tions from the given final condition. If the number of impulse functions which depend on the number of the state variables is large, this search procedure may become prohibitively tedious.

The present method can be used to handle most of the constraints and performance indexes encountered in ordinary optimum design problems. For a detailed discussion of these problems the reader is referred to the paper by Rozonoer (*6*). The method offers some possibilities for use for on-line optimizing control of a process. A special purpose analogue computer could be built for this use.

The analogue computer is ideally suited for solving two point boundary value problems. However for more complicated problems where frequent rescaling and fairly high accuracy is desired, a combined analogue-digital computer would present many advantages. The optimum gradients of temperature, pressure, and concentrations of certain chemical species in a chemical reactor are being investigated by the use of a combined analogue-digital computer.

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NOTATION

E_1, E_2 = activation energies of the first and second reactions
G = mass flow rate, g./min.
G_1, G_2 = frequency-factor constants in Arrhenius equations
H = Hamiltonian function
k_1, k_2 = reaction rate constants of the first and second reactions
N = total moles
n_1, n_2 = moles of A and B, respectively
$p_1, \ldots, p_n$ = impulse functions
R = gas constant
T = temperature
t = independent variable
$u_1, \ldots u_r$ = control variables
$x_1, \ldots, x_n$ = state variables
z = length parameter of the reactor, liter
π = total pressure, atm.
π_1, π_2 = partial pressures of A and B, respectively, atm.

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A Model Building Technique for Chemical Engineering Kinetics

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The object of much experimentation is to build or discover a suitable model for a given system. Unfortunately very little work has been published on what constitutes good strategies in these situations. This paper is an attempt to formulate an approach to this important problem of iteratively improving models in the area of chemical engineering kinetics. In this technique a statistical analysis is applied to the estimated parameters of a tentatively entertained theoretical model in such a way as to pinpoint its inadequacies, if they exist, so that it is possible to proceed in a logical manner to an appropriate modification of this model. This modified model is then analyzed in a similar way, and further modifications are suggested. In general the cycle is repeated as often as is necessary to reach an adequate model. This sequential method is illustrated by finding an adequate reaction model for the total catalytic oxidation of methane.

A simple method for iterative model building has recently been described (*4*) in which a statistical analysis is applied to the estimated parameters of a theoretical model rather than to the original observations themselves. By adopting this method it should be possible to pinpoint inadequacies of a given model in such a way as to suggest specific ways in which the model can be modified, if necessary, to yield a more useful one. The purpose of this paper is to apply this technique for model building to some kinetics data on the catalytic oxidation of methane and to indicate how the method *might* be applied to other problems of this kind. Specifically it is shown how one can proceed in a sequential manner, starting with a tentative theoretical model for the reaction, and be led in a logical way to appropriate modifications of this original formulation.

Such a systematic analysis of kinetics data is desirable particularly in situations similar to the one discussed here where no fewer than eighty mechanisms were put forward as possible. One method of approach would be to examine each of these models individually and select the best one, but there are two obvious drawbacks: it will be extremely time consuming to check each of these models carefully, and even then the most appropriate model may not be contained in this original set.

The iterative method for model building helps on both counts. Since some of the models, a priori, will be more likely to be correct, it will often be possible to start with one of them and by proper analysis be guided to the best model in the set. Moreover the analysis may lead to a particular modification of the original model that is outside the original set; that is, that has been overlooked in the initial cataloguing of possible models.

The method of analysis is based on the principle that constants should stay constant. The basic idea can be illustrated by considering a simple kinetic example where the model being entertained is the first-order decomposition of a chemical substance η:

$$-\frac{d[\eta]}{dt} = \theta[\eta] \qquad (1)$$

$$[\eta] = [\eta]_0 e^{-\theta t} \qquad (2)$$

The rate constant θ in this model should not be a function of the initial concentration of η. This fact immediately suggests one obvious way to check the adequacy of the mathematical model. For each of a number of initial concentrations $[\eta]_0$ measurements of $[\eta]$ could be taken at different times t, and the rate constant θ could be estimated by the method of least squares or some other appropriate means. It should then be possible to examine the set of estimated values $\hat{\theta}$ to determine whether they remained constant within experimental error or on the other hand whether they exhibited a dependence on the initial concentration. If the former were true, then there would be no reason to doubt the adequacy of the proposed model, at least insofar as this particular aspect of the data were concerned. If the latter were true however, then the model would be shown to be inadequate and would have to be modified in a suitable manner depending upon the way in which $\hat{\theta}$ depended on $[\eta]_0$.

In such a simple situation the experimenter usually finds an adequate model by an informal trial-and-error procedure in which he tries a number of different possibilities. Perhaps he would try different orders of reaction to see which one gave the best fit. The reaction considered here would be mth order if

$$-\frac{d[\eta]}{dt} = \theta[\eta]^m \qquad (3)$$

The experimenter therefore would be looking for that value for m which made the estimate $\hat{\theta}$ independent of the initial concentration $[\eta]_0$; that is, roughly speaking, finding the value for m which made the constant constant. This procedure as it stands of course is well known in chemical kinetics. A deeper or more elaborate analysis is perhaps unjustified in such simple cases. When there are several experimental variables however, it is not so obvious whether a given model is adequate or not. Furthermore if the model is inadequate, then careful analysis is necessary to answer two questions: what is the precise nature of the defects, and how can the model be modified to take these defects properly into account. When a complex model is being tentatively entertained, it would be helpful to have available some statistical techniques which would assist in displaying the inadequacies of the given model in a meaningful way so as to suggest useful modifications. Illustrated here is one such technique for iterative model building which makes use of a slight extension of the principle that constants by definition should stay constant.

Examples sometimes arise where the constants do not stay constant but instead change in some prescribed way when the variables are changed. For example if temperature T, measured in absolute units, were a variable in the above example, then one would expect the logarithm of the rate constant to be a linear function of the reciprocal of temperature in accordance with Arrhenius' Law. This extension of the basic idea is in fact used in this paper where the analysis is carried out on the constants c_1, which should vary linearly with the variables x if the model being entertained is correct.

In reference 4 this model building technique was illustrated with a constructed chemical example of the type

$$A + B \xrightarrow{k_1} C$$

$$A + C \xrightarrow{k_2} D$$

where C was measured at five different reaction times for each of sixteen experimental runs. It was supposed that a 2^4 factorial design was used, the controlled variables being the initial concentration of A, the initial concentration of B, the concentration of the catalyst, and the temperature. The model first considered for this system was first order with respect to the reacting components B and C and was independent of the catalyst concentration. By estimating the rate constants k_1 and k_2 for each of the sixteen runs and analyzing these estimates it was shown that this initial model was inadequate. The example illustrated how the exact nature of the defects of the model was pinpointed so that it was possible to modify the model in an appropriate manner. This diagnostic technique clearly showed for example that the data had been calculated from a system in which the rate constant k_1 for the first reaction $(A + B \rightarrow C)$ was a function of the square root of the catalyst concentration and not independent of this factor as originally supposed. It is now possible to illustrate the application of this technique to some real experimental data on the catalytic oxidation of methane, a solid-catalyzed gas reaction (7).

Before the experiments are described in detail, the motivation for this investigation is briefly indicated. Light hydrocarbons from various sources, such as automobile exhausts, have been said to contribute to the formation of smog (5). One possible way of solving this problem is to pass such exhaust gases through suitable catalytic oxidation units that will convert the unwanted hydrocarbons into carbon dioxide and water. To evaluate the practicality of such a scheme it is desirable to have quantitative information on the kinetics of the reactions. Methane is a member of the light hydrocarbon family, and being the most difficult one to oxidize it offers a good starting point for a comprehensive investigation of the catalytic oxidation of light hydrocarbons. The ultimate goal of this investigation was to determine an appropriate rate equation for the catalytic oxidation of methane. Such basic kinetic information would be useful in the design of suitable oxidation units.

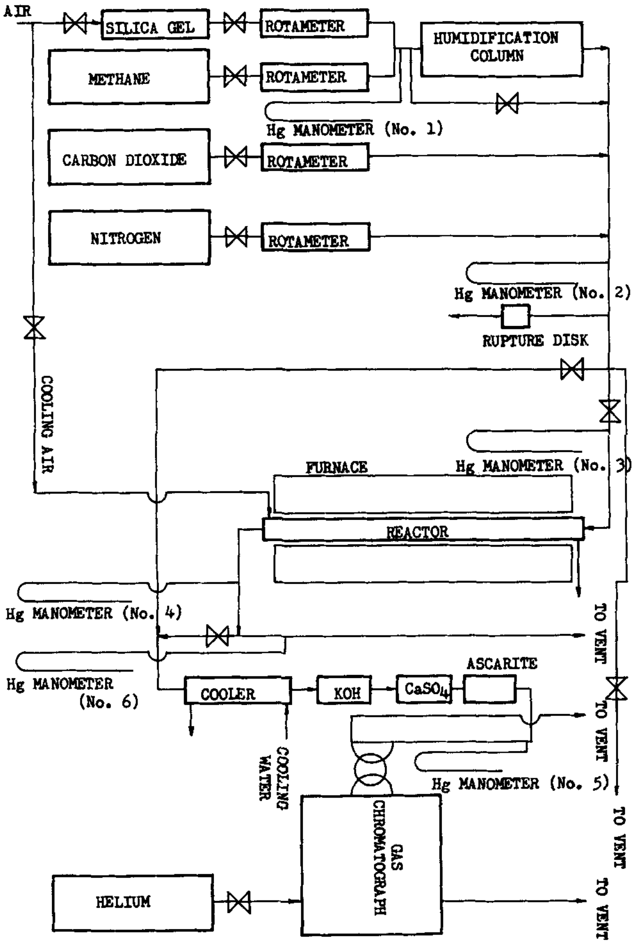

Fig. 1. Flow diagram.

EXPERIMENTAL APPARATUS

A schematic diagram of the experimental apparatus is shown in Figure 1. The feed stream consisted of nitrogen, carbon dioxide, methane, air, and water vapor. The gases (nitrogen, carbon dioxide, methane, and air) were controlled by a pressure regulating valve and needle valves. Compressed air from the laboratory lines was passed through drying tubes filled with silica gel to eliminate water. Commercially available cylinder gases were used. Water vapor was introduced into the feed stream by passing the methane and air stream through a water saturation column. Water concentration, which was regulated by changing the water temperature, was calculated from the wet and dry bulb temperatures at the outlet of the column. The feed line was heated between the column and the reactor to avoid partial condensation of water vapor in the gas.

The reactor, a 10-mm. I.D. quartz tube, 30 in. long, consisted of three sections: preheater, reaction zone, and quenching zone. Flow through the reactor was from top to bottom. The preheater section was a 25 in. empty vertical tube in which the gas was heated to the desired temperature by a surrounding electric furnace. The reaction zone, heated by a second electric furnace, consisted of a layer of catalyst. Two thermocouple wells were positioned in the catalyst bed. The reactor was surrounded by an air jacket. Compressed air was circulated inside a concentric 1-in. O.D. quartz tube, 23 in. long, to regulate the temperature. The bottom part of the reactor was the quenching zone which consisted of a ¼-in. layer of quartz chips and a 1 in. length of empty tube. The gases coming from the reactor were dried and purified to eliminate water vapor and carbon dioxide. A vapor fractometer equipped with a J column was employed for the analysis of both reactant and product gases.

A palladium catalyst (0.5% palladium deposited on the surface of γ-alumina) was used. The bulk density of the catalyst was 56 lb./cu.ft., and the surface area was 120 sq. m./g. The ⅛-in. extrusions were crushed by a mortar and pestle and screened with a U.S. sieve series set. The −12+14 mesh fraction was used for this work. The activity of the catalyst dropped during the oxidation of methane. After a 20-hr. service period however the activity reached a relatively constant value.

TENTATIVE KINETIC MODEL

Hougen and Watson (*6*) developed rate equations for isothermal gas reactions catalyzed by solids. A rate equation thought to be appropriate for the catalytic oxidation of methane was developed on the basis of the Hougen and Watson approach. The following reaction mechanism was tentatively entertained. Gaseous methane and adsorbed oxygen react producing gaseous carbon dioxide and adsorbed water. Oxygen is adsorbed on adjacent dual sites. The individual steps in the reaction are:

1. Adsorption of oxygen:

$$2O_2 + 2l \rightleftarrows 2O_2l$$

2. Surface reaction:

$$CH_4 + 2O_2l \rightleftarrows 2H_2Ol + CO_2$$

3. Desorption of water:

$$H_2Ol \rightleftarrows H_2O + l$$

Rate equations for the individual steps can now be written. For adsorption

$$r_1 = \theta_6 \left(a^2_{O_2} C_{l \cdot l} - \frac{C_{O_2 \cdot O_2}}{\theta_2} \right) \tag{4}$$

For surface reaction

$$r_2 = \theta_7 \left(a_{CH_4} C_{O_2 \cdot O_2} - \frac{C_{H_2O \cdot H_2O}\, a_{CO_2}}{\theta_5} \right) \tag{5}$$

For desorption

$$r_3 = \theta_8 \left(C_{H_2O} - \theta_4\, a_{H_2O}\, C_l \right) \tag{6}$$

where

$$C_{l \cdot l} = \left(\frac{S}{L} \right) C_l^2$$

$$C_{O_2 \cdot O_2} = \left(\frac{S}{L} \right) C^2_{O_2}$$

$$C_{H_2O \cdot H_2O} = \left(\frac{S}{L} \right) C^2_{H_2O}$$

$$L = C_l + C_{O_2} + C_{H_2O} = C_l (1 + \sqrt{\theta_2}\, a_{O_2} + \theta_4\, a_{H_2O})$$

If it is assumed that the surface reaction is the rate controlling step, the reaction rate can be expressed by the following equation:

$$r = \frac{\theta_2 \theta_7 \,(SL) \left(a_{CH_4}\, a^2_{O_2} - \frac{1}{K}\, a^2_{H_2O}\, a_{CO_2} \right)}{(1 + \sqrt{\theta_2}\, a_{O_2} + \theta_4\, a_{H_2O})^2} \tag{7}$$

The equilibrium constant *K* for the oxidation of methane as determined by a thermodynamic calculation is extremely large (approximately 10^{84}) at 350°C. Thus the equation can be simplified to give

$$r = \frac{\theta_1 \theta_2 (a_{CH_4}\, a^2_{O_2})}{(1 + \sqrt{\theta_2}\, a_{O_2} + \theta_4 a_{H_2O})^2} \tag{8}$$

where $\theta_7 SL = \theta_1$.

From stoichiometry

$$a_{CH_4} = x_1 - x_1 y$$
$$a_{O_2} = x_2 - 2x_1 y$$
$$a_{H_2O} = x_4 + 2x_1 y$$

TABLE 1. EXPERIMENTAL DESIGN WITH RESULTS

Run	ξ_2	ξ_3	ξ_4	ξ_5	Fractional conversion of methane y			Slope s
					$w = 0.0025$	$w = 0.0050$	$w = 0.0075$	
1	−1	−1	−1	+1	0.02588	0.06599	0.09539	12.41
2	+1	−1	−1	−1	*	0.30427	0.38574	52.06
3	−1	+1	−1	−1	*	0.13709	0.18025	23.78
4	+1	+1	−1	+1	0.06863	0.13162	0.21191	27.17
5	−1	−1	+1	−1	0.04344	0.09790	0.13965	18.35
6	+1	−1	+1	+1	0.03201	0.07693	0.10449	14.31
7	−1	+1	+1	+1	0.02449	0.06297	0.08221	11.47
8	+1	+1	+1	−1	0.07625	0.17175	0.23352	31.83

$$\xi_2 = \frac{x_1 - 0.015}{0.005} \qquad \xi_4 = \frac{x_3 - 0.065}{0.035}$$

$$\xi_3 = \frac{x_2 - 0.120}{0.060} \qquad \xi_5 = \frac{x_4 - 0.095}{0.055}$$

* Missing data.

Thus

$$r = \frac{\theta_1\theta_2\, x_1(1-y)\,(x_2 - 2x_1y)^2}{[1 + \sqrt{\theta_2}\,(x_2 - 2x_1y) + \theta_4\,(x_4 + 2x_1y)\,]^2} \tag{9}$$

Upon integration Equation (9) yields

$$w = \frac{1}{\theta_1\theta_2} \times \int_0^y \frac{[1 + \sqrt{\theta_2}\,(x_2 - 2x_1y) + \theta_4\,(x_4 + 2x_1y)\,]^2}{x_1\,(1-y)\,(x_2 - 2x_1y)^2}\,dy \tag{10}$$

That is

$$w = \int_0^y \frac{[c_1 + c_2y]^2}{x_1\,(1-y)\,(x_2 - 2x_1y)^2}\,dy \tag{11}$$

where

$$c_1 = \beta_0' + \beta_2'\,x_2 + \beta_4'\,x_4 \tag{12}$$

$$c_2 = -\,2(\beta_2' - \beta_4')x_1 \tag{13}$$

$$\beta_0' = \frac{1}{\sqrt{\theta_1\theta_2}}$$

$$\beta_2' = \frac{\sqrt{\theta_2}}{\sqrt{\theta_1\theta_2}}$$

$$\beta_4' = \frac{\theta_4}{\sqrt{\theta_1\theta_2}}$$

Notice that the c's are linear functions of the unknown parameters β', so that if values for the c's can be obtained, the coefficients β' can be estimated by the method of least squares. For a given run the quantity c_1 is in fact directly related to the initial slope of the y vs. w curve. Differentiating Equation (11) with respect to y one obtains

$$\frac{\partial w}{\partial y} = \frac{[c_1 + c_2y]^2}{x_1\,(1-y)\,(x_2 - 2x_1y)^2} \tag{14}$$

Hence

$$\left.\frac{\partial w}{\partial y}\right|_{y=0} = \frac{c_1^2}{x_1x_2^2} \tag{15}$$

Thus

$$c_1 = \sqrt{x_1x_2^2\left(\left.\frac{\partial w}{\partial y}\right|_{y=0}\right)} \tag{16}$$

Likewise c_2 is related to the second derivative by the equation

$$c_2 = \frac{x_1x_2}{2c_1}\left\{\left.\frac{\partial^2 w}{\partial y^2}\right|_{y=0} + (4x_1 + x_2)c_1^3\right\} \tag{17}$$

EXPERIMENTAL DESIGN

The experimental design shown in Table 1 was run at 350°C. at atmospheric pressure. This is a 2_{III}^{4-1} fractional factorial design (3). The four variables were the input concentrations of methane, oxygen, carbon dioxide, and water vapor. The eight runs for this design together with the resulting conversions y are shown in Table 1. For each run three levels of w (weight of catalyst/mass flow rate of gas) were used.

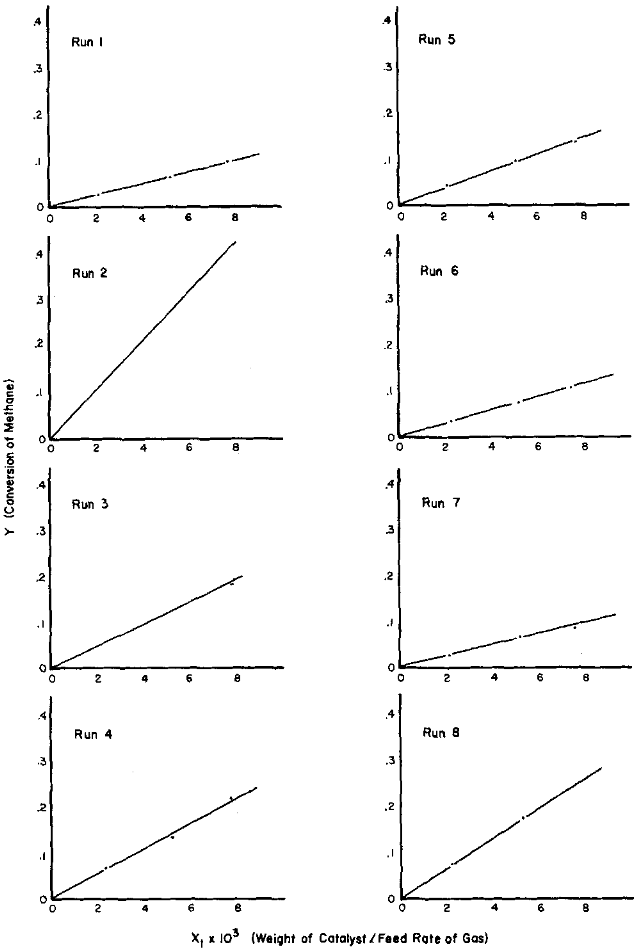

Fig. 2. Fitted curves.

Table 2. Summary of Results for Model I

$$\hat{c}_1' = b_0' + b_2'x_2 + b_4'x_4$$

$b_0' = -0.0007$	$b_2' = 0.027$	$b_4' = 0.008$
± 0.0004*	± 0.002*	± 0.002*

Run	$c_1' \times 10^4$	$\hat{c}_1' \times 10^4$	$(c_1' - \hat{c}_1') \times 10^4$
1	20.54	24.27	−3.73
2	13.93	14.35	−0.42
3	47.98	52.62	−4.64
4	58.08	59.69	−1.61
5	16.70	14.55	+2.15
6	25.27	23.45	+1.82
7	64.32	60.68	+3.64
8	53.56	50.75	+2.81

$$s(c_1') \times 10^4 = 1.72$$

* The numbers following ± signs are standard errors.

ANALYSIS OF DATA

The data which are plotted in Figure 2 can be represented to a good approximation by eight straight lines. Curvature is slight in this region, and higher values of w would be needed to show a marked departure from a linear relationship. The reaction however could not be controlled at higher values of w, and therefore no data could be obtained in this region.

The slopes of these eight straight lines were estimated by least squares and are given in Table 1. These calculations as well as all others in this paper were performed with the experimentally recorded values of the variables x and w. These values differ slightly from those given in Table 1 because it was virtually impossible because of experimental error to set all the variables exactly at the desired levels.

Model I.

The slope s estimates the derivative $\left.\frac{\partial y}{\partial w}\right|_{y=0}$ Making this replacement in Equation (16) one obtains

$$c_1' = \sqrt{\frac{x_1 x_2^2}{s}} \qquad (18)$$

Using these c_1' values in Equation (12) one can obtain by least squares the results shown in Table 2.

The residual sum of squares $\sum_{i=1}^{8} (c'_{1i} - \hat{c}'_{1i})^2$ is 67.319 $\times 10^{-8}$, and the corresponding mean square is 13.463 $\times 10^{-8}$ with 5 deg. of freedom. The ratio of this mean square to the estimated mean square error $s^2(c_1')$ [see Appendix] calculated from the fitted slopes $s_i (i = 1, 2, \ldots, 8)$ is 4.53. The upper 5% point for the F distribution with 5 and 14 deg. of freedom is only 2.96, which indicates that model I is inadequate since the value of the ratio considerably exceeds this value.

Of prime importance at this point is the unusual behavior of the residuals $c_1' - \hat{c}_1'$ which provides a valuable clue as to what modification of the model might be tried next. Notice that the sign of the first four residuals is negative and the sign of the last four is positive. As can be seen from Table 1 the signs of the residuals are perfectly correlated with the concentration of carbon dioxide. That is, model I does not take the concentration of carbon dioxide properly into account. Recall that in accordance with model I the reaction yields nonadsorbed carbon dioxide. So a logical modification would be to assume carbon dioxide is adsorbed. To keep the model as simple as possible further assume that water is not adsorbed. By doing this one ensures that the new model, model II, contains three parameters θ the same number as model I.

Model II

Following a similar development to that used in obtaining Equation (11) for model I one obtains for model II

$$w = \frac{1}{\theta_1\theta_2} \times \int_0^y \frac{[1 + \sqrt{\theta_2}\,(x_2 - 2x_1y) + \theta_3(x_3 + x_1y)]^2}{x_1(1-y)(x_2 - 2x_1y)^2}\,dy \qquad (19)$$

which can be rewritten as

$$w = \int_0^y \frac{[c_1 + c_2\,y]^2}{x_1(1-y)(x_2 - 2x_1y)^2}\,dy \qquad (20)$$

where

$$c_1 = \beta'' + \beta_2''\,x_2 + \beta_3''\,x_3 \qquad (21)$$

$$c_2 = (\beta_3'' - 2\beta_2'')\,x_1 \qquad (22)$$

$$\beta_0'' = \frac{1}{\sqrt{\theta_1\theta_2}}$$

$$\beta_2'' = \frac{\sqrt{\theta_2}}{\sqrt{\theta_1\theta_2}}$$

$$\beta_3'' = \frac{\theta_3}{\sqrt{\theta_1\theta_2}}$$

The derivatives for model II yield results which are similar to those for model I:

$$\left.\frac{\partial w}{\partial y}\right|_{y=0} = \frac{c_1^2}{x_1x_2} \qquad (23)$$

$$\left.\frac{\partial^2 w}{\partial y^2}\right|_{y=0} = \frac{2c_1c_2}{x_1x_2}\,(4x_1 + x_2)\,c_1^3 \qquad (24)$$

If $\left.\frac{\partial w}{\partial y}\right|_{y=0}$ is replaced in Equation (23) by the quantity s, a value for c_1'' can be calculated for each of the eight runs; that is

$$c_1'' = \sqrt{\frac{x_1x_2^2}{s}} \qquad (25)$$

With these values Equation (21) can be fitted by least squares and the results analyzed. The summary of the results for model II is shown in Table 3.

Table 3. Summary of Results for Model II

$$\hat{c}_1'' = b_0'' + b_2''x_2 + b_3''x_3$$

$b_0'' = -0.0003$	$b_2'' = 0.027$	$b_4'' = 0.0063$
± 0.0006*	± 0.003*	± 0.0058*

Run	$c_1'' \times 10^4$	$\hat{c}_1'' \times 10_4$	$(c_1 - \hat{c}_1'') \times 10_4$
1	20.54	16.91	+3.63
2	13.93	16.81	−2.88
3	47.98	54.66	−6.68
4	58.08	52.80	+5.28
5	16.70	21.83	−5.13
6	25.27	21.20	+4.07
7	64.32	58.05	+6.27
8	53.56	58.12	−4.56

$$s(c_1'') \times 10^4 = 1.72$$

* The numbers following ± signs are standard errors.

The residual sum of squares $\sum_{i=1}^{8} (c_{1i}'' - \hat{c}_{1i}'')^2$ is 197.06 × 10^{-8}, and the corresponding mean square is 39.41 × 10^{-8} with 5 deg. freedom. The ratio of this mean square to the mean square error $s^2(c_1'')$ is 13.27, which indicates that model II is also inadequate. Once again however by carefully examining the residuals one can gain valuable insight into the precise nature of the defects of this model. It will be noticed upon comparison with Table 1 that the signs of the residuals are now perfectly correlated with the concentration of water vapor.

Model I involved nonadsorbed carbon dioxide and adsorbed water, and model II involved adsorbed carbon dioxide and nonadsorbed water. Model I was shown to fail with regard to the manner in which carbon dioxide was taken into account, and model II was shown to be likewise inadequate with respect to water. It is apparently necessary to consider a model in which carbon dioxide and water are both adsorbed. In contrast to both models I and II which each involved three parameters, one will now be concerned with a more complex model containing four parameters.

Model III

Starting with the assumptions that both carbon dioxide and water are adsorbed and following a derivation similar to those for models I and II one obtains for model III

$$w = \frac{1}{\theta_1\theta_2} \int_0^y \frac{[1 + \sqrt{\theta_2}(x_2 - 2x_1y) + \theta_3(x_3 + x_1y) + \theta_4(x_4 + 2x_1y)]^3}{x_1(1-y)(x_2 - 2x_1y)^2} dy \qquad (26)$$

which can be rewritten as

$$w = \int_0^y \frac{[c_1 + c_2\, y]^3}{x_1(1-y)(x_2 - 2x_1y)^2} dy \qquad (27)$$

where

$$c_1 = \beta_0''' + \beta_2'''\, x_2 + \beta_3'''\, x_3 + \beta_4'''\, x_4 \qquad (28)$$

$$c_2 = (2\beta_4''' + \beta_3''' - 2\beta_2''')\, x_1 \qquad (29)$$

$$\beta_0''' = \frac{1}{\sqrt[3]{\theta_1\theta_2}} \qquad (30)$$

$$\beta_2''' = \frac{\sqrt{\theta_2}}{\sqrt[3]{\theta_1\theta_2}} \qquad (31)$$

$$\beta_3''' = \frac{\theta_3}{\sqrt[3]{\theta_1\theta_2}} \qquad (32)$$

$$\beta_4''' = \frac{\theta_4}{\sqrt[3]{\theta_1\theta_2}} \qquad (33)$$

The derivatives for model III differ from those of models I and II:

$$\left.\frac{\partial w}{\partial y}\right|_{y=0} = \frac{c_1^3}{x_1x_2^2} \qquad (34)$$

$$\left.\frac{\partial^2 w}{\partial y^2}\right|_{y=0} = \frac{(4x_1 + x_2)}{x_2} c_1^3 + \frac{3}{(x_1x_2^2)^2} c_1^2c_2 \qquad (35)$$

A value of c_1''' for each run can be calculated by replacing $\left.\frac{\partial w}{\partial y}\right|_{y=0}$ in Equation (34) by the estimated slope s; that is

$$c_1''' = \sqrt[3]{\frac{x_1x_2^2}{s}} \qquad (36)$$

TABLE 4. SUMMARY OF RESULTS FOR MODEL III

$$\hat{c}_1''' = b_0''' + b_2'''x_2 + b_3'''x_3 + b_4'''x_4$$

$b_0''' = 0.0007$	$b_2''' = 0.113$	$b_3''' = 0.038$	$b_4''' = 0.041$
±0.0011*	±0.005*	±0.008*	±0.005*

Run	$c_1''' \times 10^3$	$\hat{c}_1''' \times 10^3$	$(c_1 - \hat{c}_1''') \times 10^3$
1	15.57	15.99	−0.42
2	11.94	11.03	+0.91
3	25.99	27.04	−1.05
4	31.53	30.92	+0.61
5	13.56	14.08	−0.52
6	18.52	18.55	−0.03
7	34.03	34.14	−0.11
8	29.87	29.26	+0.61

$$s(c_1''') \times 10^3 = 0.65$$

* The numbers following ± signs are standard errors.

The results of fitting Equation (28) by least squares are shown in Table 4. The residual sum of squares $\sum_{i=1}^{8} (c_{1i}''' - \hat{c}_{1i}''')^2$ is 3.013 × 10^{-6}, and the residual mean square is 0.784 × 10^{-6} with 4 deg. of freedom. The ratio of this residual mean square to $s^2(c''')$ [see Appendix] is 1.83, which indicates that the model is adequate since $F_{4,14}(0.95) = 3.11$. Also the residuals show no obvious systematic pattern but seem to be random. Therefore model III appears to be adequate. Not only can one say that the present mechanism offers a satisfactory explanation of the data, but also this is so when one has severely strained the model and carefully considered plausible alternatives. Thus the major objective of this paper is accomplished. An appropriate form for a reaction rate equation for the catalytic oxidation of methane has been found.

The analysis can now be carried a step further by determining estimates for the four parameters θ. Rough estimates can most easily be found by substituting b's for the corresponding β's in Equations (30), (31), (32), and (33), and solving for the θ's. The values so obtained can be used as initial guesses for the parameters in a nonlinear least-squares calculation (*1, 2*) to obtain better estimates. Incidentally one of the practical aspects which is of critical importance in using nonlinear estimation successfully is obtaining good first guesses for the parameters, and the approach outlined above provides such initial values. The results were

	$\hat{\theta}_1$	$\hat{\theta}_2$	$\hat{\theta}_3$	$\hat{\theta}_4$	Residual sum of squares $\sum_{k=1}^{22} (y_k - \hat{y}_k)^2$
By solving equations	118,000	30,300	58.7	63.1	3.18×10^{-3}
By using nonlinear estimation	125,000	33,400	52.4	63.4	1.39×10^{-5}

Although there is fairly good agreement between the corresponding $\hat{\theta}$ values, the residual sum of squares for nonlinear estimation is considerably smaller. The principal reason for this fact is that in this treatment the authors have restricted themselves to the consideration of straight-line relationships between y and w for each run, whereas in fact not only is curvature to be expected, but also it can be detected from a closer statistical analysis. An examination of the residuals from the fitted straight lines for example reveals a negative value for seven out of the eight final residuals, that is $y - s\,w$ for the highest value of w in each of the runs. Furthermore the ratio of $s^2(y) = 1.33 \times 10^{-4}$ [computed from the residuals from the straight lines (see Appendix)] to $s^2 = 1.41 \times 10^{-6}$ (based on four pairs of duplicate runs in previous work indicates lack of fit, the ratio being 94.3 as compared with $F_{4,14}(0.95) = 5.9$. Consequently the second derivative could have been estimated, and the corresponding c_2 values could have been calculated. An analysis similar to that applied to the c_1 values could have been applied to the c_2 values. In some cases this procedure of using higher-order derivatives may be useful.

DISCUSSION

The main aim of this paper has been to show how one can proceed in a sequential manner in a model building situation starting with a tentative model which has a theoretical basis. The data are analyzed in the light of this particular model in such a way as to pinpoint precisely the inadequacies of this original conjecture. The model is modified in a logical manner, and the data are then reanalyzed. Defects are once again revealed, and the model is modified further and so forth. One eventually arrives at an adequate model by using this iterative, diagnostic technique. The emphasis has been on an attempt to formulate a method for improving models, as opposed to a procedure for proving or disproving (that is, accepting or rejecting) them.

In any least-squares analysis of course it is possible to check the lack of fit by examining the residuals and in particular the residual sum of squares. As has been shown however residuals can be further analyzed in a way that is particularly meaningful. The object of the analysis is not especially to establish lack of fit but to provide some indication of the nature of this lack of fit to help the experimenter in deciding how the model might be modified.

The technique has been illustrated by an example in which statistically designed experiments were employed. A number of questions arise. Could the method have been used if the experiments had not followed a factorial arrangement? The answer is yes, but in the example the implications of the residuals could not have been so readily interpreted. Nevertheless it would have been possible to proceed exactly as before in fitting the linear relationship between c_1 and the x's [for example, Equation (12) for model I] provided only that the data points yielded at least as many such independent equations as there were coefficients to be estimated. The correlation between the residuals and the variables x however would probably not have been so obvious, although it could have been discovered either graphically by a plot of the residuals vs. x or by making the corresponding analytical calculation.

Fractional designs are usually employed for estimating coefficients similar to the β's above. However since experimenters are primarily interested in the θ's and not the β's, should it not be possible to devise better designs for their purposes by focusing attention more directly on the problem of estimating the θ's? That is although the method is a valid one, as demonstrated by the kinetic example, could it not be made more efficient. This question is presently under investigation.

A number of other things must also be considered when designing an experiment in a model building situation. For instance in the example quoted above no fewer than eighty mechanisms were put forward as possible. It is of course well known that no mechanistic theory can be mathematically proved. It can only be said that the experimental data have failed to contradict a proposed mechanism. It can happen however that a model or group of models is never really placed in jeopardy by a particular set of experimental runs. That is to say the mechanism could be wrong in particular specific ways, and yet these discrepancies could not be revealed by the particular experiments performed. It is hoped that further work will be forthcoming on the specific problem of how best to plan experiments which will reveal and verify a particular mechanism, that is which will discriminate among rival candidate models.

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NOTATION

a_{CH_4} = activity of methane
a_{CO_2} = activity of carbon dioxide
a_{H_2O} = activity of water vapor
a_{O_2} = activity of oxygen
b = estimate of β
c_1 = true quantity defined for model I by Equation (16), for model II by Equation (21), and for model III by Equation (28)
c_2 = true quantity defined for model I by Equation (17), for model II by Equation (22), and for model III by Equation (29)
c_1' = calculated value of c_1 defined by Equation (18)
c_1'' = calculated value of c_1 defined by Equation (25)
c_1''' = calculated value of c_1 defined by Equation (36)
c_l = total concentration of empty active sites
$C_{l \cdot l}$ = concentration of adjacently located empty active sites
C_{H_2O} = total concentration of adsorbed water
$C_{H_2O \cdot H_2O}$ = concentration of adjacently adsorbed water
C_{O_2} = total concentration of adsorbed oxygen
$C_{O_2 \cdot O_2}$ = concentration of adjacently adsorbed oxygen
k_1 = rate constant
k_2 = rate constant
K = thermodynamic equilibrium constant of the methane oxidation reaction
L = total concentration of active sites
m = constant in Equation (3)
n = number of observations in a given run
r = overall reaction rate
r_1 = adsorption rate for oxygen
r_2 = rate of surface reaction
r_3 = desorption rate for water
s = slope of fitted y vs. w curve
S = number of equidistant active centers adjacent to each other
$s(\ )$ = standard deviation of ( )
$s^2(\ )$ = variance of ( )
t = time of reaction
w = (weight of catalyst)/(mass flow rate of gas)
w_{ij} = the jth value of w in the ith run
x_1 = mole fraction of methane
x_2 = mole fraction of oxygen
x_3 = mole fraction of carbon dioxide
x_4 = mole fraction of water vapor
y = fractional conversion of methane
y_{ij} = the jth value of y in the ith run
$\hat{y}_{ij}$ = the least-squares estimate of y_{ij}, namely $s_i w_{ij}$

Greek Letters

β = true parameter value
$[\eta]$ = concentration of chemical substance η at time t
$[\eta]_0$ = initial concentration of η at time $t = 0$
θ = first-order rate constant
θ_1 = overall reaction rate constant
θ_2 = adsorption equilibrium constant for oxygen
θ_3 = adsorption equilibrium constant for carbon dioxide
θ_4 = adsorption equilibrium constant for water vapor
θ_5 = equilibrium constant of surface reaction
θ_6 = adsorption rate constant of oxygen
θ_7 = surface reaction rate constant
ν = degrees of freedom
ξ = standardized variable defined in Table 1

Superscripts

$\wedge$ = estimated quantity
$'$ = model I
$''$ = model II
$'''$ = model III

Subscripts

i = run number $(i = 1, 2, \ldots, 8)$
j = experiment number within a run $(1, \ldots, n_i)$
k = experiment number $(1, 2, \ldots, 22)$

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APPENDIX: ERROR ANALYSIS

After the eight slopes s_i have been determined by least squares, that is

$$s_i = \frac{\sum_{j=1}^{n_i} w_{ij} y_{ij}}{\sum_{j=1}^{n_i} w_{ij}^2} \quad (i = 1, 2, \ldots, 8)$$

it is possible to obtain a pooled estimate $s^2(y)$ of the experimental error variance σ^2 from

$$s^2(y) = \frac{\sum_{i=1}^{8} \sum_{j=1}^{n_i} (y_{ij} - \hat{y}_{ij})^2}{\sum_{i=1}^{8} \nu_i} = \frac{18.703 \times 10^{-4}}{14} = 1.3359 \times 10^{-4}$$

or

$$s(y) = 1.156 \times 10^{-2}$$

Therefore a pooled estimate $s^2(s)$ of the variance of the slope is

$$s^2(s) = \frac{\sum_{i=1}^{8} \nu_i s^2(s_i)}{\sum_{i=1}^{8} \nu_i}$$

where

$$\nu_i = n_i - 1$$

$$s^2(s_i) = s^2(y) / \sum_{j=1}^{n_i} w_{ij}^2$$

or

$$s^2(s) = s^2(y) \frac{\sum_{i=1}^{8} \left\{ \nu_i \Big/ \sum_{j=1}^{n_i} w_{ij}^2 \right\}}{\sum_{i=1}^{8} \nu_i} = \frac{1.3359 \times 10^{-4}}{14} \sum_{i=1}^{8} \frac{\nu_i}{\sum_{j=1}^{n_i} w_{ij}^2}$$

$$s^2(s) = \frac{1.3359}{14} 18.3217 = 1.7483$$

that is

$$s(s) = 1.3222$$

To determine $s(c_i')$ let us use the linear approximation

$$s(c'_{1i}) = \left| \frac{dc_{1i}}{ds_i} \right| s(s)$$

Now for model I

$$c_1{}'_i = x_1{}^{1/2} x_2 s_i{}^{-1/2} \; (i = 1, 2, \ldots, 8)$$

and

$$\left| \frac{dc'_{1i}}{ds_i} \right| = \frac{1}{2} \frac{c_1{}'_i}{s_i}$$

Thus

$$s(c'_{1i}) = \frac{1}{2} \cdot \frac{c'_{1i}}{s_i} \cdot 1.3222 = 0.6611 \frac{c'_{1i}}{s_i}$$

from which one can obtain the pooled estimate

$$s^2(c_1') = \frac{\sum_{i=1}^{8} \nu_i s^2(c'_{1i})}{\sum_{i=1}^{8} \nu_i} = \frac{41.60 \times 10^{-8}}{14} = 2.9715 \times 10^{-8}$$

and

$$s(c_1') = 1.7238 \times 10^{-4}$$

For model II one obtains identical results; that is

$$s^2(c''_1) = s^2(c'_1) = 2.9715 \times 10^{-8}$$

$$s(c''_1) = s(c'_1) = 1.7238 \times 10^{-4}$$

Analogously for model III

$$c'''_{1i} = x_{1i}{}^{1/3} \, x_{2i} \, s_i{}^{-1/3}$$

and

$$\left| \frac{dc'''_{1i}}{ds_i} \right| = \frac{1}{3} \frac{c'''_{1i}}{s_i}$$

Thus

$$s(c'''_{1i}) = \frac{1}{3} \frac{c'''_{1i}}{s_i} 1.3222 = 0.4407 \frac{c'''_{1i}}{s_i}$$

from which one can obtain the pooled estimate

$$s^2(c'''_1) = \frac{\sum_{i=1}^{8} \nu_i s^2(c'''_{1i})}{\sum_{i=1}^{8} \nu_i} = \frac{6.0015 \times 10^{-6}}{14} = 0.4287 \times 10^{-6}$$

and

$$s(c'''_1) = 0.6548 \times 10^{-3}.$$