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A MODEL-BUILDING TECHNIQUE FOR CHEMICAL ENGINEERING KINETICS *

by

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A MODEL-BUILDING TECHNIQUE FOR CHEMICAL ENGINEERING KINETICS

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 report 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 80 mechanisms were put forward as possible.

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 \( \eta \),

\[
- \frac{d[\eta]}{dt} = \theta[\eta] ,
\]

that is,

\[
[\eta] = [\eta]_0 e^{-\theta t} .
\]
where \([\eta]\) = concentration of chemical substance \(\eta\) at time \(t\)

\([\eta]_0\) = initial concentration of \(\eta\) at time \(t = 0\)

\(\theta\) = first-order rate constant

\(t\) = time of reaction.

The rate constant \(\theta\) in this model should not be a function of the initial concentration of \(\eta\). 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 \(\hat{\theta}\) 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 manner 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 \(n\)-th order if
\[- \frac{d[\eta]}{dt} = \theta[\eta]^n. \tag{3}\]

The experimenter, therefore, would be looking for that value for \(n\) which made the estimate \(\hat{\theta}\) independent of the initial concentration \([\eta]_0\), that is, roughly speaking, finding the value for \(n\) 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:

1) What is the precise nature of the defects?

2) 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 we would expect the logarithm of the rate "constant"
to be a linear function of the reciprocal of temperature $T^{-1}$ in accordance
with Arrhenius' Law. This extension of the basic idea is, in fact, used in
this report where the analysis is carried out on the "constants" $c_i$, 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

$$
A + B \xrightarrow{\theta_1} C
$$

$$
A + C \xrightarrow{\theta_2} D
$$

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 $A$, $B$, and $C$. By estimating the rate constants $\theta_1$ and $\theta_2$ 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 first
reaction ($A + B \rightarrow C$) was not first-order with respect to the initial concentration.
of A, as originally supposed, but instead was second-order. 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 describing the experiments in detail, let us indicate briefly
the motivation for this investigation. 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 compre-
prehensive 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.

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 inches 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-inch empty vertical tube in which the gas was heated up 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-inch O.D. quartz tube, 23 inches long, to regulate the temperature. The bottom part of the reactor was the quenching zone which consisted of a 1/4-inch layer of quartz chips and a 1-inch length of empty tube. The gases coming from the reactor were dried and purified to eliminate water vapor and carbon dioxide. A Perkin-Elmer Model 154-C 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 pounds per cubic foot and the surface area was 120 square meters per gram. These physical properties were supplied by Engelhard Industries, Inc. The 1/8" 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-hour 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 \[ 2O_2 + 2l \rightleftharpoons 2O_2l \]
2. Surface reaction \[ CH_4 + 2O_2l \rightleftharpoons 2H_2O + CO_2 \]
3. Desorption of water \[ H_2O \rightleftharpoons H_2O + l \]

Rate equations for the individual steps can now be written.

For adsorption, \[ r_1 = \theta_6 \left( a_{O_2}^2 \cdot C_l \cdot l - \frac{C_{O_2} \cdot O_2}{\theta_2} \right) \] (4)

For surface reaction, \[ r_2 = \theta_7 \left( a_{CH_4} \cdot C_{O_2} \cdot O_2 - \frac{C_{H_2O} \cdot H_2O \cdot a_{CO_2}}{\theta_5} \right) \] (5)

For desorption, \[ r_3 = \theta_8 \left( C_{H_2O} - \theta_4 \cdot a_{H_2O} \cdot C_l \right) \] (6)

where
\[ C_l \cdot l = \left( \frac{S}{L} \right) C_l^2 \]
\[ C_{O_2} \cdot r_2 = \left( \frac{S}{L} \right) C_{O_2}^2 \]
\[ C_{H_2O} \cdot H_2O = \left( \frac{S}{L} \right) C_{H_2O}^2 \]
\[ L = C_l + C_{O_2} + C_{H_2O} = C_l \left( 1 + \sqrt{\theta_2} \cdot a_{O_2} + \theta_4 \cdot a_{H_2O} \right) \]
If it is assumed that the surface reaction is the rate controlling step, the reaction rate can be expressed by the following equation.

\[
r = \frac{\theta_2 \theta_7 \text{(SL)}(a_{\text{CH}_4} a_{\text{O}_2}^2 - \frac{1}{k} a_{\text{H}_2\text{O}} a_{\text{CO}_2})}{\left(1 + \sqrt{\frac{\theta_2}{\theta_3}} a_{\text{O}_2} + \theta_4 a_{\text{H}_2\text{O}} \right)^2}
\]  

(7)

The thermodynamic 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

\[
r = \frac{\theta_1 \theta_2 \left( a_{\text{CH}_4} a_{\text{O}_2}^2 \right)}{\left(1+\sqrt{\frac{\theta_2}{\theta_3}} a_{\text{O}_2} + \theta_4 a_{\text{H}_2\text{O}} \right)^2}
\]

(8)

where \( \theta_7 \text{SL} = \theta_1 \).

From stoichiometry

\[
a_{\text{CH}_4} = x_2 - x_2 y
\]

\[
a_{\text{O}_2} = x_3 - 2x_2 y
\]

\[
a_{\text{H}_2\text{O}} = x_5 + 2x_2 y
\]

Thus

\[
r = \frac{\theta_1 \theta_2 x_2(1-y)(x_3-2x_2y)^2}{\left[1+\sqrt{\theta_2} (x_3 - 2x_2y) + \theta_4(x_5+2x_2y) \right]^2}
\]

(9)

Upon integration, Equation 9 yields

\[
x_1 = \frac{1}{\theta_1 \theta_2} \int_0^Y \frac{\left[1 + \sqrt{\theta_2} (x_3 - 2x_2y) \right] + \theta_4(x_5+2x_2y)]^2}{x_2(1-y)(x_3-2x_2y)^2} \, dy,
\]

(10)

that is,

\[
x_1 = \int_0^Y \frac{[c_1 + c_2y]^2}{x_2(1-y)(x_3-2x_2y)^2} \, dy,
\]

(11)
where

\[ c_1 = \beta_0 + \beta_3 x_3 + \beta_5 x_5 \]  \hspace{1cm} (12)

\[ c_2 = -2(\beta_3 - \beta_5) x_2 \]  \hspace{1cm} (13)

\[ \beta_0 = \frac{1}{\sqrt{\theta_1 \theta_2}} \]

\[ \beta_3 = \frac{\theta_2}{\sqrt{\theta_1 \theta_2}} \]

\[ \beta_5 = \frac{\theta_4}{\sqrt{\theta_1 \theta_2}} \]

Notice that the \( c \)'s are linear functions of the unknown parameters \( \beta \) so that, if values for the \( c \)'s can be obtained, the coefficients \( \beta \) 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. \( x_1 \) curve. Upon differentiating Equation 11 with respect to \( y \), we obtain

\[ \frac{\partial x_1}{\partial y} = \frac{[c_1+c_2y]^2}{x_2(1-y)(x_3-2x_2y)^2} \]

Hence

\[ \frac{\partial x_1}{\partial y} \bigg|_{y=0} = \frac{c_1^2}{x_2 x_3^2} \]

Thus

\[ c_1 = \sqrt{x_2 x_3^2 \left( \frac{\partial x_1}{\partial y} \bigg|_{y=0} \right)} \]

Likewise, \( c_2 \) is related to the second derivative by the equation

\[ c_2 = \frac{x_2 x_3}{2c_1} \left\{ \frac{\partial^2 x_1}{\partial y^2} \bigg|_{y=0} + (4x_2 + x_3)c_1^3 \right\} \]

(17)
EXPERIMENTAL DESIGN

The experimental design shown in Table 1 was run at 350°C. at atmospheric pressure. This is a $\frac{4}{3}$ 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 $x_1$ (weight of catalyst/mass flow rate of gas) were used.

<table>
<thead>
<tr>
<th>Run</th>
<th>$\xi_2$</th>
<th>$\xi_3$</th>
<th>$\xi_4$</th>
<th>$\xi_5$</th>
<th>Fractional Conversion of Methane $y$</th>
<th>Slope $s$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$x_1=0.0025$</td>
<td>$x_1=0.0050$</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>+1</td>
<td>0.02588</td>
<td>0.06599</td>
</tr>
<tr>
<td>2</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>*</td>
<td>0.30427</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>+1</td>
<td>-1</td>
<td>-1</td>
<td>*</td>
<td>0.13709</td>
</tr>
<tr>
<td>4</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>+1</td>
<td>0.06863</td>
<td>0.13162</td>
</tr>
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<td>+1</td>
<td>-1</td>
<td>0.04344</td>
<td>0.09790</td>
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<td>+1</td>
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<td>0.07693</td>
</tr>
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<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>0.02449</td>
<td>0.06297</td>
</tr>
<tr>
<td>8</td>
<td>+1</td>
<td>+1</td>
<td>+1</td>
<td>-1</td>
<td>0.07625</td>
<td>0.17175</td>
</tr>
</tbody>
</table>

$\xi_2 = \frac{x_2 - 0.015}{0.005}$

$\xi_3 = \frac{x_3 - 0.120}{0.060}$

$\xi_4 = \frac{x_4 - 0.065}{0.035}$

$\xi_5 = \frac{x_5 - 0.095}{0.055}$

$x_1$ = weight of catalyst/mass flow rate of gas

$x_2$ = mole fraction of methane

$x_3$ = mole fraction of oxygen

$x_4$ = mole fraction of carbon dioxide

$x_5$ = mole fraction of water vapor

$y$ = conversion of methane

* missing data
Figure 2  Fitted Curves
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 \( x_1 \) would be needed to show a marked departure from a linear relationship. The reaction, however, could not be controlled at higher values of \( x_1 \) 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 report were performed with the experimentally recorded values of the variables \( x_i \), which differ slightly from those given in Table 1.

**Model I.** The slope \( s \) estimates the derivative \( \frac{\partial y}{\partial x_1} \bigg|_{y=0} \). Making this replacement in Equation 16, one obtains

\[
c_1' = \frac{\sqrt{x_3 x_5}}{s}
\]

(18)

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

---

### Table 2. Summary of Results for Model I

\[
\hat{c}_1 = b_0 + b_1 x_3 + b_3 x_5
\]

\[
b_0 = -0.0007 \pm 0.0004^* \quad b_1 = 0.027 \pm 0.002^* \quad b_3 = 0.008 \pm 0.002^*
\]

<table>
<thead>
<tr>
<th>Run</th>
<th>( c_1 x 10^4 )</th>
<th>( \hat{c}_1' x 10^4 )</th>
<th>((c_1' - \hat{c}_1') \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.54</td>
<td>24.27</td>
<td>-3.73</td>
</tr>
<tr>
<td>2</td>
<td>13.93</td>
<td>14.35</td>
<td>-0.42</td>
</tr>
<tr>
<td>3</td>
<td>47.98</td>
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<td>58.08</td>
<td>59.69</td>
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</tr>
<tr>
<td>5</td>
<td>16.70</td>
<td>14.55</td>
<td>+2.15</td>
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<td>6</td>
<td>25.27</td>
<td>23.45</td>
<td>+1.82</td>
</tr>
<tr>
<td>7</td>
<td>64.32</td>
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</tr>
<tr>
<td>8</td>
<td>53.56</td>
<td>50.75</td>
<td>+2.81</td>
</tr>
</tbody>
</table>

\[
s(\hat{c}_1') \times 10^4 = 1.72
\]

* The numbers following ± signs are standard errors.
The residual sum of squares \( \sum_{i=1}^{8} (c_{i1}' - \hat{c}_{i1}')^2 \) is 67.319 \( \times 10^{-8} \) and the corresponding mean square is 13.463 \( \times 10^{-8} \) with five degrees 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 five and fourteen degrees of freedom is 2.96 which indicates that Model I is inadequate.

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 should 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 Model I the reaction yields one adsorbed product, water, and one non-adsorbed product, carbon dioxide.

**Model II.** Let us now consider a reaction that produces adsorbed carbon dioxide and non-adsorbed water. Following a similar development to that used in obtaining Equation 11 for Model I, one obtains for Model II

\[
x_1 = \frac{1}{\theta_1 \theta_2} \int_0^y \frac{[1 + \sqrt{\theta_2} (x_3 - 2x_2y) + \theta_3 (x_4 + x_2y)]^2}{x_2(1-y)(x_3 - 2x_2y)^2} \, dy \quad (19)
\]

which can be rewritten as

\[
x_1 = \int_0^y \frac{[c_1 + c_2 y]^2}{x_2(1-y)(x_3 - 2x_2y)^2} \, dy \quad (20)
\]
 where

\[ c_1 = \beta_1'' + \beta_3'' x_3 + \beta_4'' x_4 \]  
(21)

\[ c_2 = (\beta_4'' - 2\beta_3'') x_2 \]  
(22)

\[ \beta_0'' = \frac{1}{\sqrt{\theta_1 \theta_2}} \]

\[ \beta_3'' = \frac{\theta_1}{\sqrt{\theta_1 \theta_3}} \]

\[ \beta_4'' = \frac{\theta_3}{\sqrt{\theta_1 \theta_2}} \]

The derivatives for Model II yield results which are similar to those for Model I,

\[ \left. \frac{\partial x_1}{\partial y} \right|_{y=0} = \frac{c_1'^2}{x_2 x_3} \]  
(23)

\[ \left. \frac{\partial^2 x_1}{\partial y^2} \right|_{y=0} = \frac{2c_1 c_2}{x_2 x_3} \left( 4x_2 + x_3 \right) c_1^3 \]  
(24)

If \[ \left. \frac{\partial x_1}{\partial y} \right|_{y=0} \] 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,

\[ c_1'' = \frac{\sqrt{x_2 x_3^2}}{s} \]  
(25)

Using 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

\[ \hat{c}_{1}'' = b_{0}'' + b_{3}'x_{3} + b_{4}''x_{4} \]

\[ b_{0}'' = -0.0003 \pm 0.0006^* \quad b_{3}'' = 0.027 \pm 0.003^* \quad b_{5}'' = 0.0063 \pm 0.0058 \]

<table>
<thead>
<tr>
<th>Run</th>
<th>( c_{1}'' \times 10^4 )</th>
<th>( \hat{c}_{1}'' \times 10^4 )</th>
<th>( (c_{1}'' - \hat{c}_{1}''') \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.54</td>
<td>16.91</td>
<td>+3.63</td>
</tr>
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<tr>
<td>8</td>
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<td>-4.56</td>
</tr>
</tbody>
</table>

\[ s(c_{1}'') \times 10^4 = 1.72 \]

* 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 \times 10^{-8} and the corresponding mean square is \( 3.41 \times 10^{-8} \) with five degrees of 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 we 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 III. A reasonable model to entertain at this stage, therefore, is one in which water and carbon dioxide are adsorbed. Proceeding as before, one obtains

\[ x_1 = \frac{1}{\theta_1 \theta_2} \int_0^Y \left[ 1 + \sqrt{\theta_2} \left( x_3 - 2x_2y \right) + \theta_3 (x_4 + x_2y) + \theta_4 (x_5 + 2x_2y) \right]^3 \frac{dy}{x_2(1-y)(x_3 - 2x_2y)^2} \]  

which can be rewritten as

\[ x_1 = \int_0^Y \frac{\left[ c_1 + c_2 y \right]^3}{x_2(1-y)(x_3 - 2x_2y)^2} \, dy \]  

where

\[ c_1 = \beta_0''' + \beta_3''' x_3 + \beta_4''' x_4 + \beta_5''' x_5 \]  
\[ c_2 = (2\beta_5''' + \beta_4''' - 2\beta_3''') x_2 \]  
\[ \beta_0''' = \frac{1}{3 \sqrt{\theta_1 \theta_2}} \]  
\[ \beta_3''' = \frac{\sqrt{\theta_2}}{3 \sqrt{\theta_1 \theta_2}} \]  
\[ \beta_4''' = \frac{\theta_3}{3 \sqrt{\theta_1 \theta_2}} \]  
\[ \beta_5''' = \frac{\theta_4}{3 \sqrt{\theta_1 \theta_2}} \]  

The derivatives for Model III differ from those of Models I and II.

\[ \frac{\partial x_1}{\partial y} \bigg|_{y=0} = \frac{c_1^3}{x_2 x_3^2} \]  

\[ \frac{\partial^2 x_1}{\partial y^2} \bigg|_{y=0} = \frac{(4x_2 + x_3)}{x_3} c_1^3 + \frac{3}{(x_1 x_3^2)} c_1^2 c_2 \]  

A value of \( c_1''' \) for each run can be calculated by replacing...
\[ \frac{\delta x_1}{\delta y} \bigg|_{y=0} \] in Equation 34 by the estimated slope \( s \), that is,

\[ c_1''' = \sqrt[3]{s} \frac{x_3^2}{x_3} \cdot \] (36)

The results of fitting Equation 28 by least squares are shown in Table 4.

<table>
<thead>
<tr>
<th>Run</th>
<th>( c_1''' \times 10^3 )</th>
<th>( \hat{c}_1''' \times 10^3 )</th>
<th>( (c_1''' - \hat{c}_1''') \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.57</td>
<td>15.99</td>
<td>-0.42</td>
</tr>
<tr>
<td>2</td>
<td>11.94</td>
<td>11.03</td>
<td>0.91</td>
</tr>
<tr>
<td>3</td>
<td>25.99</td>
<td>27.04</td>
<td>1.05</td>
</tr>
<tr>
<td>4</td>
<td>31.53</td>
<td>30.92</td>
<td>0.61</td>
</tr>
<tr>
<td>5</td>
<td>13.56</td>
<td>14.08</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>18.52</td>
<td>18.55</td>
<td>0.03</td>
</tr>
<tr>
<td>7</td>
<td>34.03</td>
<td>34.14</td>
<td>0.11</td>
</tr>
<tr>
<td>8</td>
<td>29.87</td>
<td>29.26</td>
<td>0.61</td>
</tr>
</tbody>
</table>

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

* The numbers following ± signs are standard errors.

The residual sum of squares \[ \sum_{i=1}^{8} (c_{1i'''} - \hat{c}_{1i'''}^2) \] is \( 3.013 \times 10^{-6} \) and the residual mean square is \( 0.784 \times 10^{-6} \) with four degrees 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.

Model III appears to be adequate and, consequently, Equations 30, 31, 32 and 33 can be solved to give estimates \( \hat{\theta} \) for the parameters \( \theta \) if the quantities \( \beta \) are replaced by their corresponding estimates \( b \). The values obtained in this way were used as the initial guesses for the parameters in a non-linear least squares calculation (1, 2). Incidentally, one of the practical aspects which is of critical importance in using non-linear estimation successfully is obtaining good first guesses for the parameters, and the approach outlined above provides such initial values. The results were:

<table>
<thead>
<tr>
<th>( \hat{\theta}_1 )</th>
<th>( \hat{\theta}_2 )</th>
<th>( \hat{\theta}_3 )</th>
<th>( \hat{\theta}_4 )</th>
<th>Residual Sum of Squares</th>
</tr>
</thead>
<tbody>
<tr>
<td>118,000</td>
<td>30,300</td>
<td>58.7</td>
<td>63.1</td>
<td>( \sum_{k=1}^{22} (y_k - \hat{y}_k)^2 )</td>
</tr>
<tr>
<td>By solving equations</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>By using Non-Linear Estimation</td>
<td>125,000</td>
<td>33,400</td>
<td>52.4</td>
<td>63.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( 1.39 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

Although there is fairly good agreement between the corresponding \( \hat{\theta} \) values, the residual sum of squares for non-linear estimation is considerably smaller. The principal reason for this fact is that in our treatment we have restricted ourselves to the consideration of straight line relationships between \( y \) and \( x_1 \) 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, for example, from the fitted straight lines reveals a negative value for seven out of the eight final residuals, i.e., \( y - s x_1 \) for the highest value of \( x_1 \) 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 to $F_{14, 4}(0.95) = 5.9$. 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 report 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 re-analyzed. 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" (i.e., accepting or rejecting) them.

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 (e.g., 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. $x_4$ or by making the corresponding analytical calculation of the correlation coefficient.

Fractional designs are usually employed for estimating coefficients similar to the $\beta$'s above. However, since we are primarily interested in the $\theta$'s and not the $\beta$'s, should it not be possible to devise better designs for our purposes by focusing our attention more directly on the problem of estimating the $\theta$'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 80 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.
APPENDIX: ERROR ANALYSIS

After determining the eight slopes $s_i$ by least squares, i.e.,

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

where

$x_{ij}$ = the $j$-th value of $x_i$ (weight of catalyst/mass flow rate of gas) in the $i$-th run

$y_{ij}$ = the $j$-th value of $y$ (conversion of methane) in the $i$-th run

$n_i$ = total number of observations in the $i$-th run,

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

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

or

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

where

$y_{ij}$ = the $j$-th value of $y$ (conversion of methane) in the $i$-th run

$\hat{y}_{ij}$ = the least squares estimate of $y_{ij}$, viz., $s_i x_{ij}$

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

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

\[ \nu_i = n_i - 1 \]
\[ s^2(s_i) = s^2(y) / \sum_{j=1}^{n_i} x_{ij}^2 \]

or,
\[ s^2(s) = s^2(y) \left( \frac{8}{\sum_{i=1}^{8} \nu_i} \right) = \frac{1.3359 \times 10^{-4}}{14} \sum_{i=1}^{8} \frac{\nu_i}{\sum_{j=1}^{n_i} x_{ij}^2} \]

\[ s^2(s) = \frac{1.3359}{14} \times 18.3217 = 1.7483 \]

i.e.,
\[ s(s) = 1.3222 \]

To determine \( s(c_{i1}') \) let us use the linear approximation
\[ s(c_{i1}') = \left| \frac{dc_{i1}'}{ds_i} \right| s(s) \]

Now for Model I,
\[ c_{i1}' = x_2 \frac{1}{x_3} x_3 s_i - \frac{1}{2} \quad (i = 1, 2, \ldots, 8) \]

and
\[ \left| \frac{dc_{i1}'}{ds_i} \right| = \frac{1}{2} \frac{c_{i1}'}{s_i}. \]

Thus
\[ s(c_{i1}') = \frac{1}{2} \frac{c_{i1}'}{s_i} \times 1.3222 = 0.6611 \frac{c_{i1}'}{s_i} \]

from which we can obtain the pooled estimate
\[ s^2(c_{i1}') = \frac{\sum_{i=1}^{8} \frac{n_i}{\nu_i} \times s^2(c_{i1}')}{8} = \frac{41.60 \times 10^{-8}}{14} = 2.9715 \times 10^{-8} \]
and
\[ s(c'_1) = 1.7238 \times 10^{-4} \]

For Model II we obtain identical results, i.e.
\[ s^2(c''_1) = s^2(c'_1) = 2.9715 \times 10^{-8} \]
\[ s(c''_1) = s(c'_1) = 1.7238 \times 10^{-4} \]

Analogously, for Model III
\[ c''_{i1} = x_{2i}^{\frac{1}{3}} x_{3i} s_i^{-\frac{1}{3}} \]
and
\[ \left| \frac{dc''_{i1}}{ds_i} \right| = \frac{1}{3} \frac{c''_{i1}}{s_i} \]

Thus
\[ s(c''_{i1}) = \frac{1}{3} \frac{c''_{i1}}{s_i} 1.3222 = 0.4407 \frac{c''_{i1}}{s_i} \]
from which we can obtain the pooled estimate
\[ s^2(c''_1) = \frac{\sum_{i=1}^{8} \nu_i s^2(c''_{i1})}{14} = \frac{6.0015 \times 10^{-6}}{14} = 0.4287 \times 10^{-6} \]
and
\[ s(c''_1) = 0.6548 \times 10^{-3} \]
**NOMENCLATURE**

\[ a_{\text{CH}_4} \] = activity of methane

\[ a_{\text{CO}_2} \] = activity of carbon dioxide

\[ a_{\text{H}_2\text{O}} \] = activity of water vapor

\[ a_{\text{O}_2} \] = activity of oxygen

\[ b \] = estimate of \( \beta \)

\[ c_1 \] = 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

\[ c_1'' \] = 25

\[ c_1''' \] = 36

\[ c_l \] = total concentration of empty active sites

\[ c_{l\cdot l} \] = concentration of adjacently located empty active sites

\[ c_{\text{H}_2\text{O}} \] = total concentration of adsorbed water

\[ c_{\text{H}_2\text{O}\cdot\text{H}_2\text{O}} \] = concentration of adjacently adsorbed water

\[ c_{\text{O}_2} \] = total concentration of adsorbed oxygen

\[ c_{\text{O}_2\cdot\text{O}_2} \] = concentration of adjacently adsorbed oxygen

\[ K \] = thermodynamic equilibrium constant of the methane oxidation reaction

\[ L \] = total concentration of active sites

\[ n \] = number of observations in a given run
\( r \) = over all 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. \( x_1 \) curve
\( S \) = number of equidistant active centers adjacent to each other

\( s(c_1') = \text{standard deviation of } c_1' \)
\( s(c_1'') = \text{standard deviation of } c_1'' \)
\( s(c_1''') = \text{standard deviation of } c_1''' \)
\( s(s) = \text{slope of fitted y vs. } s \)
\( s(y) = \text{slope of fitted y vs. } y \)

\( s^2(c_1') = \text{variance of } c_1' \)
\( s^2(c_1'') = \text{variance of } c_1'' \)
\( s^2(c_1''') = \text{variance of } c_1''' \)
\( s^2(s) = s^2 \)
\( s^2(y) = y^2 \)

\( x_1 = (\text{weight of catalyst})/(\text{mass flow rate of gas}) \)
\( x_2 = \text{mole fraction of methane} \)
\( x_3 = \text{mole fraction of oxygen} \)
\( x_4 = \text{mole fraction of carbon dioxide} \)
\( x_5 = \text{mole fraction of water vapor} \)
\( y = \text{fractional conversion of methane} \)
Greek Letters

\[ \beta \] = true parameter value

\[ \theta_1 \] = overall reaction rate constant

\[ \theta_2 \] = adsorption equilibrium constant for oxygen

\[ \theta_3 \] = adsorption equilibrium constant for carbon dioxide

\[ \theta_4 \] = adsorption equilibrium constant for water vapor

\[ \theta_5 \] = equilibrium constant of surface reaction

\[ \theta_6 \] = adsorption rate constant of oxygen

\[ \theta_7 \] = surface reaction rate constant

\[ \nu \] = degrees of freedom

\[ \xi \] = 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 \((j, \ldots, n_i)\)

\[ k \] = experiment number \((k = 1, 2, \ldots, 22)\)
LITERATURE CITED


(4) Box, G. E. P. and Hunter, W. G., Technometrics, 4, 301 (1962).


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