Obtaining Precise Parameter Estimates for Nonlinear Catalytic Rate Models

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A method is reviewed which allows data points to be chosen in such a fashion that precise estimates of the parameters in nonlinear reaction rate models can be obtained. This method allows each future data point to be selected such that the confidence region of the estimated parameters is smaller with it than with any other possible data point within the region of experimentation. This procedure is applied for Hougen-Watson models with hypothetical experimental data which were generated with the guidance of an example from the current chemical engineering literature. It is found that, for the same number of data points, the parameters in the model can be estimated eighteen times more precisely by using this suggested experimental design than by another commonly used design. Confidence regions are presented for the parameters of the Hougen-Watson models with two types of designs.

It is found that the positions of the data points in the well-designed experiments are more sensitive to the functional form of the model than to the current estimates of the magnitudes of the parameter values.

An experimenter in heterogeneous catalysis frequently is called upon to produce a mathematical model giving the reaction rate as a function of temperature and the partial pressures of the reaction components. He is faced with a dual problem: obtaining the correct functional form of the model and then reporting the best estimates of the parameters within the model. The first part of the problem has been discussed, among other places, in references *1*, *2*, and 3. This paper is concerned with obtaining good parameter estimates for nonlinear catalytic rate models. Since Hougen-Watson (Langmuir-Hinshelwood) models (*4*, *5*) have been used often for describing and interpreting catalytic rate data, these models will be utilized here.

An experimental design technique is to be reviewed which allows parameter estimation with a smallest volume of their joint confidence region. The procedure is to be demonstrated by hypothetical data generated with the guidance of an example from the 1962 chemical engineering literature. Confidence regions are to be presented for the parameters of a Hougen-Watson model for data generated by a one-factor-at-a-time design and that generated by the minimum volume design.

NATURE OF CONFIDENCE REGIONS FOR HOUGEN-WATSON MODELS

The nature of the confidence regions commonly associated with parameter estimation for Hougen-Watson models is frequently not entirely appreciated. A typical region for this model is shown in Figure 1 and is characteristically large and attenuated. This shape implies that the parameter values are poorly estimated; a small spherical shape is more desirable. The long, narrow shape of the region in Figure 1 results primarily from important covariance terms, that is, a high degree of correlation among the various parameter estimates. One practical implication of this high correlation is that, if a high value of one parameter is inadvertently chosen, this value can be balanced in a fitting procedure by a suitable choice of compensating values of the other parameters. The overall fit of the equation to the data will then be nearly as good as that obtained by using the best estimates of the parameter values. For example, rates calculated for parameter values corresponding to the apparently distant points *C*, *D*, and *E* of Figure 1 are compared in Figure 2. It can be seen that little difference in predicted rates is obtained. This condition is evident from a qualitative examination of Figure 2. Since the exact position of the maximum and the behavior of the curve at pressures higher than the maximum are not defined by experimental data, many combinations of parameter values can produce predicted rates near the existing data points.

In general, an unsatisfactory confidence region such as that in Figure 1 can result partly from a poor experimental design (that is, plan of experimentation) and partly from the model itself. Box (*6*) has discussed this latter contribution due to the model form. It is pointed out that the large attenuated shape of the confidence region can be due to the inherent functional form of the model under investigation. A particular model leading to such difficulties was

$$r = \frac{1 + K_1 x_1}{K_2 + K_3 x_1} \qquad (1)$$

It has also been indicated from a geometrical point of view why this behavior might be expected (*7*).

It is of interest, however, to minimize these difficulties through an efficient and effective experimental design. Blakemore and Hoerl (*2*) discussed the use of fractional factorial designs in the context of fitting nonlinear rate equations. For the comparison of designs, they defined a "usefulness of experimentation" as $\sqrt{\Sigma(x_i - \bar{x}_i)^2}$, which

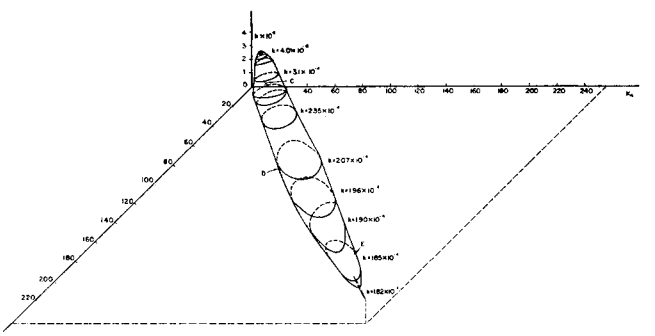

Fig. 1. Approximate confidence region of parameters from one-variable-at-a-time design.

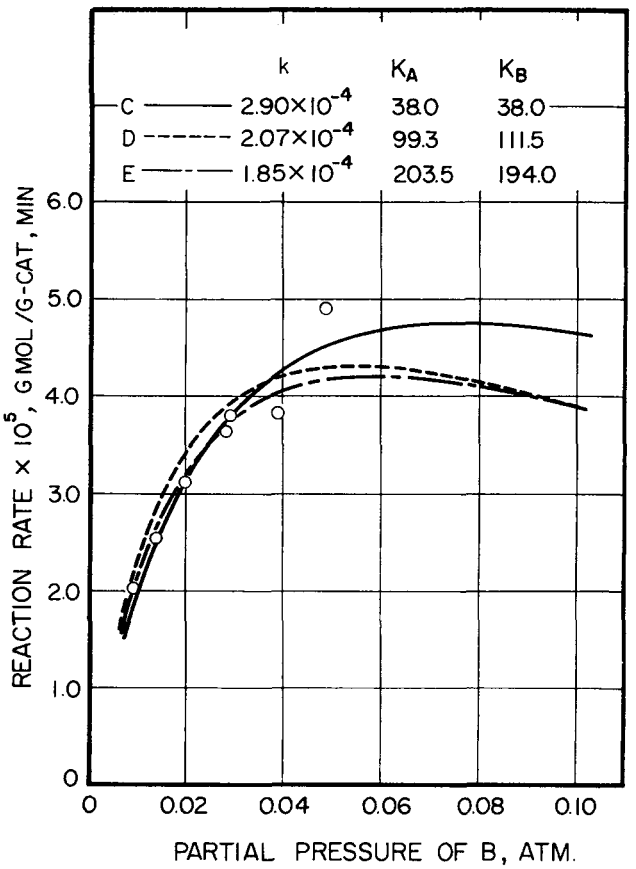

Fig. 2. Predicted and observed rates for different parameter estimates.

is approximately inversely proportional to the standard deviation of the estimated parameters of a linear model. This quantity was about twice as great for factorially designed experiments as for undesigned experiments. In other words, the same degree of knowledge of the parameter values could be obtained with about one-half the number of data points by using a fractional factorial design rather than by carrying out undesigned experimentation. However, one might expect to obtain even better results if a design were selected to accomplish the particular task of yielding, for nonlinear models, parameter estimates possessing a desirable confidence region.

One criterion for this type of design, which has been suggested by several authors, is to choose the data points in such a fashion that the volume of the joint confidence region of the estimated parameters is minimized. This seems to be a reasonable criterion, but certainly cases may arise when the best design does not meet this minimum volume criterion. For example, a spherical region may in some cases be preferable to a highly elongated ellipsoid of a slightly smaller volume. Thus, this criterion is not applicable in all situations and perhaps should be used with some other criteria to provide a better compromise design. Several other design criteria have been reviewed by Box and Hunter (8). Although the volume minimization is probably not the ultimate criterion, it is certainly an attractive design procedure and also is one of the most fully developed in a practical sense. This criterion will be used in this paper.

MINIMUM VOLUME DESIGN CRITERION

Suppose that after suitable model-building experiments have been carried out, a given nonlinear model has been singled out as being adequate. Furthermore, suppose that it is desired to obtain estimates of the parameters **K** in this known reaction rate model:

$$r = g(x_1, x_2, \ldots, x_m; K_1, K_2, \ldots, K_p) \qquad (2)$$

or, more compactly

$$r = g(\mathbf{x}; \mathbf{K})$$

Suppose also, as is usually the case, that the space of the experimental variables is limited to some particular region of experimentation. For example, a reaction temperature may be restricted to lie between the ignition temperature and the temperature at which the reaction becomes uncontrollable. Alternatively, the upper bound may be the temperature at which the product decomposes, at which point operations become economically unfeasible.

Let the partial derivative of the nonlinear rate expression of Equation (2) with respect to any parameter K_i evaluated at the u^{th} set of experimental conditions and taken at some set of parameter values $\mathbf{K}_o$ be given by g_{iu}. That is

$$g_{iu} = \left[\frac{\partial g(\mathbf{x}_u; \mathbf{K})}{\partial K_i} \right]_{\mathbf{K}=\mathbf{K}_o} \qquad (3)$$

As an illustration of the form of this derivative consider a rate expression of the form

$$r_u = K_1 p_{Au}^{K_2} p_{Bu}^{K_3} \qquad (4)$$

This derivative would correspond to, for example

$$g_{2u} = \left[\frac{\partial r_u}{\partial K_2} \right]_{\mathbf{K}=\mathbf{K}_o} = K_{1o} p_{Au}^{K_{2o}} p_{Bu}^{K_{3o}} \ln p_{Au} \qquad (5)$$

Note that this derivative *is* generally dependent upon both the parameter values and the settings of the independent variables. The matrix of these derivatives, which will contain N rows (observations) and p columns (parameters), may be written:

$$\mathbf{G} = \{g_{iu}\} \qquad (6)$$

Box and Lucas (4) have indicated that, under certain plausible assumptions, a choice of experimental points which will maximize the determinant of **G'G** (**G** transpose **G**) will also be that choice of data points which will minimize the volume of the joint confidence region of the parameters. The square root of this determinant is, in fact, inversely proportional to the volume of the joint confidence region. For their examples, the problem was restricted to one in which the number of experimental runs was equal to the number of parameters to be estimated. Behnken (9) employed two point designs of this nature to estimate copolymer reactivity ratios containing two parameters.

Box and Hunter (8) arrived at essentially the same criterion as did Box and Lucas by using a Bayesian ap-

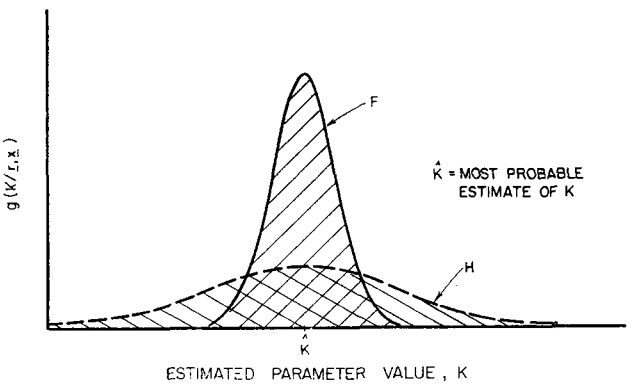

Fig. 3. Possible distributions of estimated parameter values.

proach, in which the most desirable posterior distribution was taken to be that which yielded the maximum posterior density for the most probable values of the parameter estimates. In other words, if it is desired to obtain a distribution of the parameters about the point estimate approaching the nature of distribution F instead of distribution H of Figure 3, one should choose an experimental design which maximizes the determinant of G'G. Distribution F is, of course, generally more desirable than distribution H, since the parameters would be more precisely defined in distribution F.

Now only the question of how to maximize the determinant of G'G remains. It has been pointed out that this determinant will, in general, be a function of all the parameters **K** and the experimental variables **x**. Of course, the true values of the parameters which are to be estimated are not known, so it has been suggested (7) that the best available estimates of the parameters could be used in place of their true values. In addition, a sequential scheme has been suggested (8) for using these best estimates to arrive at a good design. The sequential approach, for a limited number of parameters, involves calculating the determinant at every point on a grid in the space of the independent variables (see Figure 4) and obtaining the coordinates at which the maximum occurs. Then, one can run the next experiment at this point, get new estimates of the parameters by using this latest run in addition to the others, and find the maximum determinant for the next experiment to be run. This procedure can be continued until the desired number of experiments has been completed.

APPLICABILITY OF DESIGN PROCEDURE TO KINETICS

Before this design procedure can be useful to chemical engineers interested in obtaining optimum estimates of the parameters in Hougen-Watson models, one main point should be investigated. In view of the additional difficulty necessary to select experimental designs in this fashion, one must determine the approximate magnitude of the expected decrease of the volume of the confidence regions below the volume of the region expected with conventional experimental designs. One would then be in a position to judge whether the volume decrease is worth the investment and effort, and hence whether this procedure is profitable. The result of the comparison is, of course, somewhat dependent upon the model under consideration but some light may be thrown upon the question for Hougen-Watson models by means of a practical example. This approach also indicates the shapes and sizes of the confidence regions to be expected with Hougen-Watson models.

It should be apparent at this point that estimates of the true parameters, which are subject to experimental error, must be inserted into the G'G matrix for calculational purposes. Thus, for practical applications, one must be concerned with the sensitivity of the choice of the next experimental point to these parameter estimates. For example, if the regions of the experimental variables in which the points were to be taken were more dependent upon the functional form of the model than upon the actual parameter values, one could use this design criterion with some confidence and not be too concerned about temporarily poor parameter estimates. On the other hand, if the choice of the next experimental point were to depend heavily upon the particular values of the parameter estimates, one might either use this method after numerous experimental points were taken and the parameters already relatively well-defined, or one might wish to discard the design criterion altogether.

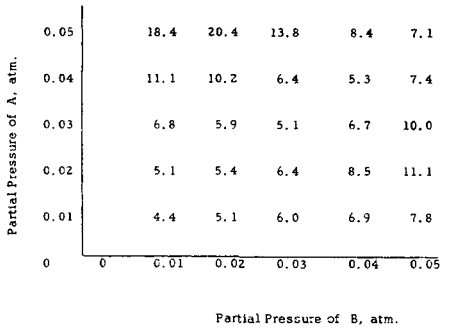

Fig. 4. Matrix of determinant values for minimum volume design, $|G'G| \times 10^{27}$.

An initial examination of this point has indicated that the regions of experimentation selected by this criterion are remarkably insensitive to deviations of the parameter estimates from the true parameter values. In a hypothetical example, of course, one could examine the degree of this insensitivity in one of two ways. Different initial estimates could be selected for a given set of true parameter values in the model. The procedure described in this paper could be applied, the results could be compared for the various initial estimates, and any differences could be observed. A sensitivity study of this type could also be applied to an experimental system. An equivalent procedure which is computationally easier and which takes advantage of the hypothetical nature of the example, however, is to select one group of initial estimates and to vary the true parameter values of the reaction rate model in the computer program. This latter procedure was applied in this particular case. It was found that the regions of the experimental space within which the observations fell were identical regardless of the magnitudes chosen for the true parameter values in the reaction rate model. Thus, it would appear that one need not be overly concerned about the initially poor parameter estimates. These results are presented in Appendix A.*

This insensitivity of the desirable regions of experimentation to the current estimated parameter values suggests the possibility of choosing several experimental points at a time before reestimating the parameter values. Appendix B* presents the results of several case studies of hypothetical data in which the reestimation of the parameters was delayed for several data points rather than being carried out after each individual data point is taken. This delay in the reestimaton did result in a slight decrease in efficiency. However, the volumes of the joint confidence regions were nearly identical regardless of whether the parameters were reestimated after each of twelve data points were taken or only after the fourth and the twelfth data points were taken.

EXAMPLE

The reaction to be simulated is the reduction of nitric oxide, data for which were presented by Ayen and Peters (10). The experiments in the study by Ayen and Peters were conducted over a solid catalyst under conditions such that no appreciable reverse reaction took place. The gaseous reaction was

$$NO + H_2 \rightleftharpoons H_2O + \frac{1}{2}N_2$$

or in abbreviated form

$$A + B \rightleftharpoons R + \frac{1}{2}S \qquad (7)$$

* Due to the necessarily qualitative nature of Appendices A and B, the details of the two studies are not included here. Rather, Appendices A and B have been deposited as Document No. 8549 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

A reasonably satisfactory Hougen-Watson mechanism found by Ayen and Peters was the reaction between an adsorbed nitric oxide molecule and one adjacently adsorbed hydrogen molecule, thus generating the model

$$r = \frac{kK_AK_Bp_Ap_B}{(1 + K_Ap_A + K_Bp_B)^2} \qquad (8)$$

In this particular study it was desired to illustrate clearly the design method presented here and to provide some insight into the type of confidence regions to be expected for the parameters in Hougen-Watson models. Also, in assessing the applicability of this method to chemical engineering problems, it was desirable to have a knowledge of the true values of the parameters being estimated. Consequently, it was felt that hypothetical data generated to follow the behavior of an actual experimental system would best suit these purposes. The hypothetical data points utilized in this example were constructed by using $k = 4.94 \times 10^{-4}$ g.-mole/(g.-catalyst)(min.), $K_A = 14.64$ atm.$^{-1}$, and $K_B = 19.00$ atm.$^{-1}$ as the true parameter values in Equation (8). These numerical values were obtained by conducting a nonlinear least squares analysis of the date reported by Ayen and Peters (*10*) at the 375°C. level. To the rate values thus obtained was added independent normal error with variance equal to 9.508×10^{-12} [g.-mole/(g.-catalyst)(min.)]^2. This corresponds to the residual mean square using all the data of the original paper.

Inadequate Design

The one-variable-at-a-time design used by Ayen and Peters (*10*) was first examined to obtain the associated confidence region. The partial pressures and the reaction rates reported by these authors and the hypothetical reaction rates generated at these conditions are shown in Table 1.* A nonlinear least squares analysis of these data yielded the results shown in Table 2. In Table 2, the determinant of the G'G matrix is also shown. The square root of this determinant is approximately inversely proportional to the volume of the confidence region of the estimated parameters. The approximate 95% confidence region for these parameters in Table 2 is shown in Figure 1. It is interesting to note that the confidence region does not contain the true value of the forward rate constant. This might be expected to happen about one time in twenty and, in fact, a different choice of twelve data points did contain the true parameter values.

Minimum Volume Design

In order to begin constructing this design, initial parameter estimates are necessary. In view of the insensitivity of this experimental design to the parameter values, one might use somewhat arbitrary parameter estimates to select the three initial data points necessary to obtain revised estimates of the three parameters. However, in this case a two-level factorial design was set up at an arbitrary position in the space of the variables to obtain estimates of the parameters. Then, with these four observations, revised parameter estimates were obtained. The G'G determinant was calculated by taking, as a possible fifth point, each of the points on a grid with intervals of 0.005 atm. between 0.0 and 0.05 atm. partial pressures of the components. A condensed matrix of the determinant values which were calculated at each point (run 6) is shown in Figure 4. The matrix thus generated was then searched to find the maximum. For example, in Figure 4 the maximum determinant value would be obtained if the next data points were taken at a partial pressure of A of 0.05 atm. and of B of 0.02 atm. Then the experiment was run at this point and a similar grid was searched to find the best position to take the next point. This procedure was continued until twelve data points were obtained, the same number as reported for the one-variable-at-a-time variation.

For one set of twelve data points the allowable region of experimentation was rather arbitrarily required to remain less than a maximum component partial pressure of 0.05 atm. (see Figure 4), since the design of Table 1 possesses this maximum. When the twelve well-designed data points were taken in this fashion, it was observed that they fell into three distinct regions, shown in Figure 5. The first four observations are, of course, at the points of two-level factorial design. Then, observations 7 and 10 fell into region J; 6, 9, and 12 into K; and 5, 8, and 11 into L. The parameter estimates and their individual confidence intervals are recorded in Table 3.

An examination of Figure 2 shows why the design criterion guided the experimentation into regions J, K, and L. For partial pressures up to 0.05 atm., all the data points fall on the rising portion of the curve. Thus, the experimenter should, if possible, raise the maximum partial pressure used in order to take observations on the decreasing side of the curve and thus define the parameters describing this curve more precisely. It is interesting to note from Figure 5 that the data points of the one-variable-at-

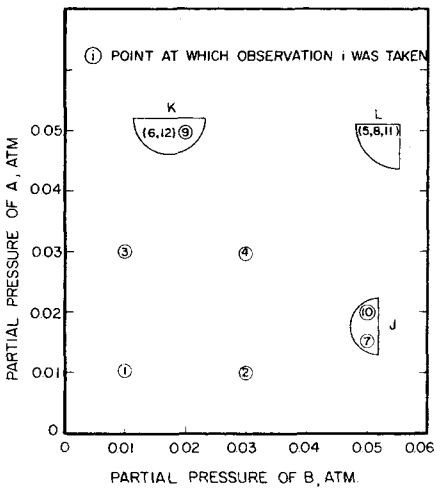

Fig. 5. Regions of experimentation for minimum volume design.

* The complete set of hypothetical data, which closely approximates the actual data, has been deposited as Document No. 8549 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

TABLE 2. RESULTS OF ANALYSIS OF ONE-VARIABLE-AT-A-TIME DESIGN

$k \times 10^4$, g.-moles / (min.)(g.-catalyst)	K_B, atm.$^{-1}$	K_A, atm.$^{-1}$	Residual sum of squares, $\left(\frac{\text{g.-moles}}{\text{(min.)(g.-catalyst)}}\right)^2$	G'G, determinant value
2.9 ± 0.92	38.0 ± 24.9	38.0 ± 26.1	4.62×10^{-11}	2.53×10^{-27}

a-time design used earlier fortuitously fall closer to the minimum volume design points than did the points of the two-level factorial design. This is due to the observed necessity of defining the higher partial pressure regions of the reaction rate surface and would not necessarily be true in general. This points out an additional advantage of this minimum volume design. It indicates regions of the experimental space which require attention in parameter estimation. Although these regions are, in retrospect, often apparent from an application of common sense, they are not necessarily obvious in more complex situations.

The partial pressure limit was then raised to 0.10 atm. and an analysis similar to that described above was carried out. Table 3 is a summary of the parameter estimates and confidence intervals for this set of runs for comparison with Table 2. It can be seen that a very significant decrease in the confidence region of the estimated parameters has been obtained by using the well-designed experiments. Note that the confidence interval of the forward rate constant k is greater in one entry of Table 3 than in Table 2. This is allowed by a large decrease in the intervals of the two adsorption constants, which results in a volume decrease of the joint confidence region in spite of the elongation of the interval of the forward rate constant. The confidence region of the "0.10 atm. maximum" parameter estimates of Table 3 is shown in Figure 6. Its volume should be compared to that of Figure 1, the confidence region for the design consisting of the one-variable-at-a-time variation. A pictorial representation corresponding to that of Figure 5 could be presented for this set of experiments, but it would be very similar to that of Figure 5 except with the regions J, K, and L shifted to 0.10 atm. In this case, observations 1 through 4 were maintained as in Figure 5; observations 6 and 9 were in region J; 5, 7 and 10 were in K; and 8 and 11 were in L. The twelfth point was taken at partial pressures of A and B equal to 0.03 atm., thus indicating that the region of high partial pressure of Figure 2 was becoming relatively well known.

A typical determinant surface, described by contours of constant determinant magnitude, is shown in Figure 7. Three very distinct peaks can be seen, one of which is higher than the others. In this case this peak corresponds to region K of Figure 5. As the experimentation proceeds, first one of these peaks appears higher than the others, then a different one does. Also, as the experimentation proceeds, this surface becomes relatively flatter and the benefit of selecting a point by this design procedure diminishes. It should be noted that these three maxima tend to remain in the same positions in the space of the variables as the experimentation proceeds, for example in regions J, K, and L of Figure 5. This is favorable to a procedure in which several optimum design points are to be selected at the same time.

CONCLUSIONS

It can be seen from this example, then, that certainly a more effective planning of experimentation can be obtained by this procedure. It was indicated, through Figure 5, that if the partial pressures could be increased the parameters could be estimated more precisely. Also, the regions of experimentation that were important in obtaining precision parameter estimates were selected. This latter characteristic of the design method is very important for its own sake. If it were not desired to use the procedure for designing experiments, the technique would still be valuable in determining the potential for a decrease in the confidence region and in directing the attention of the experimenter to critical regions of the experimental space. Moreover, a very substantial reduction in the volume of the confidence region was obtained by this approach, an eighteenfold reduction in this case. This decrease is sufficiently great to compensate for the additional difficulty encountered by using the sequential design discussed here.

Hence, the procedure illustrated in this paper is very promising for situations in which the experimenter is

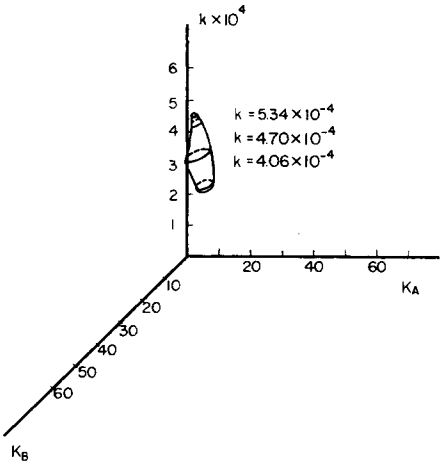

Fig. 6. Approximate confidence region of parameters from minimum volume design.

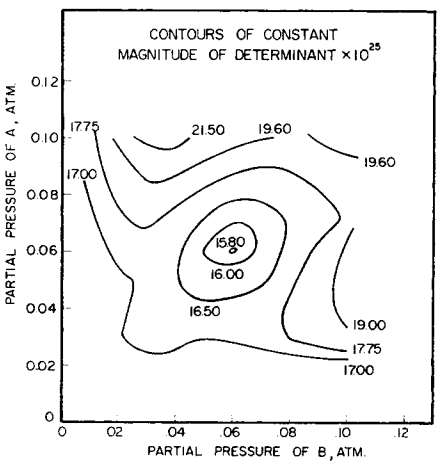

Fig. 7. G'G determinant surface for experimental region studied.

TABLE 3. RESULTS OF ANALYSIS OF MINIMUM VOLUME DESIGN

Maximum obtainable pressure, atm.	$k \times 10^4$, g.-moles / (min.)(g.-catalyst)	K_B, atm.$^{-1}$	K_A, atm.$^{-1}$	Residual sum of squares, (g.-moles / (min.)(g.-catalyst))	G'G, determinant value
0.05	5.75 ± 2.1	20.7 ± 6.0	10.8 ± 5.5	4.8×10^{-11}	3.19×10^{-26}
0.10	4.70 ± 0.53	20.2 ± 4.2	16.9 ± 4.0	6.88×10^{-11}	8.15×10^{-25}

planning experiments in order to estimate the parameter values of a nonlinear model.

ACKNOWLEDGMENT

The authors wish to express their gratitude to the National Science Foundation, under Grant No. GP-2755, for financial support. A grant of computer time by the Wisconsin Alumni Research Foundation through the University Research Committee is also acknowledged. One of us (JRK) held a National Science Foundation Graduate Fellowship.

NOTATION

A = reactant nitric oxide
B = reactant hydrogen
$\mathbf{G}$ = matrix of partial derivatives defined by Equations (3) and (6)
g_{iu} = partial derivative of a function g with respect to the parameter K_i evaluated at the u^{th} set of experimental conditions and some set of parameter values $\mathbf{K}_o$
K_i = parameter defined by Equation (4), $i = 1, 2,$ or 3
K_j = equilibrium adsorption constant for component j, atm.$^{-1}$
$\hat{K}_j$ = best estimate of parameter K_j
K_{jo} = estimate of parameter K_j
k = forward rate constant, g.-moles/(min.)(g.-catalyst)
N = number of observations
m = total number of independent variables required in a model
p = number of parameters in a model
p_i = partial pressure of component i, atm.
R = product water
r = reaction rate, g.-moles/(min.)(g.-catalyst)
S = product nitrogen
T = absolute temperature, °K.
x_i = independent variable
$\bar{x}_i$ = arithmetic mean of a set of independent variables x_i

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Manuscript received October 7, 1964; revision received July 10, 1965; paper accepted July 26, 1965. Paper presented at A.I.Ch.E. Houston meeting.

Mechanism of Dispersed-Phase Mass Transfer in Viscous, Single-Drop Extraction Systems

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The theory of solute extraction in viscous single-drop systems is extended to show (1) the dependence of the asymptotic Nusselt number on the Peclet number from $N_{Pe} = 0$, the molecular diffusion limit, to $N_{Pe} = \infty$, the Kronig and Brink limit, and (2) the dependence of the diffusion entry region Nusselt number on the Peclet number and the initial concentration profile.

A numerical solution of the diffusion equation, limited to dilute solute concentrations and solute transport by viscous convection and molecular diffusion, is presented from which the nature of the Nusselt number is deduced. The observed oscillatory behavior of the Nusselt number in the diffusion entry region, as $N_{Pe} \to \infty$, is given a simple physical interpretation in terms of the circulation period of the drop liquid.

The model is based upon the Hadamard stream function which theoretically is limited to creeping flow; however some experimental evidence indicates that flow fields similar to the Hadamard stream function exist at continuous phase Reynolds numbers of the order of ten.

It is customary to analyze and correlate the results of single-drop extraction experiments in terms of mathematical models. For example, experiments with viscous drops normally are related to either the stagnant-drop model, at the extreme of vanishing circulation or to the Kronig and Brink (*10*) model at the opposite extreme; whereas experiments with turbulent drops frequently are related to the Handlos and Baron model (*15*).

This paper presents the solution to a viscous flow model which reduces to the stagnant-drop and the Kronig and Brink models in the respective limits, that is, $N_{Pe} = 0$ and $N_{Pe} \to \infty$, and complements these models on the interval $0 < N_{Pe} < \infty$. A mathematical formulation of the model will be given after a brief summary of the problem and a presentation of the major assumptions.

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