CHE 4063

INSTRUCTIONS FOR PREPARING THE PROJECT

1. All pages should be 8 ½" x 11". Make xerox copies of all pages over 8 ½" x 11" including computer programs if necessary. Do not include any foldout pages.
2. Staple the project once in the upper left-hand corner. Do not use folders of any type.
3. Cooperation among students is forbidden.
4. Follow this format:
    a. Cover page
    b. Statement of the problem and data you were given.
    c. Theoretical development
    d. Results
        i. Explanation and final numbers
        ii. Graphical plots
    e. Appendix – Computer program and raw data output.
5. Neatness and organization counts 10% of the project!

CHE 4063: PROJECT 1

DETERMINATION OF REACTOR ORDER AND RATE CONSTANT

Each student is given a set of data which represent a set of 18 reaction runs each starting with a different initial concentration. Each run is sampled every minute for nine minutes. We will assume this reaction to be:

$$A \rightarrow \text{Products}$$

With rate expression:

$$r = k\, C_A^{\,N}$$

You are to determine N and k for the following assumptions:

1. Minimization of:

$$S(N) = \sum_i (kt_{i,\,MEASURED} - kt_{i,\,CALCULATED})^2$$

which is a "simple" method described in lecture.

2. Minimization of:

$$S(\lambda) = \sum_i (z_i^{(\lambda)} - bt_i)^2$$

which is the method of Kittrell, Mezaki, and Watson, Ind. Eng. Chem., 50 (1966). Also, compute the 99% confidence limit on N.

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:

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

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*)

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

where

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

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*):

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

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

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

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

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

where $\hat{y}$ 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:

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

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

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

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:

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

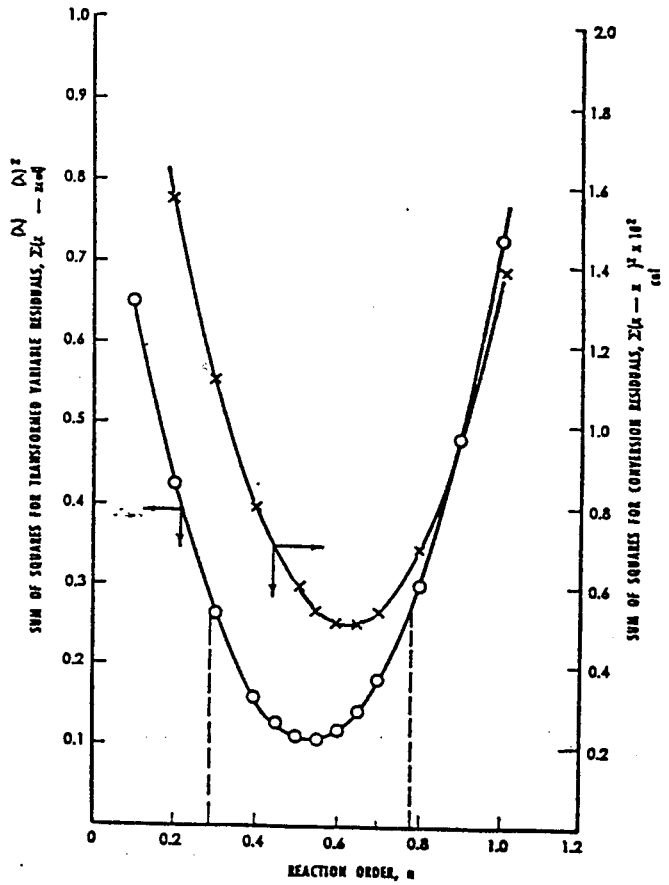

Figure 1. Sum of squares curve for 395° C. NiS_2 decomposition

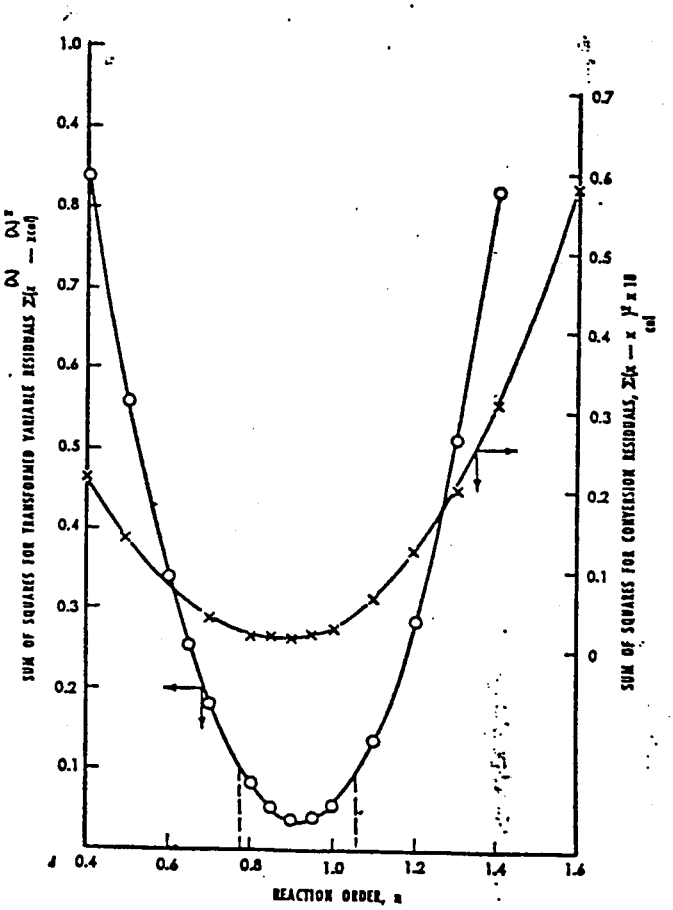

Figure 3. Sum of squares curve for 415° C. NiS_2 decomposition