or

$$T_o = 0.944\, C_o^{1/6}\, (1 - T_o^2)^{2/3} \qquad (28b)$$

since $D_o = T_o C_o^{1/2}$ by definition. Equation (28) has been found experimentally to be valid over a 20,000-fold range of dimensionless speed C_o (*6*).

As compared with the theory previously developed for power model fluids, this Ellis model theory agrees with Newtonian results over a wider range of C_o. It also incorporates the behavior at low stress, as well as at intermediate stress. Therefore, it is believed that this new theory will predict the behavior of Ellis fluids. However, final verification must await suitable data.

ACKNOWLEDGMENT

This paper was supported by National Science Foundation Grant GK-1206.

NOTATION

a_0, a_1 = rheological constants, Equation (1)
C_o, C_1 = dimensionless speed, Equations (11) and (12)
D_o = dimensionless thickness, Equation (20)
e = small dimensionless number
g_x, g = gravitational acceleration, cm./sec.^{2}
h = film thickness, cm.
h_o = film thickness in the constant thickness region 1, cm.
L = dimensionless coordinate, Equation (7)
m = parameter as defined by Equation (3)
P = capillary pressure, dyne/sq.cm.
Q_1, Q_2 = flux in regions 1 and 2, Equations (5*b*) and (4*b*)
R = radius of curvature, cm.
R_1, R_2, R_3 = dimensionless coordinate, Equations (8), (18), and (24*b*)
T_o, T_1, T_2 = dimensionless thickness, Equations (9), (10), and (15)
U = vertical fluid velocity, cm./sec.
U_s, U_w = velocity at surface and of the wall, cm./sec.
x, y = rectangular coordinates, see after Equation (2*a*)

Greek Letters

α = rheological exponent, Equation (1), dimensionless
ρ = fluid density, g./cc.
σ = fluid-gas surface tension, dyne/cm.
τ_{yx} = shear stress, dyne/sq.cm.

LITERATURE CITED

1. Gutfinger, Chaim, and J. A. Tallmadge, *A.I.Ch.E. J.*, **11**, 403 (1965).
2. Levich, V. G., "Physicochemical Hydrodynamics," Chap. 12, Prentice Hall, Englewood Cliffs, N. J. (1962).
3. Matsuhisa, Seikichi, and R. B. Bird, *A.I.Ch.E. J.*, **11**, 588 (1965).
4. Reiner, M., "Deformation, Strain, and Flow," 2 ed., Lewis, London (1960).
5. Tallmadge, J. A., *A.I.Ch.E. J.*, **12**, 810 (1966).
6. White, D. A., and J. A. Tallmadge, *Chem. Eng. Sci.*, **20**, 33 (1965).

The Use of Diagnostic Parameters for Kinetic Model Building

J. R. KITTRELL, W. G. HUNTER, and REIJI MEZAKI

University of Wisconsin, Madison, Wisconsin

In a previous paper (*1*) it was shown how an analysis of residuals of a diagnostic parameter could not only indicate the inadequacy of a proposed model for a heterogeneous chemical reaction but also could indicate *how* the model might be modified to yield a more satisfactory model. In this communication, we wish to present additional results on the exploitation of the functional form of a proposed model through the use of diagnostic parameters. The use of such a diagnostic analysis will be illustrated by *building* an adequate Hougen-Watson model from conversion-space time data on the complete vapor phase oxidation of methane over a solid palladium-alumina catalyst. The essence of the model building procedure is the analysis of the residuals of a certain diagnostic parameter occurring in the Hougen-Watson models (*2*).

The success of this technique depends to a certain extent upon the model initially considered. For instance, suppose that instead of beginning with the models of reference *1*, we had considered the grossly inadequate model

$$r = \frac{x_1(1-y)(x_2 - 2x_1 y)^2}{\hat{C}_1 + \hat{C}_2 y} \qquad (1)$$

where

$$\hat{C}_1 = \frac{1}{k_1 K_1} + \frac{1}{k_1} x_1 + \frac{K_3}{k_1 K_1} x_3 \qquad (2)$$

or

$$\hat{C}_1 = b_o + b_1 x_1 + b_3 x_3 \qquad (3)$$

and

$$\hat{C}_2 = \left(\frac{K_3}{k_1 K_1} - \frac{1}{k_1}\right) x_1 y \qquad (4)$$

Equation (1) corresponds to the surface reaction controlled reaction of adsorbed methane with gaseous oxygen to form adsorbed carbon dioxide and vapor phase water. Hence, the expected value of the residual can be obtained by using the $\hat{C}_1$ of Equation (3) and the true value of C_1 from the previous paper (*1*):

$$C_1 = \beta_o + \beta_2 x_2 + \beta_3 x_3 + \beta_4 x_4 + \epsilon \qquad (5)$$

The expected value of the residual thus becomes

$$E(C_1 - \hat{C}_1) = E(\beta_o - b_o)$$
$$2x_1\, E(b_1) + x_2\, E(b_2) + x_3\, E(\beta_3 - b_3) + x_4\, E(b_4) \quad (6)$$

J. R. Kittrell is at Chevron Research Company, Richmond, California.

or, for a factorial design

$$E(C_1 - \hat{C}_1) = \beta_2 x_2 + \beta_4 x_4$$

In the former case, the residual will be correlated with the weighted sum of variables x_1, x_2, x_3, and x_4. Although a trend may still be detectable, we will not generally be able to determine with which of the variables the residual is correlated and thus we will not know how to correct the model. The next section suggests one method of obtaining a good starting model for the model building technique.

INITIAL MODEL SELECTION

As previously mentioned the diagnostic parameter C_1 can be effectively utilized in an iterative model building analysis, *provided* a reasonably good initial model is employed. We shall now show how the experimenter can be guided in the selection of an appropriate initial model with the aid of the second parameter C_2. Consider the general representation of a surface reaction controlling model for the complete oxidation of methane.

$$r = \frac{k x_1 (1-y)(x_2 - 2x_1 y)^2}{[1 + K_1 x_1 (1-y) + \sqrt{K_2}(x_2 - 2x_1 y) + K_3(x_3 + x_1 y) + K_4(x_4 + 2x_1 y)]^n} \tag{7}$$

The problem of specifying an adequate model will then be to determine the exponent n (by means of C_2) and to determine which of the denominator terms may be omitted (by means of C_1). Utilizing the continuity equation for the plug flow integral reactor and collecting terms, we obtain

$$\frac{\partial w}{\partial y} = \frac{[(1 + K_1 x_1 + \sqrt{K_2} x_2 + K_3 x_3 + K_4 x_4) + (K_3 + 2K_4 - 2\sqrt{K_2} - K_1) x_1 y)]^n}{k x_1 (1-y)(x_2 - 2x_1 y)^2} \tag{8}$$

or

$$\frac{\partial w}{\partial y} = \frac{[\hat{C}_1 + \hat{C}_2 y]^n}{x_1 (1-y)(x_2 - 2x_1 y)^2} \tag{9}$$

Now, as before, C_1 is obtained from the experimental data through

$$C_1 = \left\{ x_1 x_2^2 \left. \frac{\partial w}{\partial y} \right|_{y=0} \right\}^{1/n} \tag{10}$$

The derivative in this equation is the reciprocal of the initial slope of the conversion-space time data. By taking the second derivative, the observed value of C_2 is found:

$$C_2 = \frac{x_1 x_2}{n C_1^{n-1}} \left\{ x_2 \left. \frac{\partial^2 w}{\partial y^2} \right|_{y=0} - \frac{C_1^n}{x_1 x_2^2}(x_2 + 4x_1) \right\} \tag{11}$$

The values of C_1 and C_2 predicted from the generalized model are, respectively

$$\hat{C}_1 = b_o + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 \tag{12}$$

$$\hat{C}_2 = b x_1 \tag{13}$$

Note that, as described before, $\hat{C}_1$ changes greatly, depending upon the model assumed; $\hat{C}_2$, however, remains the same for all surface reaction models. A combination of Equations (11) and (13) yields

$$b x_1 = \frac{x_1 x_2}{n C_1^{n-1}} \left\{ x_2 \left. \frac{\partial^2 w}{\partial y^2} \right|_{y=0} - \frac{C_1^n}{x_1 x_2^2}(x_2 + 4x_1) \right\} \tag{14}$$

This contains only two parameters, b and n, and known experimental variables [C_1 is given by Equation (10)]. Hence, it is possible to estimate the magnitude of the parameter n, the power of the denominator of Equation (7), from a set of experimental data. This estimation can be effected by any of several methods, such as linear least squares, a grid-search procedure (3), or nonlinear least squares. Once the number of participating active sites n is specified, the number of possible describing models is greatly decreased. Generally, the selection of any of these models will be a sufficiently good model for a subsequent diagnostic analysis on the parameter C_1. The entire procedure is illustrated in the following example.

EXAMPLE

The experimental system to be studied here is the complete vapor phase oxidation of methane over a palladium-alumina catalyst:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

An integral reactor was used to study this reaction, with conversion-space time data taken at 350°C. and at approximately 1 atm. total pressure. A complete description of the experimental apparatus and the reacting system has been presented elsewhere (*1*). For this study, eight different conditions of the initial partial pressures of the reacting gases were used, with the levels of these variables set approximately according to the 2^{4-1}_{III} fractional factorial design of Table 1. For these eight runs, twenty-two conversion points were obtained and are presented in the earlier article. In the analysis to follow, the average initial partial pressures of the reacting components during each of the eight runs will be required; these differ only slightly from the levels of Table 1 (due to errors in setting the variables) and are presented in Table 2.*

TABLE 1. EXPERIMENTAL DESIGN

Run No.	ξ_1	ξ_2	ξ_3	ξ_4
1	−1	−1	−1	+1
2	+1	−1	−1	−1
3	−1	+1	−1	−1
4	+1	+1	−1	+1
5	−1	−1	+1	−1
6	+1	−1	+1	+1
7	−1	+1	+1	+1
8	+1	+1	+1	−1

$$\xi_1 = \frac{x_1 - 0.015}{0.005} \qquad \xi_2 = \frac{x_2 - 0.120}{0.060}$$

$$\xi_3 = \frac{x_3 - 0.065}{0.035} \qquad \xi_4 = \frac{x_4 - 0.095}{0.055}$$

---

*Tables 2 and 3 have been deposited as document 8980 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.

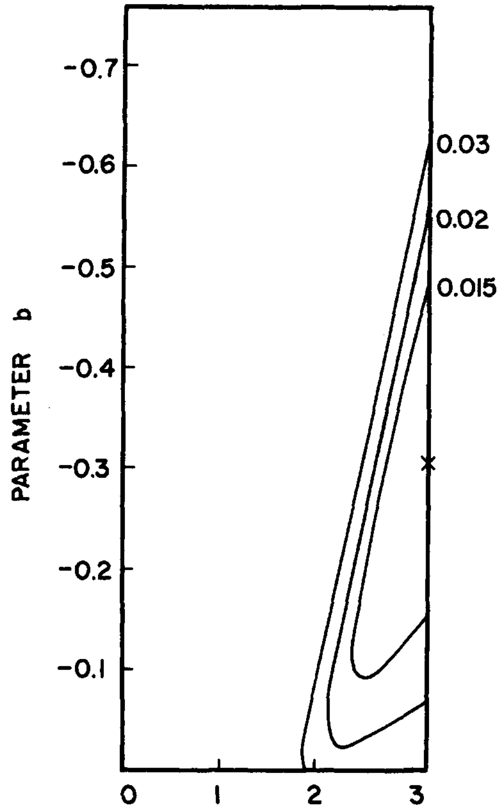

Fig. 1. Contours of sums of squares surface for Equation (14).

In the estimation of the parameter n of Equation (11), linear least squares may sometimes be used. A visual inspection of the data, plotted in Figure 1 of the earlier paper, indicates that these low conversion data may be representable by a straight line. If this were the case, the second derivative of Equation (14) would vanish and the equation would simplify to

$$\ln\left(\frac{x_1x_2^2}{r_0}\right) = n\ln\left(\frac{x_1x_2}{4x_1+x_2}\right) + n\ln(-bn) \quad (15)$$

Here, r_0 denotes the initial slope of the conversion-space time data; C_1 of Equation (14) has been written as defined in Equation (10). Using the left-hand side of Equation (15) as the dependent variable in an unweighted linear least squares analysis, we estimated a value of 2.61 for n, with a standard error of 1.2. This suggests, although not precisely, that only models with three active sets participating in the reaction need be considered. In this example, however, there is some evidence of lack of fit in assuming a linear conversion-space time relationship; hence since a nonzero second derivative may exist, the above linear least squares analysis is of questionable value here.

In order to estimate this second derivative, the conversion-space time data were fitted by a second-order polynomial. The fitted coefficients were then used to obtain estimates of the first and second derivatives. Using these derivatives shown in Table 3* and the average partial pressures of Table 2, we calculated the sums of squares of residuals of the second derivative over a grid of possible values of the parameters b and n. In calculating these residuals, the predicted value of the second derivative is obtained from Equation (14), while the observed value is obtained from Table 3. A portion of the results of this analysis is shown in Figure 1. The minimum sum of squares of this plot yields the estimates of the parameters b and n best describing the data, which are, respectively, -0.3 and 3.0. It may now be seen more conclusively that the best value of n is three. Higher values of n are not considered here because they are theoretically improbable. A nonlinear least squares analysis will also yield this result if n is constrained to be three or less.

TABLE 4. MATRIX OF TERMS COMPRISING POSTULATED MODELS*

Model No.	Methane, x_1	Oxygen, x_2	Carbon dioxide, x_3	Water, x_4
1	1	1	0	0
2	1	1	0	1
3	1	1	1	0
4	1	0	1	1
5	0	1	1	1
6	1	1	1	1

* 0 and 1: gaseous and adsorbed state, respectively.

With n set at 3, the possibility of considering a grossly wrong model and hence reducing the effectiveness of the C_1 residual analysis is diminished. With $n = 3$, one model with a minimum number of parameters is model 1 of Table 4. By choosing a model with the smallest number of parameters, of course, we tend to prevent including parameters in the models unless their presence is absolutely necessary (principle of parsimonious parameterization). The residuals of the diagnostic parameter C_1 for this model are shown in Table 5, for use in an analysis such as that proposed in the earlier paper (*1*). Note that the perfect correlation of the signs of the residuals with the water partial pressure of Table 1 suggests that model 1 should be modified by changing the manner in which the effect of water is taken into account. To maintain $n = 3$, this requires the inclusion of an additional parameter, resulting in model 2 of Table 4. The residuals of model 2 of Table 5, being perfectly correlated with the carbon dioxide level of Table 1, suggest that the effect of carbon dioxide is improperly described by model 2. Keeping the number of parameters to a minimum, we are thus led to model 3 of Table 4. However, the residual trends of model 3 as shown in Table 5 would indicate that the effect of water is not described adequately by the model. Utilizing the principle of parsimonious parameterization, one can consider both water and carbon dioxide to be adsorbed and oxygen to be nonadsorbed, resulting in the three-parameter model 4. The residuals in Table 5 for model 4, however, are correlated with the oxygen level. Hence, model 5 would perhaps be preferable, for it likewise contains only three parameters while allowing adsorbed oxygen. The random residuals of Table 5 for model 5 indicate that this model cannot be rejected by using the data presented. Thus, a reaction rate model adequately describing these experimental data is model 5:

TABLE 5. RESIDUALS OF PARAMETER C_1 FOR THE POSTULATED MODELS $\times 10^3$

Run No.	Residuals for model 1	2	3	4	5
1	+1.17	−1.38	+2.49	−7.18	−0.29
2	−3.61	−1.07	−2.51	−7.70	+0.50
3	−4.99	−2.21	−3.75	+7.54	−1.08
4	+2.33	−0.54	+3.43	+7.88	+0.93
5	−1.18	+1.81	−2.37	−7.00	+0.24
6	+3.39	+0.55	+2.21	−8.75	−0.51
7	+4.01	+1.42	+2.97	+8.04	−0.08
8	−1.13	+1.42	−2.46	+7.16	+0.29

---

*See foonote on page 1015.

$$r = \frac{k_1\sqrt{K_2}x_1(1-y)(x_2-2x_1y)^2}{[1+\sqrt{K_2}(x_2-2x_1y)+K_3(x_3+x_1y)+K_4(x_4+2x_1y)]^3} \qquad (16)$$

This model was also obtained in the earlier paper (*1*), where the residual mean square was shown to compare favorably with that expected from pure error. It is seen, then, that we have been led logically from one model to another within the small class of models for which $n = 3$ by the above analysis.

DISCUSSION

The foregoing development represents a substantial deviation from, and in some cases a distinct improvement on, the more usual methods of obtaining a reaction model adequately describing a set of data. In particular, for Hougen-Watson models, one often must set forth a large number of possible models and extensively search through these to find an adequate model. Common criteria for adequacy are that the data plot linearly with the proper choice of the ordinate and that the parameter estimates be acceptable (*4*). For methane oxidation, more than eighty such models could be thus considered. By contrast, we begin with the class of surface reaction controlling models, since experience has indicated that these models are generally found to represent reaction data. An exception to such an approach may sometimes be found in high-pressure processes, in which adsorption or desorption controlled reactions may exist. The analysis, then, provides first for an estimate of the number of sites participating in the reaction, n, without the necessity of the simultaneous estimation of the magnitudes of all of the individual adsorption constants in the model. Then, a model with the appropriate value of n and with the minimum possible number of adsorption constants is considered and the experimenter is *led* by the experimental data and the analysis to a model with a minimum number of parameters which adequately represents the data.

It should be noted, however, that no claim is made concerning the mechanism of the reaction or even the uniqueness of the *model* which has been set forth as adequately describing the experimental data. We do claim, however, that a logical procedure is now available for obtaining a Hougen-Watson model which adequately represents the data and which is in accordance with the principle of parsimonious parameterization. In this light, it should be noted that model 6 of Table 4, heretofore unmentioned, will also represent the data. It could happen that this model would represent the data with a zero value of the methane adsorption constant, thus reducing model 6 to model 5. Actually, a fit of this model to the data by nonlinear least squares indicates that the best estimate of the methane adsorption constant is 27 atm.$^{-1}$, but with a confidence interval so large that a zero adsorption constant fits the data almost equally well. The reason for this large confidence interval is that the methane partial pressure of Table 2 has been varied only between 1 and 2%, an insufficient variation for the precise specification of the effect of adsorbed methane on the conversion-space time data. This limited variation was used because the original study (*5*) was directed toward a study of methane oxidation in catalytic afterburning of exhaust gases for pollution control, for which low methane compositions are relevant. If, on the other hand, a precise mechanistic model is desired, wider variations of the independent variables are necessary. In fact, such an endeavor will often entail the selection of certain critical experiments, that is, it is largely concerned with experimental designs rather than only data analysis as described here. A review of the literature in the field of mechanistic modeling has been presented elsewhere (*6*).

ACKNOWLEDGMENT

The authors express their gratitude to the National Science Foundation for financial support under Grant No. GP-2755. A grant of computer time by the Wisconsin Alumni Research Foundation through the University Research Committee is also acknowledged.

NOTATION

b = estimated value of a collection of adsorption constants of Equations (8), (9), and (13)
b_i = estimated value of a collection of adsorption and rate constants generally defined in Equations (8), (9), and (12), $i = 0, 1, \ldots, 4$
C_1 = observed value of the diagnostic parameter C_1, generally defined in Equation (10)
$\hat{C}_1$ = predicted value of the diagnostic parameter C_1, generally defined in Equation (12)
C_2 = observed value of a parameter as defined in Equation (11)
$\hat{C}_2$ = predicted value of a parameter as defined in Equation (13)
$E(x)$ = expected value of any random variable x
k = estimated value of the collection of all kinetic terms in Equations (7) and (8), g.-mole/(g.-cat.) (hr.) (atm.^{3})
k_1 = estimated value of the rate constants of Equations (1), (2), (4), and (16), g.-mole/(g.-cat.) (hr.) (atm.^{2})
K_1 = adsorption equilibrium constant for methane, atm.$^{-1}$
K_2 = adsorption equilibrium constant for oxygen, atm.$^{-2}$
K_3 = adsorption equilibrium constant for carbon dioxide, atm.$^{-1}$
K_4 = adsorption equilibrium constant for water, atm.$^{-1}$
n = exponent of denominator of generalized rate expression, Equation (7)
r = reaction rate, g.-mole/(g.-cat.) (hr.)
r_o = initial slope of conversion-space time curve, g.-mole/(g.-cat.) (hr.)
w = space time, (hr.) (g.-cat.)/g.-mole
x = generalized random variable
x_1 = initial partial pressure of methane, atm.*
x_2 = initial partial pressure of oxygen, atm.*
x_3 = initial partial pressure of carbon dioxide, atm.*
x_4 = initial partial pressure of water vapor, atm.*
y = fractional conversion of methane
β_i = true values of the collections of rate and adsorption constants denoted by b_i, $i = 0, 1, 2, \ldots 4$
ϵ = experimental error associated with the determination of the diagnostic parameter C_1
ξ_i = standardized independent variables as defined in Table 1.

LITERATURE CITED

1. Hunter, W. G., and Reiji Mezaki, *A.I.Ch.E. J.*, **10**, 315 (1964).
2. Hougen, O. A., and K. M. Watson, "Chemical Process Principles, Part III," Wiley, New York (1947).
3. Kittrell, J. R., Reiji Mezaki, and C. C. Watson, *Ind. Eng. Chem.*, **57**, No. 12, 18 (1965).
4. Kittrell, J. R., W. G. Hunter, and C. C. Watson, *A.I.Ch.E. J.*, **11**, 1051 (1965).
5. Mezaki, Reiji, Ph.D. thesis, Univ. Wisconsin, Madison (1962).
6. Kittrell, J. R., Reiji Mezaki, and C. C. Watson, *Brit. Chem. Eng.*, **11**, No. 1, 15 (1966).

---

* The variables x_i in the previous paper (*1*) were erroneously defined to be mole fractions. In this communication and the previous paper they should be partial pressures.