Nonlinear Least Squares Analysis of Catalytic Rate Models

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Conventional data generation and analysis procedures used to select a descriptive Hougen-Watson reaction rate model have been reviewed and some statistical objections to these conventional procedures have been presented. In an attempt to assess the practical importance of these objections, a recently published example was analyzed with both conventional techniques and nonlinear least squares procedures, which more closely conform to theoretical weighting requirements. Comparisons were made between the results of the conventional linear least squares analysis of isothermal data and those of nonlinear least squares analyses of both isothermal and nonisothermal data. It was found that the nonlinear least squares procedures were useful for a rational selection of an acceptable model and estimation of its parameters.

General observations were made concerning good regions for further experimentation if a discrimination among rival models is desired. Additional well-designed experiments were found to be necessary to allow a reduction of the confidence region of the parameters of the Hougen-Watson models to an acceptable size.

Often it is desired to fit rate data from a heterogeneous reaction to a model, either theoretical, semitheoretical, or empirical, to predict the reaction rate within the ranges of the variables studied and, in some cases, to allow cautious extrapolation. This perhaps most frequently has been done with a family of Hougen-Watson models (*1*, *2*) as functional forms, from which one appropriate model hopefully could be selected by utilizing existing data. It is common to linearize these expressions by a rearrangement of the model so that the constants within them can be estimated by the method of unweighted linear least squares or some other simple technique. These models must then be screened to reject those that are inadequate in the light of the data.

Many criteria have been proposed for the elimination of unsatisfactory models. For example, models have been declared inadequate if the estimated adsorption or rate constants were negative, if the temperature coefficients of these estimated parameter values were of the wrong sign, or if the ability of the models in question to reproduce the data with these parameter values were unacceptable. Occasionally one, but very frequently more than one, model can be said to be plausible after following a conventional procedure such as this.

Several objections to the Hougen-Watson models have been published and it is not necessarily the authors' intent in this paper to endorse these models, even though numerous useful applications of such models exist. Apart from these theoretical inadequacies of the Hougen-Watson models, however, several objections have been raised concerning the statistical judiciousness of this conventional approach to the analysis of heterogeneous reaction rate data (*3* to *5*). These statistical considerations suggest that the conventional methods are motivated more by the requirement of an expedient analysis than by statistical justification. An analysis would, of course, be justified from a statistical point of view if all the underlying theoretical assumptions were satisfied fully. A matter of even more importance in practice, however, is that an analysis also could be justified even if the underlying statistical assumptions were violated, provided that the results of such an analysis were insensitive to these violations. If, for example, the linear analysis of the Hougen-Watson models should be inherently insensitive to violations of any underlying statistical assumptions, fitting techniques more elaborate than unweighted linear least squares would not be necessary. The example in this paper suggests, however, that the conventional linear analysis of these models may not be robust and hence more elaborate fitting techniques are desirable for the final stages of an investigation.

The purpose of the paper, then, is actually threefold:

1. The results of a conventional unweighted analysis can be quite misleading. Models can be rejected by this analysis on the basis of negative adsorption constants or improper trends of these constants with temperature when, in actuality, these constants are positive or have negative temperature coefficients. Of course, physical mechanisms which have such properties as adsorption constants with positive temperature coefficients are extremely rare and *if* the constants of a model are actually unacceptable the model should probably be rejected. However, as pointed out in this paper, these apparent inadequacies can be caused by the type of data analysis rather than by the true behavior of the experimental data.
2. A nonlinear least squares analysis (*9*) of the same rate data can result in estimates of the parameters which are compatible with our knowledge of the problem. In particular, in this paper it is found that two models were rejected in the conventional analysis for possessing negative adsorption constants. These should not have been rejected on this basis, for through a nonlinear least squares analysis of the same data these constants were found to be positive. This nonlinear analysis essentially provides a different assumption about the proper weighting of the data, which is believed to be more justifiable from an experimental point of view.
3. Finally, it is illustrated that perhaps the most important factor in the construction of reaction rate models is a good experimental design. For the models considered here, more data obtained at higher partial pressures of the reactants are desirable for an effective discrimination among the rival models.

OBJECTIONS TO CONVENTIONAL APPROACH

Specific objections to the conventional approach can in general be broken down into two areas: the plan of experimentation and the analysis of the data.

Generation of Data

The experimental designs, that is, plans of experimentation, that are used to generate data in conventional mechanism studies can follow one of two limiting strategies, both of which are subject to the severe disadvantage of not being iterative in nature. The first strategy consists of covering completely the space of the experimental variables within limits believed adequate. For example, with two variables the space would be two dimensional. Thus, if the individual experiments were represented as points in this space, they might display a gridlike pattern as shown in Figure 1. In particular, if two-component partial pressures were to be varied, data points could be taken according to such a pattern with intervals of, for example, one-tenth of an atmosphere between one and two atmospheres, inclusive, of the component partial pressures. In most cases this procedure, although thorough, is inefficient in several respects. Furthermore, even if this procedure were fully efficient, as the number of variables to be studied increases, the number of experiments required by this method increases so rapidly as to preclude this method of experimentation. In the example just cited, with two variables the number of data points that would be required would be 121; with three variables, 1,331; and with four variables, 14,641.

The second strategy, which requires fewer runs, is to select some subset of this space on an a priori basis. For example, one could take data points by varying only one variable at a time, each variable being restricted to a single traverse. At first glance this design would appear to give a clear insight into the system under study by separating the individual effects of each of the variables. However, to illustrate the effect of interactions, consider the actual rate response of our example plotted as a system of contours of constant rate in Figure 2. These experimental points, which lie along the solid lines, clearly do not give a representative description of the entire response surface. For instance, the choice of experimental points shown would make it very difficult to distinguish between a model possessing a maximum rate with a traverse at a constant component partial pressure, as represented by the contours of Figure 2, and a rival model whose rate surface continually increases with an increase of one partial pressure while the other pressure is held constant. (These cases correspond to models 3 and 1, respectively, of Figure 6.) Of course, as can be seen from Figure 2, completely covering the experimental region of partial pressures less than 0.05 atm. would not allow discrimination between these models either. Also, note that in purely empirical surface studies a one-variable-at-a-time variation could give two totally different pictures of this particular surface of Figure 2, depending upon the range and position of the observations taken. For example, observations from 0.0 to 0.14 atm. of the partial pressure of A would indicate that the rate continually increased if the observations were made at a partial pressure of B equal to 0.14 atm. However, at a partial pressure of B equal to 0.02 atm., the rate would increase and then decrease with an increasing partial pressure of A.

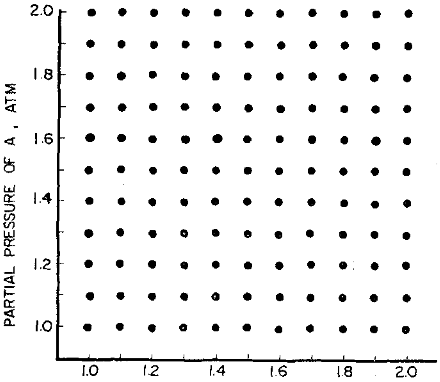

Fig. 1. Design points in the space of the experimental variables.

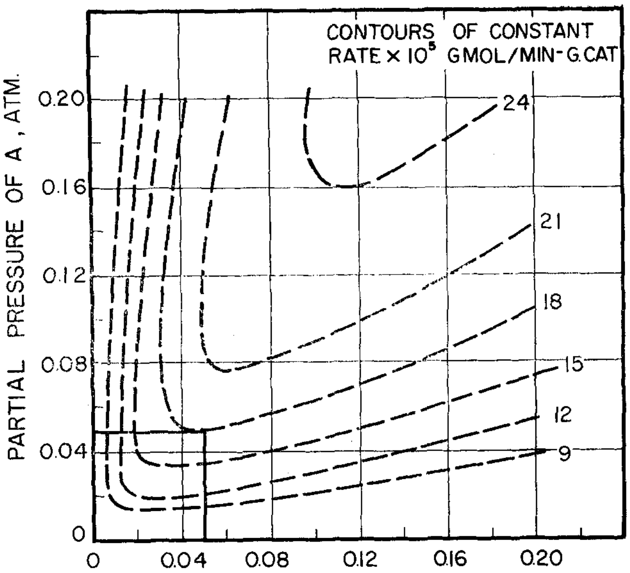

Fig. 2. One-factor design on reaction rate response surface.

Thus, if a design such as this were used for selecting a Hougen-Watson model, one would be proposing to determine the rate expression defining, and the parameter values characterizing, the entire rate surface from an insufficient sampling of the surface. It is not surprising that several surfaces corresponding to a number of reaction rate models can be found that fit this limited amount of data and that the estimates of the adsorption constants may be poorly defined as characterized by their large confidence intervals.

Analysis of Data

The objections associated with the data analysis are centered upon the linearization of the model (by a rearrangement of terms and not by a Taylor expansion) and upon the rejection criteria used in the screening of the models. In particular, an assumption that usually is made in developments of the method of linear least squares is that there be a mathematical equation with a dependent variable y, which is subject to error, on one side of the equation being equal to an expression that is linear in the parameters b_i on the other (6). For example

$$y = \sum_{i=1}^{p} b_i x_i + \text{error} \qquad (1)$$

where the x_i $(i = 1, 2, \ldots, p)$ are independent variables which are not subject to error but instead are known exactly. As a result of the linearizing transformation of the Hougen-Watson models, however, the observed dependent variable, in this case the reaction rate, need no longer be on one side of the equation with the relatively error-free independent variables on the other, as required by the linear least squares theory usually applied. Rather, combinations of the independent variables and the reaction rate could be on one or both sides of the equation, for example, as in Equation (5). Even if, in addition to this requirement, the other assumptions inherent in the least squares analysis (that is, adequacy of model, normality and independence of error, and constancy of error variance) are appropriate for the original model, they probably are not satisfied by the linearized equation. That is, if a residual is defined as the difference between any experimentally observed and calculated values, the linear least squares analysis does not minimize the sum of squares of residuals of the reaction rates but rather that of a combination of the rate and the independent variables, the error distribution for which is not necessarily as obvious. Since it is the reaction rate that is to be predicted, however, these unweighted linear least squares estimates of the parameters could be different from those that would give the best prediction of the reaction rates through, say, maximum likelihood arguments.

Thus, the method of unweighted linear least squares can give parameter estimates which guarantee neither a best prediction of reaction rates within the range of the variables studied nor reasonably satisfactory extrapolations. But perhaps of even more importance is that these estimates, which possess possible uncertainties of the same order of magnitude as the estimates themselves, can result in apparently unacceptable parameter values, for example, negative adsorption constants. The result can be an early rejection of a supposedly incorrect reaction rate expression which is, in fact, adequate. Additional objections to the rejection criteria of a qualitative nature have been set forth elsewhere (4).

There are definite indications, then, that these conventional designs and methods of analysis may be inadequate. Apart from a very few studies (3, 7) little effort has been directed toward investigating data generation and analysis procedures in heterogeneous kinetics. It is not known, for example, how important these statistical considerations are; thus the Hougen-Watson models and the concomitant conventional analysis conceivably could be inherently robust to deviations from the theoretical requirements on the design and analysis. The following example is taken from the work of Ayen and Peters (8). It allows a comparison of the results obtained by a nonlinear least squares analysis (9), which it is felt more closely fulfills the theoretical requirements in this case, with those from a conventional analysis.

EXAMPLE

The gaseous reaction to be considered (8) is the reduction of nitric oxide (component A):

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

or, for abbreviation,

$$A + B \rightleftharpoons C + \tfrac{1}{2}D$$

The reaction was conducted in a differential reactor over a commercial solid catalyst consisting of copper, zinc, and chromia. Experimental conditions were maintained such that the reverse reaction did not take place to any appreciable extent. Data were taken at three temperatures and at partial pressures of A and B ranging from 0.005 to 0.05 atm. These data, having been corrected for slight variations in catalyst activity and for minor variations in the component partial pressure being held constant, are presented in the original article. Upon reference to the original article, it will be noted that the experimental design consisted of varying one variable at a time over the ranges shown by the solid lines in Figure 2.

On the basis of plots of these data, the experimenters suspected that a surface reaction was controlling. The final three mechanisms chosen by them for further consideration were:

1. Reaction between one adsorbed A molecule and one gas phase B molecule, generating the model

$$r = \frac{kK_A\, p_A\, p_B}{(1 + K_A p_A + K_B p_B)} \tag{2}$$

2. Reaction between one adsorbed B molecule and one gas phase A molecule, generating the model

$$r = \frac{kK_B\, p_A\, p_B}{(1 + K_A p_A + K_B p_B)} \tag{3}$$

3. Reaction between one adsorbed A molecule and one adjacently adsorbed molecule of B, generating the model

$$r = \frac{kK_A\, K_B\, p_A\, p_B}{(1 + K_A p_A + K_B p_B)^2} \tag{4}$$

LINEAR LEAST SQUARES ANALYSIS

These three equations were linearized to fit them to the data by use of linear least squares techniques. For model 3, for example, the linearized equation for $p_A = 0.05$ atm. is

$$\left(\frac{p_B}{r}\right)^{1/2} = \left[\frac{K_B}{(0.05\, kK_B K_A)^{1/2}}\right] p_B + \left[\frac{1 + 0.05\, K_A}{(0.05\, k\, K_A\, K_B)^{1/2}}\right] \tag{5}$$

and for $p_B = 0.05$ atm. is

$$\left(\frac{p_A}{r}\right)^{1/2} = \left[\frac{K_A}{(0.05\, k\, K_B\, K_A)^{1/2}}\right] p_A + \left[\frac{1 + 0.05\, K_B}{(0.05\, k\, K_B\, K_A)^{1/2}}\right] \tag{6}$$

Note the importance of the one-variable-at-a-time experimental design in this particular linearization, although it is not necessary for the implementation of a least squares analysis. Also note, on the assumption of appropriately distributed rate error, that even worse violations of the

TABLE 1. LINEAR LEAST SQUARES ESTIMATES OF REACTION RATE AND ADSORPTION CONSTANTS FOR THREE MODELS

Temp., °C.	$k \times 10^4$, g.-mole/(min.) (g.-catalyst)	K_B, atm.$^{-1}$	K_A, atm.$^{-1}$
	Model 1—impinging B		
375	19.7 ± 1.8	—126.1 ± 254.5	—101.8 ± 202.0
400	26.5 ± 3.4	—48.6 ± 43.2	—44.9 ± 36.6
425	49.0 ± 18.1	—48.1 ± 40.6	—35.6 ± 20.4
	Model 2—impinging A		
375	15.9 ± 37.1	—151.3 ± 250.0	—122.1 ± 228.6
400	24.5 ± 65.0	—39.6 ± 16.0	—36.6 ± 22.7
425	36.3 ± 67.3	—50.7 ± 44.3	—37.6 ± 38.3
	Model 3—dual site		
375	4.9 ± 1.4	18.8 ± 9.2	14.6 ± 5.7
400	5.3 ± 1.7	38.6 ± 39.2	35.4 ± 22.6
425	8.8 ± 4.5	48.9 ± 62.5	30.9 ± 40.3

Table 2. Estimates of Parameters of the Dual Site Model 3, Reported by Ayen and Peters (8)

Temp., °C.	$k \times 10^4$, g.-mole/(min.) (g.-catalyst)	K_B, atm.$^{-1}$	K_A, atm.$^{-1}$
375	4.94	19.00	14.64
400	7.08	30.45	20.96
425	8.79	48.55	30.95

linear least squares requirements could occur if the reaction rate had to be included in the supposedly error-free variables on the right side of Equation (1).

The linear least squares procedures for these three models were then carried out for each of the three groups of isothermal data. The linear least squares estimates of the parameters obtained by this procedure are shown in Table 1. Also shown are their approximate 95% confidence intervals, which were obtained from twice the estimated standard deviation of the parameters and henceforth will be referred to as two sigma intervals. In this case an approximate standard deviation of a parameter of interest can be obtained by assuming approximate linearity in the region near the point estimate of the parameters. The general procedure is to linearize, by a Taylor expansion about the best parameter estimates, the equation relating the parameter of interest to the quantities in the brackets of Equations (5) and (6). The problem, then, is reduced to obtaining the variance of the resulting linear sum, a procedure set forth in most mathematical statistics texts.

From the tabulated point estimates, it can be seen that the requirement of positive adsorption constants apparently eliminates models 1 and 2. (However, it should be noted at this point that, for example, for K_B of model 1 at 375°C., the two-sigma interval is so large that K_B could conceivably be positive.) Model 3, which possesses all positive constants and which reproduces the data reasonably well, was judged to be correct by the experimenters. The temperature dependence of the parameter values listed under model 3 of Table 1 could then be obtained by linear least squares by assuming an Arrhenius type of temperature relationship. The results reported by the experimenters, however, are shown in Table 2 and these results are compared to the estimates of Table 1 in Figure 3. Apparently the validity of the 400°C. data was questioned. It is obvious from this figure that a linear least squares fit of the parameter values of Table 1 would give a somewhat different final set of parameters than those reported in Table 2.

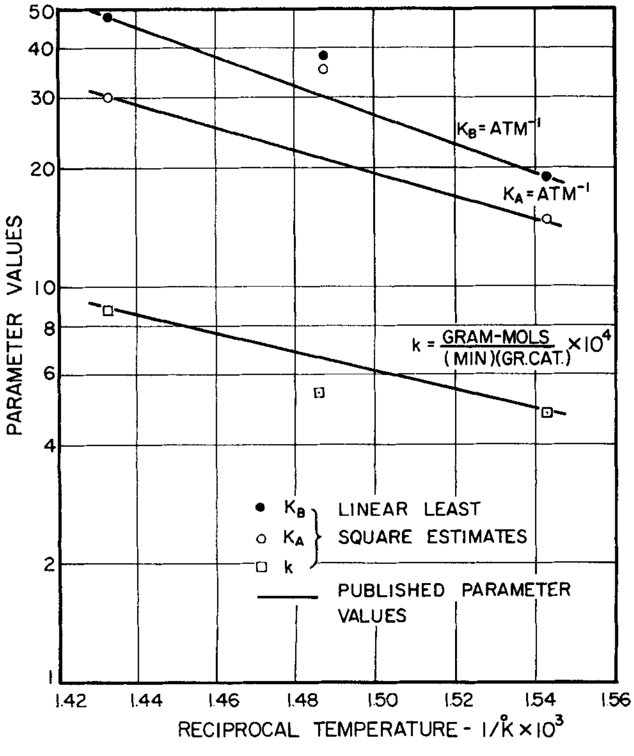

Fig. 3. Comparison of linear least squares and published parameter values for dual site model 3.

On the basis of these calculations, then, the experimenters concluded that model 3 was the proper model and that the best estimates of the parameters of the model were those of Table 2. Although adsorption phenomena commonly are thought to be exothermic, the positive temperature coefficients observed in Figure 3 for model 3 were not mentioned by the experimenters. Since it is conceivable that endothermic adsorption processes can occur in some particular cases, this behavior, although very suspicious, is not an incontrovertable reason for dropping this model. The behavior does, however, imply a need not only for an examination of the confidence intervals on the heats of adsorption, but also for an examination of the adequacy of other more acceptable models.

NONLINEAR LEAST SQUARES ANALYSIS

In an effort to obtain results that could be compared to those determined by linear least squares, these same data were fitted by using nonlinear least squares techniques. At least two important advantages of this method can be seen at this point which should make the estimated parameters equal to or better than those from a linear analysis, on the reasonable assumption of error in the rate measurements being spherically normally distributed. First, as mentioned earlier, the sum of squares of residual rates can be minimized directly instead of minimizing the residuals of some combination of variables, the error distribution for which is calculable though not simple. For example, in model 3 and the resulting Equation (5), the quantity $\Sigma\ (r_{\text{obs.}} - r_{\text{calc.}})^2$ would be minimized instead of the quantity $\Sigma\ [(p_B/r)^{1/2}_{\text{obs.}} - (p_B/r)^{1/2}_{\text{calc.}}]^2$. Second, for nonlinear least squares, little additional difficulty is encountered by requiring that the parameters in the model possess an exponential temperature dependence. All data can, therefore, be treated at once without

Table 3. Nonlinear Least Squares Estimates of Parameter Values for Three Models using Isothermal Data

Temp., °C.	$k \times 10^4$, g.-mole/(min.) (g.-catalyst)	K_B, atm.$^{-1}$	K_A, atm.$^{-1}$
	Model 1—impinging *B*		
375	20.8 ± 5.7	−142.9 ± 231.5	−105.0 ± 154.6
400	23.9 ± 4.7	−38.9 ± 16.5	−42.8 ± 19.3
425	50.3 ± 18.8	−52.1 ± 36.6	−37.2 ± 18.5
	Model 2—impinging *A*		
375	15.3 ± 2.3	−143.4 ± 251.4	−105.4 ± 171.2
400	26.3 ± 5.9	−38.9 ± 16.0	−42.7 ± 19.0
425	36.0 ± 6.4	−52.4 ± 37.2	−37.3 ± 19.2
	Model 3—dual site		
375	5.19 ± 1.9	18.5 ± 6.8	13.2 ± 6.7
400	5.51 ± 2.3	31.6 ± 25.9	36.0 ± 27.8
425	10.1 ± 6.0	34.5 ± 30.4	23.1 ± 23.1

TABLE 4. NONLINEAR LEAST SQUARES ESTIMATES OF PARAMETER VALUES FOR THREE MODELS USING NONISOTHERMAL DATA

Temp., °C.	$k \times 10^4$, g.-mole/(min.)(g.-catalyst)	K_B, atm.$^{-1}$	K_A, atm.$^{-1}$
	Model 1—impinging *B*		
375	40.2 ± 236	56.4 ± 203	27.4 ± 280
400	59.3 ± 280	81.6 ± 283	44.2 ± 394
425	85.0 ± 310	114.8 ± 393	69.1 ± 532
	Model 2—impinging *A*		
375	23.9 ± 44.4	201.1 ± 2,950	263.8 ± 3,450
400	33.2 ± 45.9	399.7 ± 5,670	330.1 ± 4,290
425	45.1 ± 42.9	756.4 ± 10,400	406.6 ± 5,270
	Model 3—dual site		
375	4.92 ± 7.41	15.5 ± 26.7	17.5 ± 22.9
400	6.58 ± 7.87	26.3 ± 36.6	23.8 ± 25.6
425	8.63 ± 7.84	42.9 ± 47.1	31.7 ± 29.1

any minor corrections to a base temperature and pressure; thus questionable discrepancies illustrated by the disagreement of Tables 1 and 2 can be avoided. In this case, then, the nonlinear least squares estimates of the parameters would be better than the unweighted linear least squares values.

Isothermal Data

The importance of the first of these advantages can be seen from a comparison of Table 3, which presents nonlinear least squares estimates of the parameters using the three sets of isothermal data, with Table 1, which contains the linear least squares estimates using the same data. The confidence intervals for the nonlinear analyses are calculated individually by approximating the rate expression by a linear Taylor expansion about the best estimate of the parameter values. Thus, they do not represent a joint confidence region. It can be seen that the discrepancies of the corresponding point estimates of these tables vary from 5 to 40%. The residual sum of squares, a measure of lack of fit in this case, was decreased only slightly by using nonlinear rather than linear least squares estimates of the parameters (for example, from 1.87×10^{-10} to 1.81×10^{-10}). As would be expected, the confidence intervals of the nonlinear least squares parameter estimates are, in general, smaller than those of the linear least squares estimates. The only exceptions to this generalization are the intervals of the forward rate constant, which will be discussed later. Thus, this first advantage is only marginal in this isothermal case, probably due to the small variation of the reaction rate within the isothermal data sets. In linearizations of other Hougen-Watson models and with other data sets this advantage could become more important.

Analysis of All Data Simultaneously

As an illustration of the effect of both advantages, a summary of the parameter estimates obtained by simultaneously fitting all the data by nonlinear least squares procedures is shown in Table 4. This table indicates that the magnitudes of the parameters for all the models are reasonable, so that no model could be discarded as inadequate on this basis. However, the two-sigma intervals here are quite large; in fact, they are greater than those of Table 1 and 3. Primarily this is because each temperature set was fitted separately for Tables 1 and 3, whereas for Table 4 the models were required to fit all the data simultaneously.

The residual mean square, that is, the residual sum of squares divided by the number of degrees of freedom, of each of these models for all the data taken simultaneously is tabulated in Table 5. These values should measure the amount of total deviation of the models from the data. Since at the 5% level an *F* statistic with the appropriate number of degrees of freedom is about 1.94 and since the largest ratio of mean squares in Table 5 is 2.03, it would be hazardous to assert simply on the basis of the residual mean square that any one of these models fits the data better than any other model. The comparison of this ratio to the *F* statistic can only be approximate here due to the lack of independence of the mean squares. It should be noted, however, that plots of residuals as a function of the experimental variables, which one would expect to be essentially random if the model were correct, exhibit systematic trends.

Comparison of Estimated Constants

Due to the severe residual trends and the positive temperature coefficients observable for these models in Table 4, the adequacy of all three models is open to serious doubt. Thus, the ensuing discussion should not be taken to imply that any one of these three models is adequate. Nevertheless, the comments concerning the model discrimination and parameter estimation remain appropriate. No attempt was made to determine a better model, since, as will be seen, further experimentation probably is necessary for an unambiguous decision.

In contrast with the linear least squares results, it can be seen from Table 4 that for nonlinear least squares, although the temperature coefficients are still positive, the magnitudes of the constants are reasonable for all of the models considered. This discrepancy in the parameter estimates from the two types of analyses has been observed elsewhere (*10*). In that work it was confirmed that the variance of the rate errors was approximately constant over the ranges of the variables studied. In addition, Table 5 indicates that the two models previously rejected by linear least squares techniques fit the data about as well as does the previously accepted model. As a further illustration of this equally good fit, the actual reaction rates and the rates predicted by each model are plotted as functions of the partial pressures of *A* and *B* in Figures 4 and 5.* It can be seen from these figures that more spread in predicted rates is obtained among the various rival models as the temperature is increased. One implication from this behavior is that, for interpolation purposes, the choice of the best model is not particularly

TABLE 5: COMPARISON OF RESIDUAL MEAN SQUARES

Model No. and parameters	Residual mean square, $\left[\frac{\text{g.-mole}}{(\text{min.})(\text{g.-catalyst})}\right]^2$
No. 1 with nonlinear least squares estimates	6.3×10^{-11}
No. 2 with nonlinear least squares estimates	4.5×10^{-11}
No. 3 with nonlinear least squares estimates	3.1×10^{-11}
No. 3 with linear least squares estimates	5.0×10^{-11}

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* Figures 5 and 7 present essentially the same information as Figures 4 and 6, respectively, except the partial pressure of *A* is the independent variable. Figures 5 and 7 have been deposited as document 8542 with the American Documentation Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

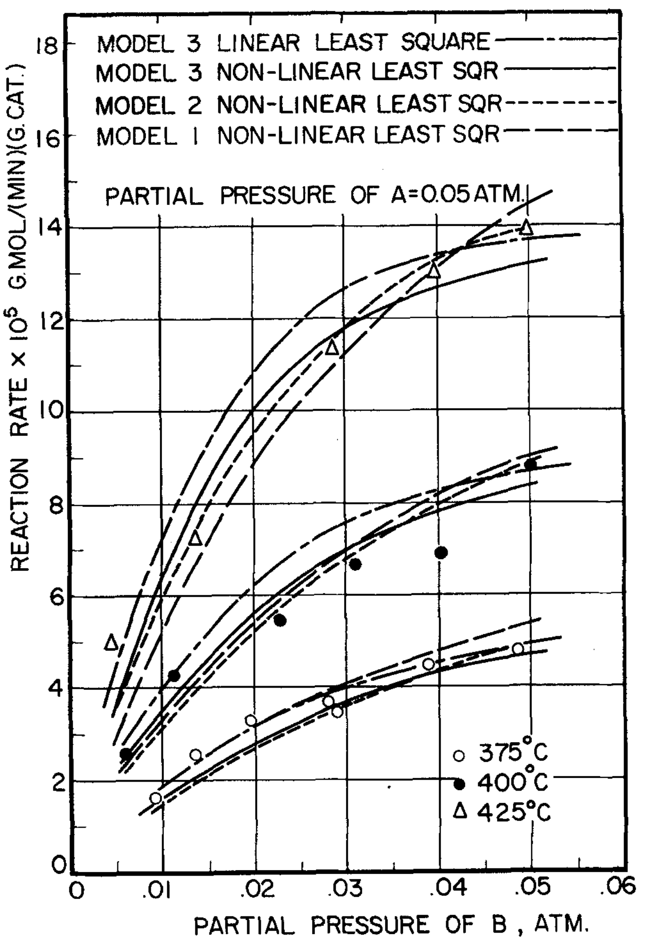

Fig. 4. Comparison of predicted and actual reaction rates for all models.

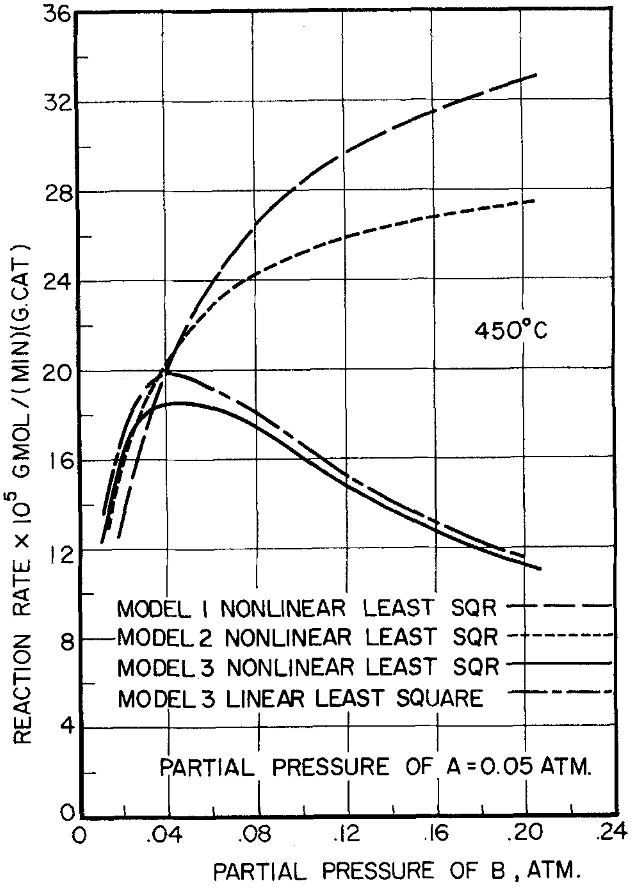

Fig. 6. Comparison of extrapolated rates for all models.

important if conditions are maintained near the low temperature regions in Figure 4. However, for the high temperature regions of Figure 4, the choice of the proper model gains more importance and any one of these models must be used with care.

For the purpose of comparing further the constants estimated by linear least squares with those obtained by nonlinear least squares, model 3 was selected for consideration since it had been chosen as apparently the most plausible by the original experimenters. For this model, the estimates of Table 4 can be compared to those reported in Tables 1, 2, and 3. It is seen that the linear least squares analysis generally provides about the same estimate of the forward rate constant as does nonlinear least squares. This is to be expected, since the forward rate constant enters the Hougen-Watson models in a linear fashion. For the adsorption constants, it can be seen that the nonlinear estimates using all the (nonisothermal) data are in one case closer to estimates which would be obtained by a linear least squares fit of the three linear estimates from the isothermal sets of data (K_A). In the other case, the nonlinear estimates using all of the data are closer to the published values reported by the experimenters (K_B). Of even more importance, however, is the fact that the temperature trends of the parameters estimated from nonlinear least squares are substantially different from the linear least squares estimates. As will be seen later, this would make extrapolations of linear least squares rate estimates somewhat less satisfactory than those of nonlinear least squares estimates. It is of practical significance, however, that this discrepancy in extrapolation is not as large as that between the predicted rates of the various models under consideration, as shown in Figures 6 and 7.* Table 6 indicates quantitatively the substantial differences that can be expected in the magnitudes and temperature trends of the constants estimated. This is in general agreement with the discrepancies reported by Blakemore and Hoerl (3). Also, it can be seen from the confidence intervals of this table that the temperature coefficient for gas A could be negative whereas the coefficient for gas B appears to be truly positive. Thus, as discussed earlier, this model could be viewed with suspicion.

CONCLUSIONS

Given that the Hougen-Watson models exist somewhere in the spectrum between purely empirical interpolation polynomials and precisely known theoretical models, one must apply a careful data analysis because the basic interpretation of the results of kinetic studies is subject to the above discussed questions. In particular, it can be seen from the above example that substantially different conclusions about the describing model and its parameter values can be drawn, depending upon what type of analysis and what type of data weighting are chosen. With the data presented, sufficient information is not yet available to allow the selection of any of the three given models. As seen previously, this may or may not be of importance if one wishes only to use these models for interpolation. However, if one wishes to determine a mechanistic model describing the reaction, then these models are not equally satisfactory. This is illustrated by the extrapolations of these models shown in Figures 6 and 7.

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* See footnote on page 1055.

TABLE 6. COMPARISON OF PARAMETER VALUES OBTAINED BY LINEAR AND NONLINEAR LEAST SQUARES FOR MODEL 3

Parameters	Linear least squares	Nonlinear least squares	% difference from nonlinear least squares
α_1	1.61	1.27 ± 8.9	26.8
α_2	498,000	67,800 ± 536,000	635
α_3	9,200,000	24,300,000 ± 190,000,000	62.2
E_1	10,400	10,000 ± 10,960	4.0
E_2	13,500	10,600 ± 11,400	27.4
E_3	16,900	18,400 ± 12,200	8.1

where

$k = \alpha_1 e^{-E_1/RT}$, g.-mole/(min.)(g.-catalyst)
$K_A = \alpha_2 e^{-E_2R/T}$, atm.$^{-1}$
$K_B = \alpha_3 e^{-E_3/RT}$, atm.$^{-1}$

In addition, several points concerning the future path of experimentation are suggested by Figures 6 and 7. First the region of experimental variables to be examined should, if possible, be raised to higher partial pressures than were used (less than 0.05 atm.) if it is hoped to reject some of these rival models. Also, temperature is important in this regard but not as much as the partial pressures. Second, the proper selection of an adequate model is of an equal or greater importance than a precise estimation of the parameters within these models. However, the relatively close approach of the two lines corresponding to model 3 with two different sets of parameter estimates should not be allowed to become misleading. The fact remains, as evidenced by Table 4, that the confidence regions for these parameter values are very large, so that little is known about their actual magnitudes as yet.

In view of this example, then, either rather refined weighting of the data for a linear least squares analysis or a (possibly weighted) nonlinear least squares analysis will be necessary as one step in the data analysis for model building in heterogeneous catalysis. Since the exact error distribution of the reaction rates was not known here, the Jacobians of the transformations were not utilized to effect weighted analyses. It should be explicitly mentioned in relation to this weighting that the linear and nonlinear analyses are not rival techniques for the treatment of kinetic data. For example, in the initial stages of an investigation in which there are numerous candidate models, linear least squares methods may be carefully used in eliminating obviously inadequate models. Furthermore, it appears that several other points need attention in a program designed to determine the best rate model and to estimate its parameters.

First, as is shown in Figure 6, one must carefully choose the experimental points to be run so that it will be possible to distinguish among several rival models of the type encountered here. That is, one cannot expect that experiments run at arbitrary levels of the experimental variables will yield adequate discriminatory power. Since the basis for this choice of experiments is insight into the physical system, and since this insight must often arise from previous experiments, the necessity for sequential experimentation is common. Also, the concept of efficiency in the selection of experimental points is clarified since one data point at a partial pressure of 0.10 atm. in the situation depicted in Figures 6 and 7 may be as valuable as several at pressures less than 0.04 atm. The problem of discriminating between rival models has been examined and experimental designs have been suggested by Hunter and Reiner (*11*) and by Box and Hill (*12*).

Second, poorly planned experimentation can contribute to the rather large, attenuated confidence regions for the parameters of the Hougen-Watson models. A sequential design scheme has been presented which minimizes the volume of the joint confidence regions of the parameters in these nonlinear models (*13*). A comparison of the confidence regions obtained by these designs with regions obtained by the designs used in the example cited here is presented elsewhere (*14*).

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NOTATION

A = reactant nitric oxide
b_i = unspecified parameter of Equation (1)
B = reactant hydrogen
C = product water
D = product nitrogen
E_i = exponential energy factor for rate or adsorption constant, cal./g.-mole
k = forward rate constant of surface reaction, g.-mole/(min.) (g.-catalyst)
K_A = adsorption equilibrium constant for component A, atm.$^{-1}$
K_B = adsorption equilibrium constant for components B, atm.$^{-1}$
p_A = partial pressure of component A, atm.
p_B = partial pressure for component B, atm.
r = reaction rate, g.-mole/(min.)(g.-catalyst)
R = universal gas constant, cal./(g.-mole)(°K.)
T = absolute temperature, °K.
W = weight of catalyst, g.
x_i = arbitrary independent variable
y_i = arbitrary dependent variable
α_i = pre-exponential factor for rate or adsorption constant, (g.-mole)/(min.)(g.-catalyst) or atm.$^{-1}$

LITERATURE CITED

1. Hougen, O. A., and K. M. Watson, *Ind. Eng. Chem.*, **35**, 529 (1943).
2. ——————, "Chemical Process Principles, Part III," Wiley, New York (1947).
3. Blakemore, J. W., and A. E. Hoerl, *Chem. Eng. Progr. Symposium Series No. 42*, **59**, 14 (1963).
4. Chou, Chan-Hui, *Ind. Eng. Chem.*, **50**, 799 (1958).
5. White, R. R., and S. W. Churchill, *A.I.Ch.E. J.*, **5**, 354 (1959).
6. Plackett, R. L., "Regression Analysis," p. 33, Oxford Press, London (1960).
7. Peterson, T. I., *Chem. Eng. Progr. Symposium Series No. 31*, **56**, 111 (1960).
8. Ayen, R. J., and M. S. Peters, *Ind. Eng. Chem. Process Design Develop.*, **1**, 204 (1962).
9. Box, G. E. P., *Ann. N. Y. Acad. Sci.*, **86**, 792 (1960).
10. Mezaki, R., Ph.D. thesis, Univ. Wisconsin, Madison (1962).
11. Hunter, W. G., and A. M. Reiner, *Technometrics*, **7**, No. 3, 307 (1965).
12. Box, G. E. P., and W. J. Hill, *Dept. Statistics Tech. Rept. No. 51*, Univ. Wisconsin, Madison (1965).
13. Box, G. E. P., and W. G. Hunter, *IBM Sci. Computing Symp. Statistics*, 113 (1965).
14. Kittrell, J. R., W. G. Hunter, and C. C. Watson, *A.I.Ch.E. J.*, to be published.

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