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The most commonly applied model for correlating reaction rate data is the power function rate equation, which requires careful data analysis for estimation of the reaction order. The authors present a method for the analysis of isothermal, constant volume data of irreversible reactions. The technique allows determination of reaction order with simultaneous testing of goodness of fit and proper transformation of error distribution

Numerous methods of studying the kinetics of particular reactions have been proposed. With the exception of extremely rapid reactions, the measurement of the concentration of an important reactant as a function of some independent variables, such as time, is frequently used as a method of conducting this study. It is generally recognized that such a study of conversion data alone cannot completely define the mechanism of a reaction, and, in fact, such a complete definition is seldom obtained. One main tool applied in the study of a reaction mechanism, however, is the mathematical model which best describes the reaction kinetics. Furthermore, this model may be immediately useful in the design of industrial equipment.

Several types of models have been used for correlating reaction rate data. The most commonly applied model is the power function rate equation, for which the reaction order is selected by an analysis of experimental data. Several techniques have been proposed for determining the reaction order in such a model. If no error were present in the data, of course, all of these methods would yield identical results and would be equally reliable although not equally easy to use. Since error is present in the data, numerous discussions of the relative merits of the several methods have arisen (*1, 4, 5, 9, 10, 14–16*). The general availability of small computers to chemists and chemical engineers has allowed advances in many computational areas unavailable at the time that most of the techniques for determining reaction orders were developed. Consequently, a method usable on small computers and generally applicable to many problems would be of value today.

The purpose of this paper is to present such a method for the analysis of isothermal, constant volume data of irreversible reactions. This technique allows the determination of a reaction order in such a way that not only is a goodness of fit of the predicted to the experimental rates attained, but also the error distribution is properly transformed. For example, a transformation may be obtained such that less weight is automatically given to low precision data. This is accomplished, of course, to the extent that the goodness of fit and proper transformation of error can be simultaneously achieved. In addition, a general computer program is described which can accomplish this estimation of the reaction order and the forward rate constant.

CONVENTIONAL DETERMINATION OF REACTION ORDER

The conventional methods of determining the reaction order and estimating the rate constant can be broken down into four primary areas. The influence of error in the data on the reaction order estimated by each of these methods is summarized here for the purpose of a later comparison to the proposed technique of this paper. More complete discussions of the mechanics of applying these techniques are available in standard texts (*1, 5, 9, 17*). Although the discussion will be centered upon isothermal, constant volume, batch reactor data, the method can be extended to certain other types of data.

Method of Integration

In this method, a reaction order is assumed and the differential rate equation is then integrated to provide an equation relating an instantaneous concentration to the time over which the reaction has taken place. For example, a second-order equation might be written:

$$-\frac{dC_A}{dt} = kC_A^2 \tag{1}$$

so that upon integration:

$$\frac{1}{C_{A_0}(1-x)} - \frac{1}{C_{A_0}} = kt \tag{2}$$

Several techniques exist for testing this integrated equation and thus the assumed reaction order. In general, this integration method is not considered to be sensitive for distinguishing between fractional orders (*9*).

To test graphically the adequacy of the integrated equation, one can plot the concentration function, such as $1/C_{A_0}(1-x)$, *vs.* time. If the correct order has been chosen, in this example second order, the data can be well correlated by a straight line, the slope of which provides an estimate of the rate constant. The graphical method becomes quite tedious, however, unless an appropriate integral or half-integral order is found early in the analysis.

One of the most commonly applied analytical methods is simply to calculate the rate constant from the integrated equation—e.g., Equation 2—at each data point.

$$k = \frac{1}{tC_{A0}(1-x)} - \frac{1}{tC_{A0}} \tag{3}$$

If trends in the constants are found with time or initial concentration, a different reaction order is then assumed. When an adequate order is found, the rate constants, calculated at each point, are averaged to obtain a "best" estimate of this constant. This method suffers from the disadvantage of placing a very high weight on the initial concentration of the reactant, because it is used in the calculation of every rate constant. Also, at either high or low conversions, the calculated rate constants can become greatly scattered due to the experimental error influencing the term corresponding to $1/C_{A_0}(1-x)$ in the second-order model of Equation 2.

Alternatively, one could calculate the rate constant using adjacent pairs of data points. Livingston discusses further the disadvantages of these and other analytical methods (*10*). The general technique of using trends of estimated constants to indicate the adequacy of the model under consideration has been discussed elsewhere (*3*).

A relatively recent technique has been to use nonlinear least squares (*13*) to determine simultaneously both the reaction order and the rate constant. This eliminates the trial-and-error procedure frequently necessary to determine the reaction order. However, the usual applications (*13*) of nonlinear estimation still assume that the reaction rate is determined with equal precison at each data point (constant error variance). This may or may not be justified in a particular set of experiments. Furthermore, one then encounters problems of initial parameter estimates, convergence, and the necessity of having available a relatively large and fast computer to apply this estimation technique.

Method of Differentiation

It is obvious that many trial integrations may be necessary for the use of the method of integration. On the other hand, it can be seen that if one can obtain the reaction rate itself—that is, the rate of change of concentration with time in Equation 1—the slope of a plot of the logarithm of the rate *vs.* concentration will directly give the reaction order. Of course, the determination of this reaction rate requires differentiation of the concentration-time data. Several methods of accomplishing this have been suggested (*5*). In addition to these, the concentration-time data can be fit by an empirical function which may then be differentiated analytically to obtain reaction rates.

With the amount of error often present in kinetic data, however, it is sometimes difficult to get sufficiently precise rate measurements so that this method can be applied satisfactorily. Although techniques are available for adjusting these rates for greater consistency with the concentration-time data (*7*), the best application of this procedure might be to obtain estimates of the reaction order for use in beginning the method of integration.

Method of Fractional Life Times

The most commonly used fractional life is the half-life, the time required for one half of a given reactant to be consumed. For this half-life, an integration of, for example, Equation 1 yields

$$t_{1/2} = \frac{1}{kC_{A_0}} \tag{4}$$

Then, the rate constant can be evaluated from measurements of the half-life for several initial concentrations and any trends with initial concentration noted to determine the adequacy of the assumed reaction order.

Again, this technique can be quite tedious if the reaction order is not approximately known initially. Of even more importance is the inability to check for a variation of the rate constant with time in assessing the correctness of the reaction order. To circumvent this difficulty partially, one can consider any point along the concentration-time curve as the start of a new reaction for which a fractional lifetime may be defined (*1*). However, few ratios of this sort can be obtained for a given reaction path.

Finally, not all of the data obtained are used in calculating the rate constant; for example, in Equation 4 only the initial and the half-way point are used. Thus, this method can be tedious for determining the reaction order, it requires considerable (unused) data, and should probably be followed by another method of estimating the rate constant and assessing the adequacy of the assumed reaction order which uses all of the data. Nevertheless, numerous useful applications of the method of fractional lifetimes exist.

Method of Reference Curves

Walas (17) discusses a method of assessing the reaction order without estimating the rate constant. Here, the ratio of the time required to reach any conversion divided by the time required to reach, say, 90% conversion is plotted against conversion. The data can be shown to be a function, then, only of the reaction order and can be plotted on a graph containing a group of reference curves for given orders. Thus, the experimental order can be obtained by matching the data to one of the curves. This is a useful technique, but it also places great weight on the time required to reach a given conversion level, such as the 90% level. In addition, the method is insensitive to deviations of the data from the reference curve unless a great number of reference curves are drawn. Other methods of dimensionless curves also exist (5).

TREATMENT OF SEVERAL REACTANTS

The previous discussion has tacitly assumed the existence of a single reactant. In fact, the method for estimating reaction orders to be presented in the next section also assumes a single reactant. Although this assumption is certainly restrictive, methods exist for partially circumventing this disadvantage.

One method of analyzing data for a rate equation of the form

$$-\frac{dC_A}{dt} = kC_A{}^nC_B{}^m \tag{5}$$

is to take reaction rate data at such large concentrations of one reactant that this concentration is effectively a constant during the entire course of the reaction. Then, the order of the other reactant can be determined by any of the previously discussed methods. This technique, called the isolation method, will allow a determination of the component reaction orders but it should be kept in mind that a very limited region of the experimental space has been covered in determining these orders. Thus, because the model has not been tested for conditions in which both concentrations are varying, the model should be used with caution here. These estimated constants, on the other hand, should provide quite good initial estimates for a nonlinear least squares program which can analyze data taken when both concentrations are varying.

A second method of analyzing data to be described by Equation 5 is to use initial reaction rates. Here, one can vary the initial concentrations of the individual reactants, holding all other reactant concentrations constant, and thus analyze the data by the previous methods. An advantage of this technique over the isolation method is that the concentrations of the reactants can be nearly equal instead of some concentrations being in large excess. The method allows reaction rates to be obtained over the entire range of composition with respect to known major reaction participants. However, these rates may not be equal to those obtained from experiments in which extensive conversions are allowed because of the presence of trace by-products generated during the reaction which affect the reaction rate.

TRANSFORMATION TO OBTAIN REACTION ORDER

It has been indicated that each type of data analysis tacitly assumes some form of data weighting. Unfortunately, this weighting is implicit in these analyses, and the experimenter may not realize what assumptions are being made. In addition, it would not be expected that this assumed method of accounting for error in the data would be identical with the demands of the actual error distribution. In particular, with the usual unweighted linear least squares analysis, one assumes that the effective error in the dependent variable, $1/C_{A_0}(1 - x)$ of Equation 2, is independently normally distributed with constant variance. A transformation is now to be discussed which allows these assumptions to be met to the extent that it is possible.

General Kinetic Formulation

The integrated form of an n^{th}-order irreversible reaction can be written:

$$\begin{aligned} C_{A_0}{}^{1-n}\,[(1-x)^{1-n} - 1] &= (n-1)kt \qquad n \neq 1 \\ -\ln(1-x) &= kt \qquad n = 1 \end{aligned} \tag{6}$$

Now, to write this in a more compact form, choose

$$\begin{aligned} \lambda &= n - 1 \\ y &= (1-x)^{-1} \end{aligned} \tag{7}$$

Thus, λ is directly related to the reaction order and y is the reciprocal of the fraction of the reactant unreacted at time t. Let the following transformation also be defined:

$$y^{(\lambda)} = \begin{cases} \dfrac{y^\lambda - 1}{\lambda C_{A0}{}^\lambda} & \lambda \neq 0 \\ \ln y & \lambda = 0 \end{cases} \tag{8}$$

Then, the integrated n^{th}-order rate expression of Equation 6 may be written in the generalized form for all reaction orders:

$$y^{(\lambda)} = kt \tag{9}$$

It is now desired to estimate λ in a manner which takes into account the error distribution of the data.

Selection of a Transformation

Box and Cox (2) have recently presented a method of choosing a transformation to achieve (a) linearity of the model, (b) constancy of error variance, (c) normality of error distribution, and (d) independence of the observations, to the extent that all are simultaneously possible. These are exactly the requirements for an unweighted linear least squares analysis. Let us examine the applicability of this transformation to the selection of a reaction order.

One family of transformations discussed by Box and Cox is

$$y^{(\lambda)} = \begin{cases} \dfrac{y^\lambda - 1}{\lambda} & \lambda \neq 0 \\ \ln y & \lambda = 0 \end{cases} \tag{10}$$

Note the similarity of Equations 8 and 10. This will allow a development analogous to that of Box and Cox, except with the inclusion of the constant.

Parallel to the development of the transformation of Box and Cox, let us assume that a λ exists for which the *transformed* dependent variable satisfies the four assumptions just tabulated. Then, the likelihood in relation to the transformed dependent variable is:

$$\frac{1}{(2\pi)^{N/2}\ \sigma^N} \exp\left\{-\frac{\sum_{i=1}^{N}(y_i^{(\lambda)} - kt_i)^2}{2\sigma^2}\right\} \qquad (11)$$

Because this can also be considered to be a distribution function of the transformed variable, one can calculate the distribution function of the untransformed variable (original observations, y) through the Jacobian of the transformation (*8*)

$$\frac{1}{(2\pi)^{N/2}\ \sigma^N} \exp\left\{-\frac{\sum_{i=1}^{N}(y_i^{(\lambda)} - kt_i)^2}{2\sigma^2}\right\} J(\lambda;\mathbf{y}) \qquad (12)$$

where

$$J(\lambda;\mathbf{y}) = \prod_{i=1}^{N}\left|\frac{dy_i^{(\lambda)}}{dy_i}\right|$$

Now it is desired to select the reaction order and the forward rate constant which have a maximum likelihood (Equation 12) of representing the concentration-time data. For a given λ, an examination of Equation 12 indicates that it is maximized when the sum of squares of the residuals for the *transformed variable* is minimized—i.e., a standard unweighted least squares problem. Then, if this is repeated for all possible values of λ, a plot can be made of these likelihoods to find that λ which provides an absolute maximum likelihood (a simplification will be made shortly). Furthermore, if the logarithm of the maximum likelihood for any given λ is defined as $L_{max}(\lambda)$ and the absolute maximum as $L_{max}(\hat{\lambda})$, then an approximate $100(1-\alpha)$ confidence interval on $\hat{\lambda}$ is given by (*2*):

$$L_{max}(\hat{\lambda}) - L_{max}(\lambda) < 1/2\ \chi_1^2(\alpha) \qquad (13)$$

or, at the 99% level,

$$L_{max}(\hat{\lambda}) - L_{max}(\lambda) < 3.31$$

Box and Cox have further pointed out that these results may be expressed even more simply if a normalized transformation is chosen

$$z^{(\lambda)} = y^{(\lambda)}/J^{1/N} \qquad (14)$$

The simplification obtained is evident upon taking the logarithm of the likelihood function. Also, this allows the determination of the reaction order without the initial reactant concentration entering the calculation. In our case

$$J^{1/N} = \begin{cases} \dfrac{\dot{y}^{\lambda-1}}{C_{A0}^{\lambda}} & \lambda \neq 0 \\ 1/\dot{y} & \lambda = 0 \end{cases} \qquad (15)$$

where $\dot{y}$ is the geometric mean of the experimental values of the untransformed variable y.

Thus, the transformation that should be used for the analysis of kinetic data is:

$$z^{(\lambda)} = \begin{cases} \dfrac{y^{\lambda}-1}{\lambda\dot{y}^{\lambda-1}} & \lambda \neq 0 \\ \dot{y}\ln y & \lambda = 0 \end{cases} \qquad (16)$$

Note that the initial concentration is not contained in the variable $z^{(\lambda)}$.

The concentration-time data for several initial concentrations may be simultaneously analyzed by replacing the initial concentration in Equation 15 by the geometric mean of the initial concentrations. In such a case, Equation 16 will no longer be independent of the initial concentration but must be multiplied by the ratio of the geometric mean of the initial concentrations to the initial concentration associated with each y, raised to the λ^{th} power.

Consequently, the steps that we should take for data of a single initial concentration are:

1. Estimate, by unweighted linear least squares, the parameter $b = k/J^{1/N}$ which minimizes the sum of squares

$$S(\lambda) = \sum_{i=1}^{N}(z_i^{(\lambda)} - bt_i)^2 \qquad (17)$$

for a given λ and calculate the sum of squares $S(\lambda)$

2. Plot this minimum sum of squares for several λ
3. Read off the minimum of this plot to obtain the best λ, $\hat{\lambda}$
4. Calculate the 99% confidence interval for this $\hat{\lambda}$ by

$$\ln S(\lambda) - \ln S(\hat{\lambda}) < \frac{\chi_1^2(0.01)}{N} = \frac{6.63}{N} \qquad (18)$$

If this procedure is followed, then a reaction order will be obtained which is not masked by the effects of the error distribution of the dependent variables. Because the transformation achieves the four qualities listed at the first of this section, an unweighted linear least squares analysis may rigorously be used. The reaction order, $n = \lambda + 1$, and the transformed forward rate constant, b, possess all of the desirable properties of maximum likelihood estimates. Finally, the equivalent of the likelihood function can be represented by the plot of the transformed sum of squares versus the reaction order. This provides not only a reliable confidence interval on the reaction order, but also the entire sum of squares curve as a function of the reaction order. Then, for example, one could readily determine whether any previously postulated reaction order can be reconciled with the available data.

EXAMPLE 1

Pannetier and Davignon (*11*) studied the solid-solid reaction:

$$NiS_2\ (s) \rightarrow NiS\ (s) + 1/2\ S_2\ (g) \qquad (19)$$

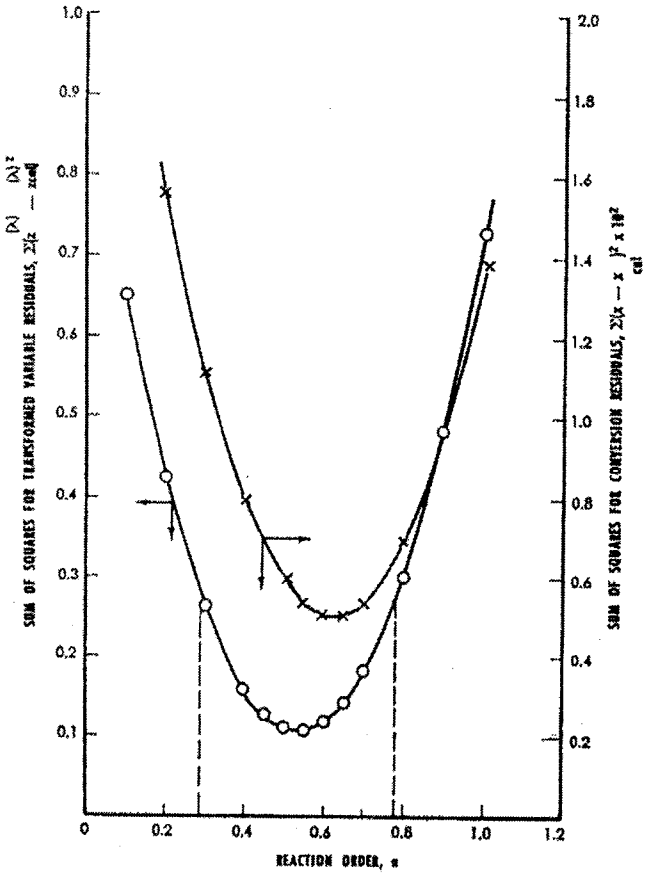

Figure 1. Sum of squares curve for 395° C. NiS_2 decomposition

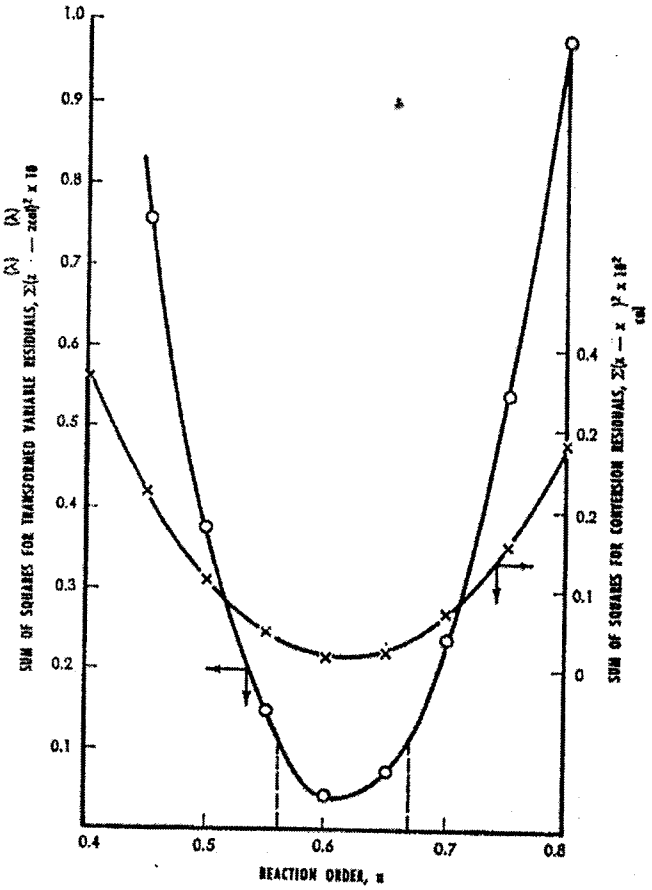

Figure 2. Sum of squares curve for 405° C. NiS_2 decomposition

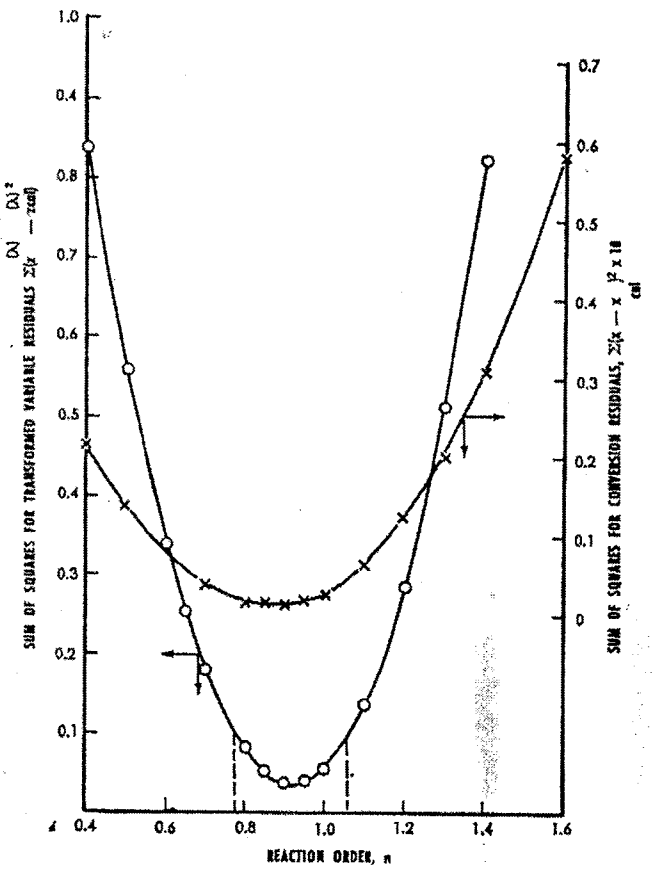

Figure 3. Sum of squares curve for 415° C. NiS_2 decomposition

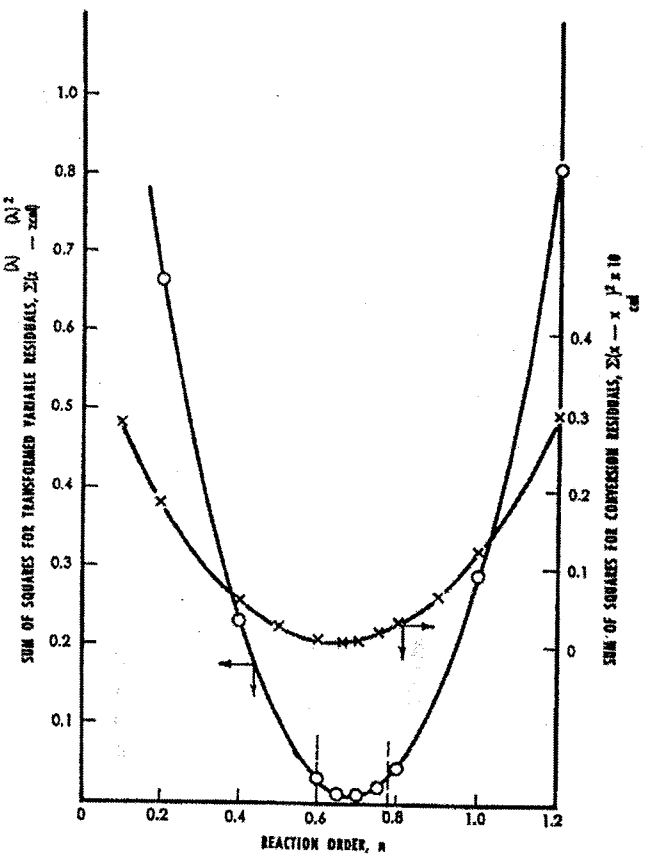

Figure 4. Sum of squares curve for 426° C. NiS_2 decomposition

They presented seven determinations of the mass of unreacted solid at each of four temperatures for an initial mass of 25 mg. of NiS_2. Data were also reported for 100 and 200 mg. of NiS_2 initially present, but these latter data will not be considered here. The 25-mg. data, taken at equal increments of the mass of NiS_2 reacted, were analyzed by those authors through the method of differentiation to obtain reaction orders of 0.67, 0.66, 0.71, and 0.67 with increasing temperatures. Thus, they concluded that the reaction is of $^2/_3$ order:

$$\frac{d\left(\frac{M}{M_0}\right)}{dt} = -k \left(\frac{M}{M_0}\right)^{2/3} \tag{20}$$

We analyzed further the data for 25 mg. of NiS_2 initially present.

Figures 1 through 4 present the sums of squares of the transformed dependent variables $z^{(\lambda)}$, and of the untransformed dependent variables, $x = (M_0 - M)/M_0$. An examination of the 99% confidence interval (enclosed by the vertical broken lines on the graphs) for the transformed variable indicates that the $^2/_3$ order reported by Pannetier and Davignon is not compatible with the 415° C. data. Although this order is adequate for the other data sets, a rather disturbing increase in the order with an increase of the temperature is present. In fact, the 395° C. data alone would commonly be considered to be $^1/_2$ order, with a relatively low probability of the $^2/_3$ order being appropriate. From an examination of the two minima in each figure, one can further observe the difference between the order predicted by this method and that obtained by considering only the conversion residuals—i.e., with no consideration of weighting or normality of the error.

A typical analysis of variance for the transformed and untransformed variables is shown in Table I. It can be seen from a comparison of the mean square due to the model with the residual mean square that the model accounts for much of the variation in the data. It was known from the published work (*11*) for this particular data set that a single reaction order could be found that would approximately describe all of the data at each temperature level. Thus, we considered only the linear model

$$y^{(\lambda)} = kt \tag{21}$$

in the analysis of variance. If it had been necessary to test for the adequacy of the model and thus for the probability of the data's being from a complex reaction, for which no simple reaction order is adequate, the quadratic term

$$y^{(\lambda)} = kt + k_2t^2 \tag{22}$$

could be included in the analysis of variance. The quadratic term in Equation 22, of course, merely describes the deviation of the data from the best n^{th} order model and has no mechanistic interpretation. Thus, the existence of an important quadratic term would only indicate that no n^{th} order model could describe the data.

An examination of Table I indicates another advan-

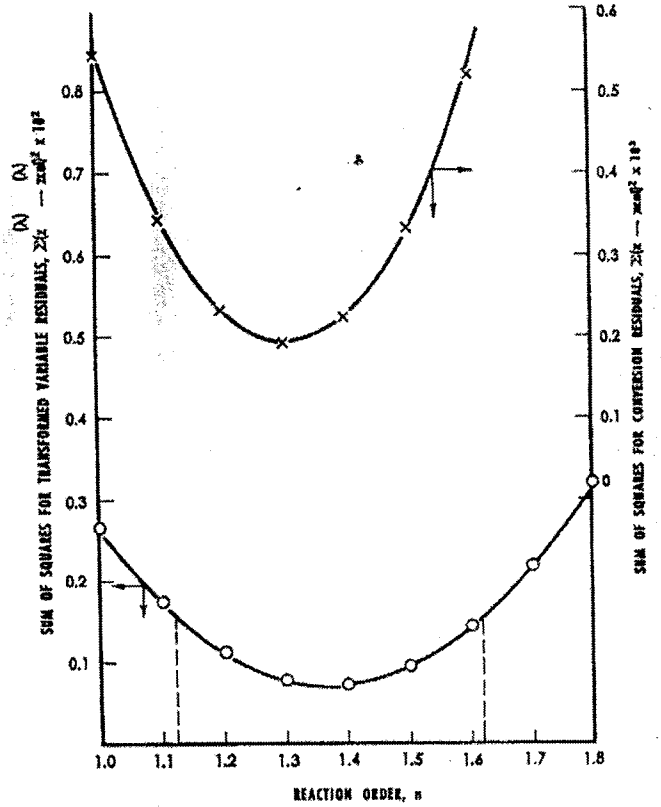

Figure 5. Sum of squares curve for 857.8° K. N_2O decomposition

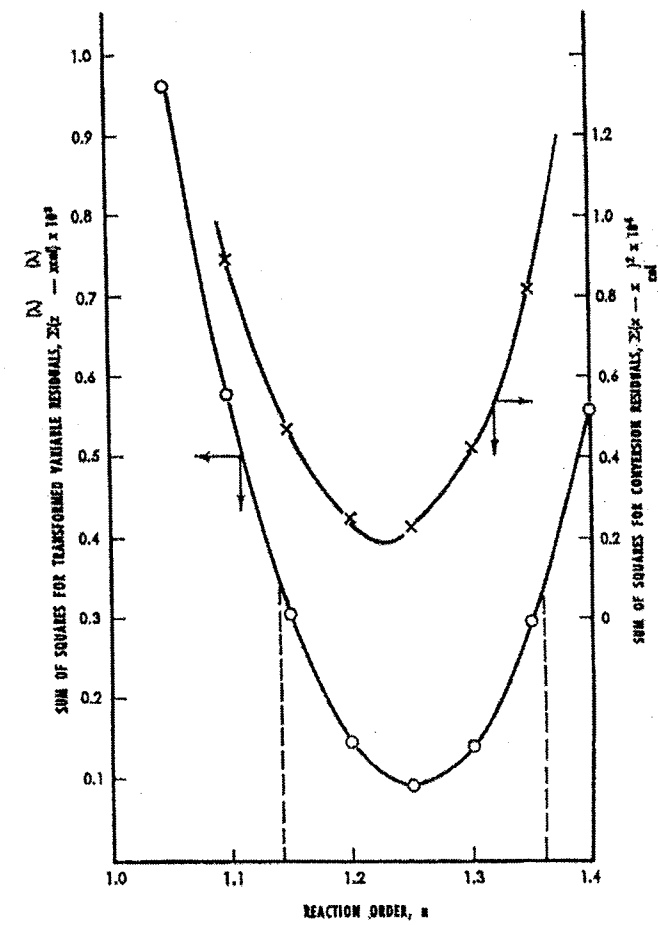

Figure 6. Sum of squares curve for 875° K. N_2O decomposition

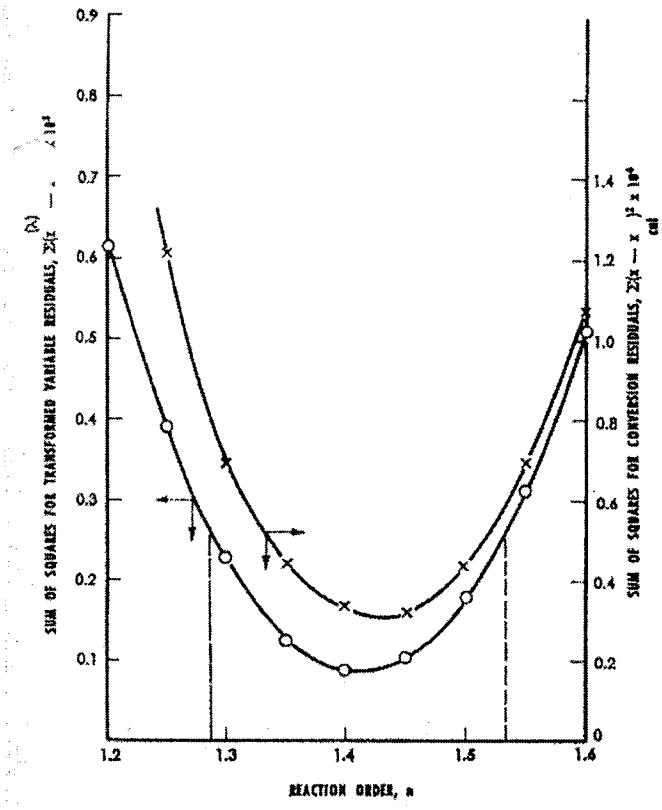

Figure 7. Sum of squares curve for 887.7° K. N_2O decomposition

e that often can be derived from such a transformation. The ratio of the linear to the residual mean square is greater for the transformed than for the untransformed variables by a factor of 1.8. This indicates that the transformation has increased the sensitivity of the analysis (*2*).

This analysis leaves some doubt as to whether a single reaction order exists which adequately can describe all of the data. In support of this, the anomalous behavior of the 415° C. data and the apparent increase of the reaction order with temperature have been pointed out. In addition, if a single order must be selected, an examination of the 95% confidence intervals (not shown) indicates that the $^2/_3$ order is a reasonable choice. For this order, however, estimates of the forward rate constants of 0.100, 0.138, 0.250, and 0.538 hour^{-1} are obtained and these deviate somewhat from an Arrhenius relationship. Finally, some trend of the residuals (*3*) of the transformed dependent variable with time exists for this reaction order.

EXAMPLE 2

Pease (*12*), in discussing the experimental basis for the theory of quasi-unimolecular reactions, analyzed data for the gaseous decomposition of nitrous oxide taken from literature. The data consisted of nine data points at 857.8° K., five at 875.0° K., and six at 887.7° K. for the reaction

$$2N_2O \rightarrow 2N_2 + O_2 \qquad (23)$$

The analysis (*12*) of other data led Hinshelwood to the conclusion that the reaction is second order, while Volmer reported it to be first order. Pease analyzed data on this reaction by the method of integration and found that the reaction order could be either 1.0 or 1.5 since little variation could be seen in any of the calculated rate constants. Upon presenting a possible mechanism yielding a 1.5-order rate equation, he concluded that the data could exhibit a 1.5 order:

$$\frac{dp_A}{dt} = -kp_A^{1.5} \qquad (24)$$

Figures 5 through 7 present the sums of squares of the transformed and untransformed dependent variables for these data. It can be seen that an acceptable reaction order for all these data is in the neighborhood of 1.3. An order of 1.5 is not inconsistent with the low and high temperature data but probably does not describe the 875° K. data. Note also that the reaction order is determined more precisely with the higher temperature data in spite of the fewer data points there. It can also be seen from these plots that a first-order reaction is not consistent with the data. This more quantitative statement about the relative acceptability of the 1.0 and 1.5 orders is possible because a quantitative measure of the goodness of fit is available with this method whereas no such measure is generally used in applications of the method of integration.

The ratios of the mean square due to the transformed model to the residual mean square for these three data sets were of the order of magnitude of 10^5, indicating that the model accounts for much of the variation in the data. Again, a quadratic term could be used for a more careful analysis of variance if it were not known from previous evidence (*12*) that a reaction order could be found which fits the data adequately.

On the basis of these graphs, it seemed reasonable to assign a $^4/_3$ order to the reaction. The rate constants for this reaction order, then, are 2.42×10^{-3}, 4.88×10^{-3}, and 7.77×10^{-3} (cc./gram mole)$^{1/3}$ sec.$^{-1}$. These rate constants follow an Arrhenius relation quite well.

EXAMPLE 3

Hinshelwood and Burk (*6*) studied the reaction of gaseous ammonia adsorbed on a tungsten wire at several temperatures and at various pressures of ammonia and ammonia-hydrogen mixtures:

$$2\,NH_3 \rightarrow N_2 + 3\,H_2 \qquad (25)$$

TABLE I. ANALYSIS OF VARIANCE OF NIS, DATA AT 395° C.

		Mean Squares	
	Degrees of Freedom	*Untransformed, n = 0.65*	*Transformed, λ = −0.45*
Due to model	1	2.212	502.5
Residual	6	0.000142	0.0179

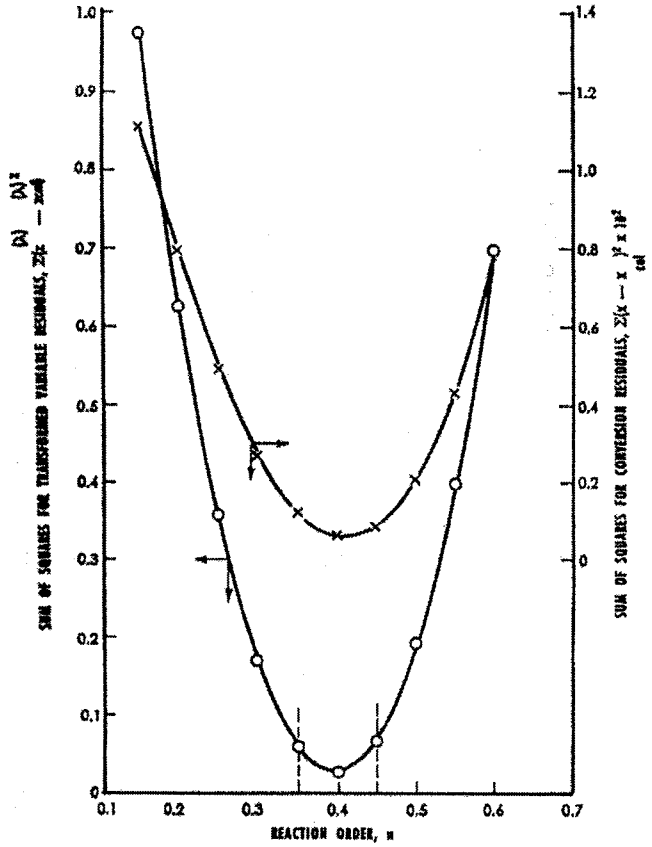

Figure 8. Sum of squares curve for 100 mm. Hg NH_3 decomposition

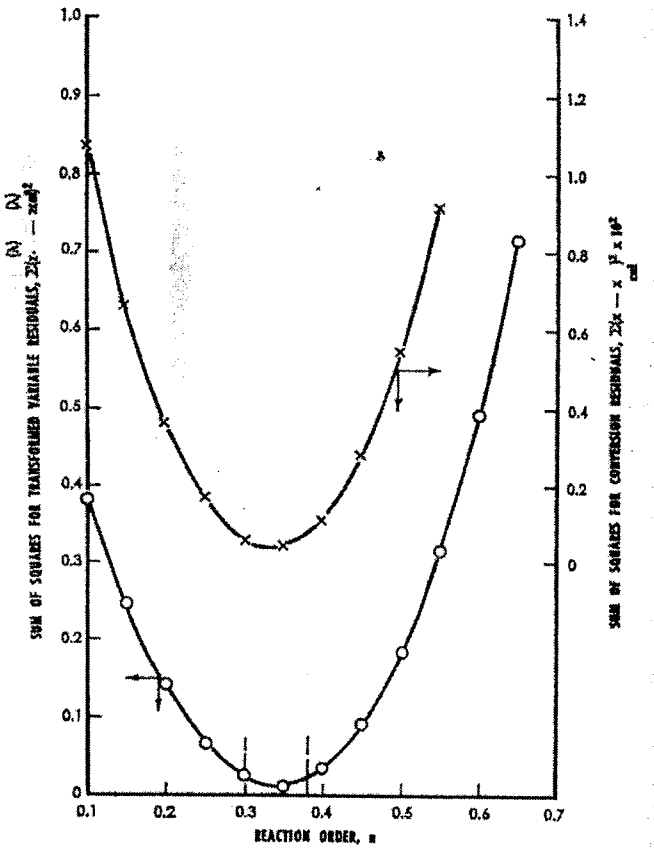

Figure 9. Sum of squares for 200 mm. Hg NH_3 decomposition

They found that the reaction was "almost zero order." Laidler (*9*) in discussing this reaction pointed out that plots of pressure of decomposed gas *vs.* time which "approach linearity more closely than they approach the type of curvature found with first-order reactions" supported zero-order kinetics. Furthermore, Laidler stated that half-lives indicate that zero-order kinetics are preferable to first-order kinetics.

The nine data at 100 and the twelve data at 200 mm. Hg of ammonia pressure and 856° K. were analyzed by us. The usual plots of the sums of squares of residuals for the transformed and untransformed dependent variables are shown in Figures 8 and 9. It can be seen from these plots that reaction orders from 0.35 to 0.40 are compatible with all of the data. Furthermore, it can be seen from the confidence intervals using all of these data that the reaction is probably neither zero nor first order. Such a deviation from zero order could be of considerable significance in a study of the reaction mechanism. Laidler (*9*) has, in fact, suggested a reason for the deviation of the data from zero order at high reaction times.

It should be noted that the same order is predicted by the minimum sum of squares of residuals of both the transformed and the untransformed variables, indicating that no adjustment of the reaction order was needed to take into account the nature of the error distribution. The ratios of the mean square due to the model to the residual mean square for the data of both ammonia pressures were of the order of magnitude of 10^4. For a 0.4-order reaction, the best estimates of the rate constant are 4.3×10^{-7} and 3.8×10^{-7} (gram mole/cc.)$^{0.6}$ sec.$^{-1}$ for initial pressures of 100 and 200 mm. Hg, respectively. This agreement is reasonably good.

This example clearly illustrates one of the implicit disadvantages of the conventional methods of determining the reaction order—the tendency to stop the analysis at the best integral or half-integral order and not to examine those reaction orders that are approximately equally capable of describing the reaction. This is partly because no quantitative way is generally used to compare the goodness of fit of several orders with the conventional methods. For data presenting a sums-of-squares curve, such as Figure 8, and without any inde-

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pendent evidence to the contrary, it is evident that an interpretation of a mechanism based upon a zero-order reaction could not only be of little value, but it could actually be misleading.

Discussion

The several conventional methods of determining reaction orders have two common disadvantages, the importance of which depends upon the amount and distribution of the error in the data. First, nearly all methods place a very large weight on the concentration at a particular point in the course of the reaction, such as the initial concentration. Second, proper consideration is rarely given to the distribution of error in the data, which should be used to give some data less weight than other data. The methods are generally tedious, and the determination of the adequacy of a particular order is only qualitative. Also, in using least squares techniques, normality and independence of the error is desirable.

The method presented here, a variation of the method of integration, transforms the dependent variable to achieve an error distribution as consistent as possible with the assumptions inherent in a least squares analysis. Hence, if these assumptions are fulfilled, the maximum likelihood estimates of the reaction order and the transformed rate constant are obtained. Furthermore, as a result of the normalization of the dependent variable by dividing by the Jacobian of the transformation, the reaction order is obtained without repeated reference to the initial concentration. The initial concentration is used only in the evaluation of the rate constant after the reaction order has been selected. Thus, this proposed method takes into account the error in the data in a more satisfactory fashion than any of the conventional methods of determining reaction orders. In addition, a dependable confidence interval can be obtained to determine the range of possible orders which is compatible with the data. The plot of the sums of squares of residuals *vs.* the reaction order, as demonstrated in Example 3, can be very valuable in studying a particular reaction.

A small computer, such as the IBM 1620, is of considerable assistance in the performance of the routine calculations in this method. A perfectly general computer program can be written for this computer which can take the time and concentration data directly from the experimenter and calculate the sums of squares in the transformed variable over suitable reaction orders. These sums of squares can be searched to find a minimum and the analysis of variance for Equation 22 completed at this minimum with little expenditure of computer time (generally less than 20 minutes). These sums of squares can then be printed as computer output. Alternatively, one can utilize an automatic plotting device to allow a direct presentation of graphs similar to those in this paper. The axes on such graphs would be defined for each problem with the aid of the confidence interval on the reaction order. With such a tool at their disposal, chemists or chemical engineers can assign reaction orders quickly and rationally.

NOMENCLATURE

b = transformed forward rate constant defined above Equation 17
C_A = concentration of component A, gram moles/cc.
C_{A0} = initial concentration of component A, gram moles/cc.
C_B = concentration of component B
g = gas
$J(\lambda; y)$ = Jacobian of the transformation of the untransformed variable, y, to the transformed variable, $y^{(\lambda)}$
k = forward rate constant
k_2 = empirical constant in Equation 22
$L_{max}^{(\lambda)}$ = maximized logarithm of the likelihood function in relation to the original observations, y (Equation 12), for any given λ
$L_{max}^{(\hat{\lambda})}$ = absolute maximized logarithm of the likelihood function in relation to the original observations for all λ
M = mass of NiS_2 not decomposed at time t
M_0 = initial mass of NiS_2
m = reaction order for component B
N = number of observations
n = reaction order for component A
p_A = partial pressure of component A
$S^{(\lambda)}$ = minimum sum of squares of residuals for transformed variable for a given λ
$S^{(\hat{\lambda})}$ = absolute minimum sum of squares of residuals for transformed variable for all λ
s = solid
t = time during which a reaction has taken place
$t_{1/2}$ = time required for one half of initial amount of a given reactant to be consumed
x = fraction of a reactant converted at time t
x_{cal} = calculated value of the fraction of a reactant converted at time t
y = reciprocal of fraction of reactant which is unreacted at time t
$\mathbf{y}$ = vector of all experimental values of the untransformed variable y
$\dot{y}$ = geometric mean of all experimental values of untransformed variable y
$y^{(\lambda)}$ = generalized transformed dependent variable given by Equation 8
$z^{(\lambda)}$ = normalized transformed dependent variable given by Equations 8 and 16
$z_{cal}^{(\lambda)}$ = predicted value of the normalized transformed dependent variable $z^{(\lambda)}$

Greek Letters

α = confidence coefficient for Chi-Squared distribution
λ = parameter related to reaction order by Equation 7
$\hat{\lambda}$ = best estimate of parameter λ minimizing the sum of squares of Equation 17
σ = constant standard deviation of experimental error in transformed dependent variable $y^{(\lambda)}$
$\chi_1^2(\alpha)$ = abscissa value below which is $100(1 - \alpha)$ per cent of the area under the curve of a Chi-Squared distribution with one degree of freedom

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