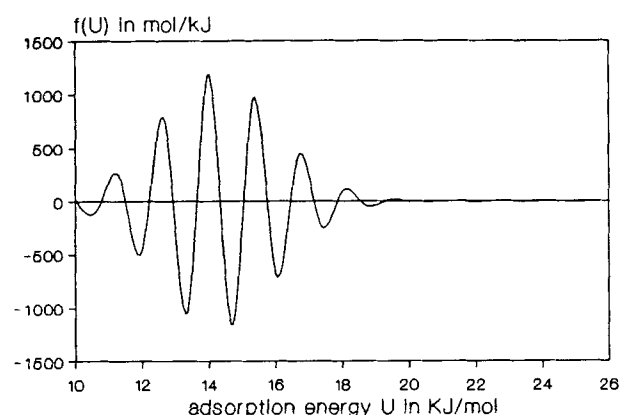
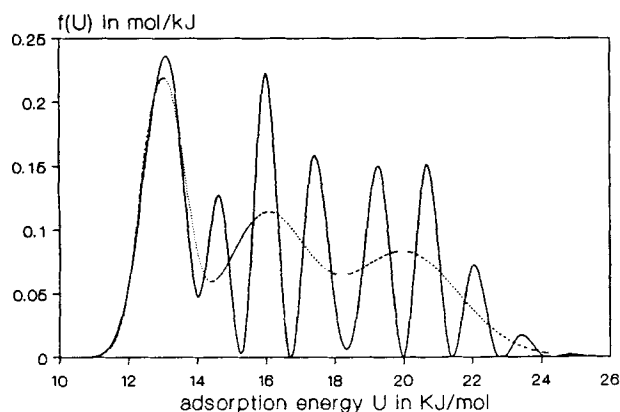
To some extent Figures 3(a) and 3(b) represent limits of the regularized solutions of the adsorption integral equations for $\gamma \rightarrow 0$. At this point it is necessary to discuss a general behavior of the calculated distribution functions in dependence on the regularization parameter. This behavior changes when additional restrictions of the solution region are made. In the case of the common regularization (eq. (20)), we found almost always strong oscillations on the distribution function for any regularization parameter, which is smaller than the maximal digit accuracy used in the calculation. These extreme oscillations are normally caused by numerical roundoff errors. They disappear very rapidly on increasing regularization parameter and the obtained distribution functions become smoother. When the isotherm data are adequately represented by the selected adsorption model, negative points in the distribution functions appear only very seldom. It can happen that near a very sharp peak the obtained distribution function has a very small peak in the negative range. This is commonly observed and is caused by the smoothing properties of the integral equations. The appearance of stable oscillations in the distribution function, which cover the negative range even when the regularization parameter is chosen relatively large, should be understood always as a clear indication to a nonadequacy between the isotherm data and the chosen adsorption model.^{21,45} In the case of the regularization principle (43), called the nonnegative regularization, we found that the behavior of the solution on the regularization parameter is very different from that of the common regularization. Due to the restriction of the solution region to the nonnegative values, the calculated distribution functions are relatively stable even at very small values of the regularization parameter. Whereas, for the common regularization we observed many of peaks resulting from the oscillations, but their negative parts have been suppressed. The obtained peak heights correspond to the expectations (compare with Figure 3(b)). Only when the regularization parameter is a few levels higher than that used for the common regularization, do these peaks disappear. Above this regu-

Table I. Theoretical adsorption isotherm for the postulated energy distribution consisting of three Gaussian peaks (Fig. 2(a)).

Number	p (Torr)	$\theta_i(p)$	Number	p (Torr)	$\theta_i(p)$
1	1×10^{-4}	1.6705×10^{-4}	14	2	0.29669
2	2×10^{-4}	3.3322×10^{-4}	15	4	0.36140
3	4×10^{-4}	6.6297×10^{-4}	16	10	0.45392
4	1×10^{-3}	1.6330×10^{-3}	17	20	0.52869
5	2×10^{-3}	3.1932×10^{-3}	18	40	0.60666
6	4×10^{-3}	6.1396×10^{-3}	19	100	0.71282
7	1×10^{-2}	1.3991×10^{-2}	20	200	0.79134
8	2×10^{-2}	2.4983×10^{-2}	21	400	0.86094
9	4×10^{-2}	4.2529×10^{-2}	22	1000	0.92870
10	1×10^{-1}	7.8828×10^{-2}	23	2000	0.96029
11	2×10^{-1}	0.11720	24	4000	0.97887
12	4×10^{-1}	0.16417	25	10000	0.99119
13	1	0.23638			

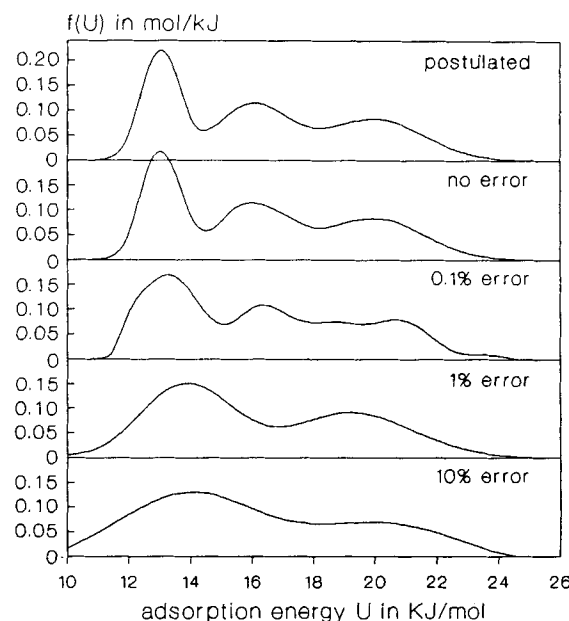
larization parameter the non-negative regularization behaves similar to the common regularization. In the case when a non-negative distribution function is calculated by the common regularization method absolutely the same result will be obtained with the non-negative regularization.

Figure 4 shows the distribution functions with 3

**Figure 3(a).** Reproduced adsorption energy distribution from the theoretical adsorption isotherm using the least squares method.**Figure 3(b).** Reproduced adsorption energy distribution from the theoretical adsorption isotherm using the nonnegative least square method in comparison with the postulated distribution (...)

peaks reproduced from the simulated isotherms with 0, 0.1, 1, and 10% error by means of the nonnegative regularization method. It turns out:

1. The reproduction of the postulated distribution function from the theoretical isotherm without experimental errors occurs with nearly complete agreement.
2. The resolution decreases as the experimental errors increase. Closely neighbouring peaks overlap and form peaks with decreasing peak heights.
3. The values of the regularization parameter required for a sensible solution increase with increases in experimental error. The used regularization parameters were 10^{-10} , 10^{-5} , 10^{-3} , and 3×10^{-2} .

**Figure 4.** Reproduced adsorption energy distribution from the simulated adsorption isotherm with random errors of 0, 0.1, 1, and 10% using nonnegative regularization method in comparison to the postulated adsorption energy distribution.

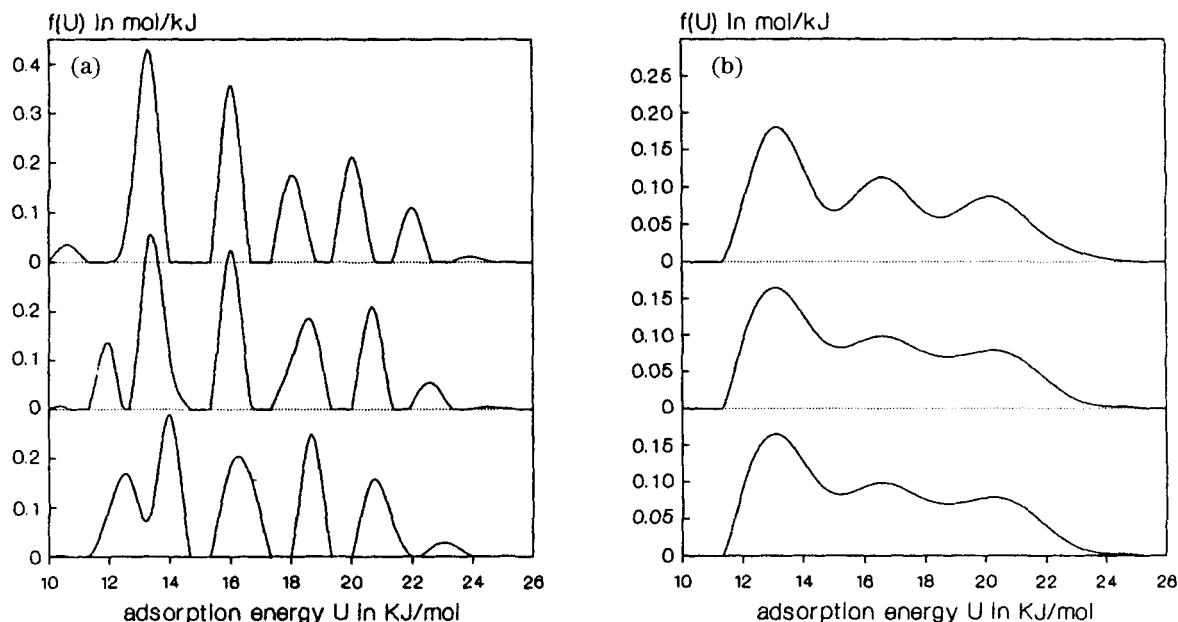


Figure 5. Reproduced adsorption energy distribution from three, irrespective of each other, simulated adsorption isotherms with 0.1% random errors using the nonnegative condition with the least squares method without regularization (Fig. 5(a)) and nonnegative regularization method (Fig. 5(b)).

The intention of Figure 5 is to demonstrate the danger of the sole use of the NNLS method for solution of the adsorption integral equations. For illustration, three isotherms with 0.1% error in each case were simulated from the theoretical isotherm. Figure 5(a) shows the results of calculation using the NNLS method without regularization. Each simulated isotherm yields a different solution. Moreover, more peaks are obtained than are postulated. Using the regularization method (Fig. 5(b)) all three simulated isotherms yield comparable results. Thus, it has to be stated that up to a certain degree the host of peaks in the distribution functions obtained by use of the NNLS Method,^{24,29,46} is only a reflection of the random experimental errors in the investigated isotherms. Also, on the basis of extensive applications of the nonnegative regularization it is apparent that the value of a sensible determined regularization parameter by this method differs hardly from that chosen by common regularization. Accordingly, in most cases the distribution functions obtained by both methods are very similar. Insignificant values of the function obtained by the common regularization are suppressed using the nonnegative regularization, which does not change significantly the result in the positive region. So a basic improvement of the results in comparison to the common regularization method can not be expected by use of the nonnegative regularization method. Some improvements are possible with regard to the adequacy between the adsorption model and experimental data, but the restriction to nonnegative results makes it more difficult to recognize a possible inadequacy. Therefore, an exclusive use of the nonnegative regularization method should be avoided.

All previous examples simulated the real experimental situation exclusively by application of random errors to a theoretical isotherm. But often, we find experiments in which only a few measuring points are employed or in which only a restricted pressure range is measured. The influence of both these experimental restrictions on the reproduced distribution function is shown in Figure 6. In the first case only each second isotherm point was used for the

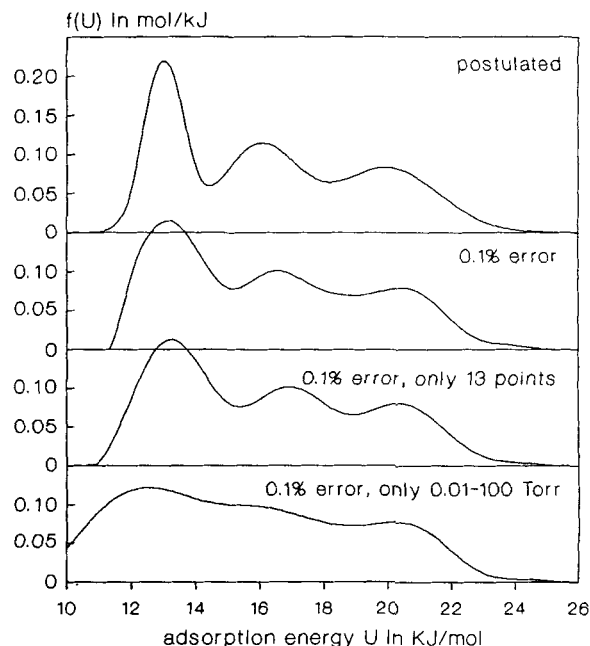


Figure 6. Reproduced adsorption energy distribution from the simulated adsorption isotherm with 0.1% errors and restricted number of isotherm points using the nonnegative regularization method.

calculation. The influence on the result is not large, because the recorded range of $\theta_i(p)$ by this restricted number of the measured points encompasses the same coverage region (compare Table I) as before. In the case of the restricted pressure range sample from 0.01 to 100 Torr, $\theta_i(p)$ includes only 1.4–71.2% of the maximal adsorbed amount. The resolution in this case is considerably worse. Especially, the low energy peak is strongly influenced. This is understandable when one keeps in mind that the low energy adsorption sites are occupied at higher coverages. In addition to the requirement for higher accuracy of adsorption experiments, it is recommended that adsorption isotherms be measured over a wide range of coverages. This demand is especially important for the range of small amounts adsorbed in micropores of solid adsorbents.

With Figure 7 we want to return again to the question of the resolution of the calculated distribution functions from the adsorption integral equations. For this purpose, distribution functions with five and seven peaks (Langmuir model for nitrogen adsorption at 78 K) were postulated in a relatively close range of the adsorption energy. The simulated experimental errors are one order of magnitude less than in Figure 4. The reproduced distribution functions show a good agreement with the postulated distribution functions when the data are free of errors. But in the error range, which is to be expected for the real experimental isotherm data of above 0.1%, the resolution is significantly worse as already observed elsewhere.²³ Therefore, the search for a large number of peaks in adsorption energy distributions and their interpretation seems to be doubtful.

Experimental Adsorption Isotherms

Application of the regularization method to experimental data is illustrated by using the adsorption isotherms of nitrogen at 77 Kelvin on the carbon blacks: Spheron, Spheron heated at 800°C, Graphon and Sterling measured by Wesson.⁴⁶ These data were already investigated in several articles,^{24,26,29} so that a comparison with these results is possible.

First, let us regard in detail the situation of analysis of the experimental data using the regularization method. During the treatment of the simulated isotherms it was always possible to compare the obtained distribution function with the postulated one. In the case of analysis of the real experimental data only small possibilities exist for judgment of the results. Here, one must distinguish between additional information, which is known for the experimental data, and the information about the expected distribution function.

As regards the experimental data, we have certain information in those cases about their average error. The deviation between the experimental data and the calculated points using eq. (6) with the obtained distribution function should have the same order as these errors; its small value suggests that the regularization parameter is chosen too small. A distinctly larger value indicates a nonadequacy between the experimental data and the selected adsorption model. But mostly we have no information about the average error of the experimental data. In this case, one is forced to judge the result on the basis of general properties of the experimental data. For instance, in gas adsorption the isotherms are always

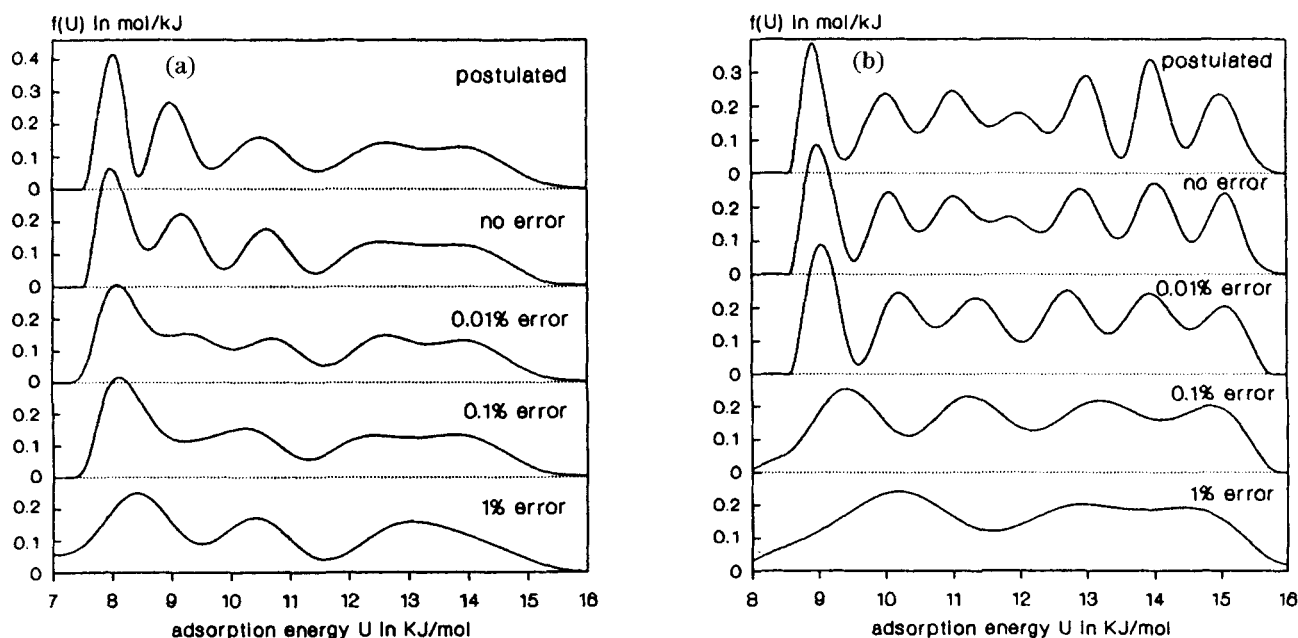


Figure 7. Reproduced adsorption energy distribution from the simulated adsorption isotherms and with random errors of 0, 0.01, 0.1 and 1% using the nonnegative regularization method in comparison to the postulated adsorption energy distributions with five (Fig. 7(a)) or seven peaks (Fig. 7(b)).

monotonically increasing. This monotony of the experimental data is often violated by their errors when closely neighbouring points are measured. The isotherm generated by the obtained distribution function (eq. (6)) should have a monotonically increasing curve again. Otherwise, the calculated distribution function contains information generated by the experimental errors.

Besides the residual $\|\mathbf{Af} - \mathbf{g}\|$ there are some other numerically quantifiable properties of the obtained solution \mathbf{f} . A useful quantity is the relative mean error^{26,29}

$$\delta = \frac{1}{m} \sum_{i=1}^m \left| \frac{g_{\text{calc},i} - g_i}{g_i} \right|, \quad (75)$$

where

$$\mathbf{g}_{\text{calc}} = \mathbf{Af}. \quad (76)$$

Compared to the residual $\|\mathbf{Af} - \mathbf{g}\|$ the relative mean error covers a range, which is easier to handle. For extreme small values of g_i , the relative mean error is strongly oscillating and is not useful.

In addition to the comparison with experimental data, the a priori information concerning the expected distribution function can be used, e.g., information about the number and position of individual peaks, monotony, smoothness, positivity, or the integral over the expected distribution function.

All these possibilities to judge the obtained distribution function can be used to select a sensible value of the regularization parameter. A disagreement with the expected a priori information gives a

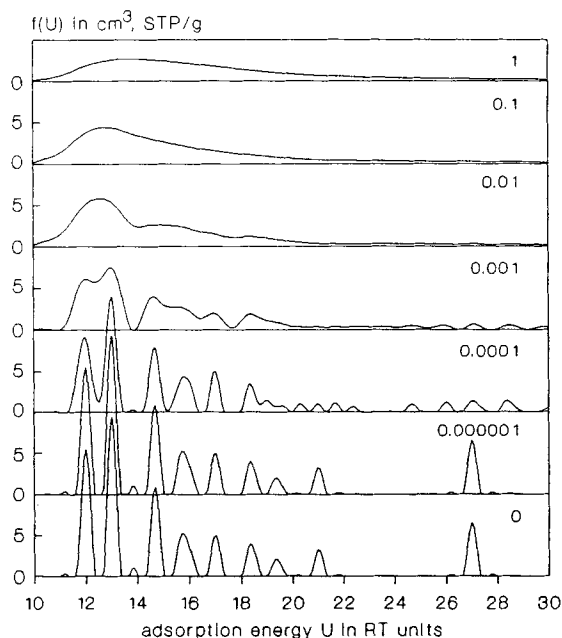


Figure 8. Evaluated adsorption energy distributions from the experimental nitrogen adsorption isotherm on Spheron calculated by means of the nonnegative regularization method for different values of the regularization parameter.

Table II. The residual $\|\mathbf{Af} - \mathbf{g}\|$, V_m and δ of the calculated distribution functions for Spheron for different values of the regularization parameter γ .

γ	$\ \mathbf{Af} - \mathbf{g}\ $ (cm ³ , STP/g)	V_m (cm ³ , STP/g)	δ (%)
0	0.888	26.06	1.399
10 ⁻⁶	0.888	26.06	1.400
10 ⁻⁴	0.900	26.15	1.412
10 ⁻³	0.928	26.28	1.431
10 ⁻²	1.008	26.90	1.511
10 ⁻¹	1.750	25.50	2.344
1	1.967	21.22	10.638

suggestion concerning nonadequacy of the chosen adsorption model with all or only certain experimental points. But the reverse of this statement is *not* true. An observed adequacy between the adsorption model and the experimental data has a purely numerical character. So it happens, for example, that the Langmuir adsorption isotherm can be evaluated under the assumption of the homotactic-patch approximation with the Fowler–Guggenheim adsorption model without any violation of the expected a priori information. The obtained distribution function is only shifted to lower energy values. The numerical mathematics, in our case the regularization method, can indicate when a model is not adequate, but other cases require careful physicochemical considerations. For that reason, questions associated with the influence of an incorrect adsorption model are not part of this article. In the authors' opinion this is not a numerical problem.

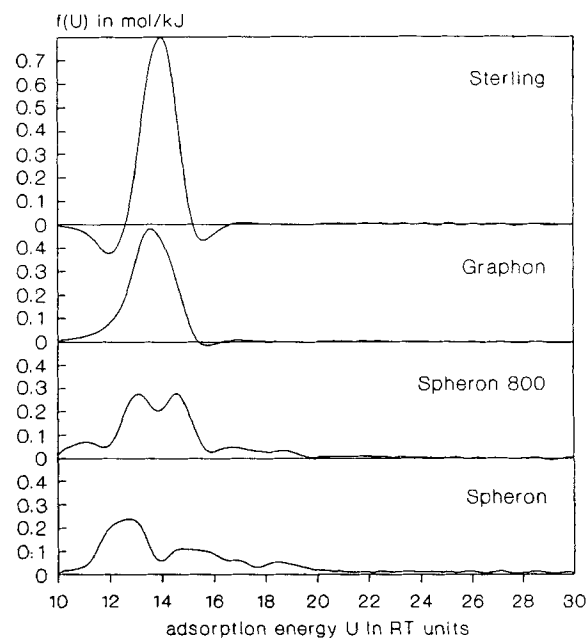


Figure 9. Calculated adsorption energy distributions from the experimental nitrogen adsorption isotherm on Spheron, Spheron 800, Graphon, and Sterling calculated by means of the common regularization method with the maximum of possible result points.

Table III. The used parameters for calculating $f(U)$ and the obtained values for residual $\|Af - g\|$ and V_m .

	n	m	Δ (RT)	γ	$\ Af - g\ $ (cm ³ , STP/g)	δ (%)	V_m (cm ³ , STP/g)
Speron	39	101	10–30	0.002	0.957	1.46	26.76
Spheron-800	60	101	10–30	0.002	1.438	2.86	26.08
Graphon	56	101	10–30	0.002	1.020	2.96	34.48
Sterling	49	101	10–30	0.002	0.155	4.74	3.086

Analysis of the experimental data was carried out analogously as in references^{24,26,29,46} by using the virial equation to represent the local isotherm $\theta_i(x, y)$ in eq. (6). The isotherm points were taken from reference 26. But the received values with CAESAR²⁶ for δ could not be confirmed by us using the regularization method. Also an extension of the upper boundary of the adsorption energy interval Δ to 30 RT was necessary. A hint to this is given especially by the isotherm on Spheron, which already at a pressure of only 1×10^{-3} Torr exhibits a significant adsorption.

Figure 8 shows the obtained distribution functions for Spheron using the nonnegative regularization method for several values of the regularization parameter. In Table II the appropriate values for the residual $\|Af - g\|$, the integral $V_m = \int_{\Delta} f(x) dx$ and δ are specified. It can be clearly seen that for $\gamma \leq 1 \times 10^{-4}$ a relatively stable solution is obtained. This means, as already shown in Figure 5, that only a reflection of the experimental errors although the calculated values for the residual are quite realistic. If we use the common regularization method, then the appearing oscillations cover widely the negative region and the obtained values for the residual $\|Af - g\|$ and δ are some orders less than expected. The solutions obtained for $\gamma \geq 1 \times 10^{-2}$ seem to be too smooth and the values of δ too high. Thus, the most acceptable solution should be found in the range of the regularization parameter between 1×10^{-4} and 1×10^{-2} . The GCV criterion proposed by Merz²¹ for finding the optimal regularization parameter yields $\gamma_{opt} = 3 \times 10^{-3}$. For that reason, as in many other cases, only a subjectively manual choice of the regularization parameter is possible.

Figure 9 shows the calculated distribution functions for all four isotherms⁴⁶ using the common regularization method. The regularization parameter was determined manually for all adsorbents to 2×10^{-3} . It is often found that experimental data measured under the same experimental conditions require similar regularization parameters. Table III shows the parameters employed and the obtained values for the residual $\|Af - g\|$ and V_m .

In spite of a certain subjectivity during the determination of the regularization parameter it appears that the number of significant peaks in the adsorption energy distribution for these adsorbents is less than previously found.^{24,26,29} Beyond it, the obtained results bear a great likeness to the results with

CAEDMON using the virial equation calculated by Wesson.⁴⁶ Meantime, the expected degradation of the energetic heterogeneity in the sequence Spheron, Spheron-800, Graphon, and Sterlin caused by their preparation is confirmed by the results shown. The appearance of negative regions in the distribution function for Sterling suggests that the virial equation gives only an approximate representation of the local isotherm.

CONCLUSIONS

The examples presented in this article prove unambiguously the applicability of the regularization method for solving adsorption integral equations. The information provided by the distribution function depends strongly on the experimental errors and on the range of the measured adsorption isotherm. In many practical cases, only limited information can be expected.

With the regularization method the user possesses a sufficiently exact and model-independent numerical technique for studying adsorption integral equations with any adsorption model. The formulation and the application of adsorption models as local isotherms can occur without further consideration of the analytical solvability of the integral equation or other special numerical questions. The use of the regularization method for solving adsorption integral equations should facilitate the physicochemical studies of adsorption on heterogeneous adsorbents.

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