FORTRAN II PROGRAM FOR REDUCTION OF SPECTROPHOTOMETRIC REACTION KINETICS DATA

by

G. J. Werkema

RELEASED FOR ANNOUNCEMENT IN NUCLEAR SCIENCE ABSTRACTS

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80402
U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1196
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.
FORTRAN II PROGRAM FOR REDUCTION OF SPECTROPHOTOMETRIC REACTION KINETICS DATA

by

G. J. Werkema

LEGAL NOTICE

This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission, makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights. or

A. Assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report. As used in the above, "person acting on behalf of the Commission," includes any employee, or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor, is provided access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80402
U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106
ACKNOWLEDGMENT

The author is grateful to Dr. J. M. Cleveland for suggesting the writing of this program and for supplying the data used for testing the code.
# CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENT</td>
<td>ii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>v</td>
</tr>
<tr>
<td>MATHEMATICAL METHODS</td>
<td>1</td>
</tr>
<tr>
<td>A. Derivation of Integrated Rate Laws</td>
<td>1</td>
</tr>
<tr>
<td>1. First-Order Rate Law</td>
<td>1</td>
</tr>
<tr>
<td>2. Second-Order Rate Law</td>
<td>2</td>
</tr>
<tr>
<td>3. Third-Order Rate Law</td>
<td>2</td>
</tr>
<tr>
<td>B. Reduction of Observational Data</td>
<td>3</td>
</tr>
<tr>
<td>1. Absorbance at $\lambda_1$</td>
<td>3</td>
</tr>
<tr>
<td>2. Absorbance at $\lambda_2$</td>
<td>5</td>
</tr>
<tr>
<td>3. Selection of Routines</td>
<td>6</td>
</tr>
<tr>
<td>C. Fortran Notation</td>
<td>7</td>
</tr>
<tr>
<td>D. Running Time</td>
<td>8</td>
</tr>
<tr>
<td>E. Input</td>
<td>8</td>
</tr>
<tr>
<td>F. Output</td>
<td>9</td>
</tr>
<tr>
<td>G. Operating Procedure</td>
<td>10</td>
</tr>
<tr>
<td>SAMPLE PAGES</td>
<td>11</td>
</tr>
<tr>
<td>Sample Input</td>
<td>11</td>
</tr>
<tr>
<td>Sample Output</td>
<td>12</td>
</tr>
<tr>
<td>Fortran Listing</td>
<td>14</td>
</tr>
<tr>
<td>PROGRAM FLOW CHART</td>
<td>16</td>
</tr>
<tr>
<td>APPENDIX A</td>
<td>17</td>
</tr>
</tbody>
</table>
The program described computes first-, second-, and third-order reaction rate constants by reduction of spectrophotometric absorbancy data using the respective integrated rate laws. The computer output tabulates the computed rate constants ($k_1$, $k_2$, and $k_3$), their time products ($k_1t$, $k_2t$, and $k_3t$), and the number of gram-molecular-weights of starting material that have reacted, as a function of time.
INTRODUCTION

The ERLF* program is designed around the spectrophotometric experiment in one of its applications. The specific problem is that of observing the decrease in concentration of a given reactant, or conversely, observing the increase in concentration of some product, during a chemical reaction. It is a required condition that one of the reaction constituents have a measurable absorption, for visible or ultraviolet light, which is free of major interferences from that of other constituents. At low concentrations, absorbancy is a direct linear function of concentration. Absorbancy readings constitute the major portion of the observational data required for this program.

The program allows the user to compensate for a minor interference from one constituent. The mathematical derivation is discussed in the next section.

It is useful to regard a computer as a fast, versatile, and capacious desk calculator. The FORTRAN language makes it possible to compute values of transcendental and other frequently-used functions through the simple expedient of a single code symbol.

* ERLF: Abbreviation for Exact Rate Law Fortran
In general, this program has been designed to perform all of the tedious calculations that are required for accurate determination of rate constants for chemical reactions. It has been written specifically for chemical reactions of the type $A + B \rightarrow C + D$ which proceed according to first-, second-, or third-order rate laws.
MATHEMATICAL METHODS

A. DERIVATION OF INTEGRATED RATE LAWS

We define a general stoichiometry factor, \( P \), such that the stoichiometric equation may be written

\[
d[A] = P \cdot d[B]
\]

(1)

This equation states that one gram-molecular-weight of \( B \) reacts stoichiometrically with \( P \) gram-molecular-weights of \( A \). \( P \) need not be integral insofar as this program is concerned.

1. First-Order Rate Law

The subprogram has been written for the special case in which the reaction rate is first-order in reactant \( B \), that is,

\[
\frac{-d[A]}{dt} = k_1 \cdot [B]
\]

in which \( k_1 \) is the first-order rate constant. The integrated form of this first-order rate equation is:

\[
k_1 t = P \cdot \ln[B]_0, \quad \frac{[B]}{[B]}
\]

where \([B] = \) concentration of component \( B \) at any time in moles/liter, \([B]_0 = \) initial concentration of component \( B \) in moles/liter, and \( P = \) stoichiometry factor.
2. **Second-Order Rate Law**

The subprogram has been written for the special case in which the reaction rate is first-order in each reactant A and B, that is

\[
\frac{-d[A]}{dt} = k_2[A][B],
\]

in which \( k_2 \) is the second-order rate constant. The integrated form of this second-order rate equation is

\[
k_2t = \frac{P \ln [A]_o[B]}{P[B]_o[A]_o - [A]_o[B]_o[A]}
\]

where \([A] = \) concentration of component A at any time, in moles/liter, \([A]_o = \) initial concentration of component A, in moles/liter, and similarly for \([B] \) and \([B]_o \).

3. **Third-Order Rate Law**

The subprogram has been written for the special case in which the reaction rate is second-order in component A and first-order in component B, that is

\[
\frac{-d[A]}{dt} = k_3 [A]^2[B],
\]

in which \( k_3 \) is the third-order rate constant. The integrated form of this third-order rate equation is

\[
k_3t = \frac{P}{P[B]_o[A]_o} \left( \frac{1}{[A]} - \frac{1}{[A]_o} \right) + \frac{P}{(P[B]_o[A]_o)^2} \ln [B]_o[A],
\]

with the symbolic significances as before.
B. REDUCTION OF OBSERVATIONAL DATA

In dilute solution, the absorbance of a species \( \text{A} \) in solution for a given wavelength of light \( \lambda \) is equal to the product of its molar extinction coefficient \( \varepsilon_A^\lambda \) and its concentration, \([\text{A}]\), that is

\[
(\text{Absorbance})^\lambda_A = \varepsilon_A^\lambda [\text{A}]. \tag{6}
\]

The total observed absorbance \( A^\lambda \) of a solution at a given wavelength is equal to the sum of contributions due to all absorbing species, and may be expressed as

\[
A^\lambda = \varepsilon_A^\lambda [\text{A}] + \varepsilon_B^\lambda [\text{B}] + \varepsilon_C^\lambda [\text{C}] + \ldots \tag{7}
\]

This program has been written to accommodate two absorbing species, one of which is a reactant, the other a product. In the ensuing discussion it is assumed that \( \text{A} \) is a reactant, \( \text{C} \) is a product, the contribution to the absorbance at \( \lambda_1 \) is due primarily to \( \text{A} \), and the contribution to the absorbance at \( \lambda_2 \) is due primarily to \( \text{C} \). In addition, it is required that \( -d[\text{A}] = d[\text{C}] \). The following paragraphs develop the relationships among these elements.

1. **Absorbance at \( \lambda_1 \):** following the disappearance of \( \text{A} \), with \( \varepsilon_A^{\lambda_1} > \varepsilon_C^{\lambda_1} \).

   The absorbance at \( \lambda_1 \) is equal to the sum of absorbances of the individual species present, that is, species \( \text{A} \) and \( \text{C} \). Thus we have

   \[
   A^{\lambda_1} = \varepsilon_A^{\lambda_1} [\text{A}] + \varepsilon_C^{\lambda_1} [\text{C}], \tag{8}
   \]

   with the contribution due to \( \text{A} \) being much larger. The amount of product \( \text{C} \), \([\text{C}]\), present is equal to the sum
of the amount initially present plus that which was pro-
duced at the expense of A during the reaction, that is
\[
[C] = [C]_o + \{[A]_o - [A]\}.
\] (9)
Equation (9) is valid only if \( -d[A] = d[C] \).
Substituting (9) in (8) gives
\[
\alpha_{\lambda l} = e_{\lambda A}^l [A] + e_{\lambda C}^l [C]_o + e_{\lambda C}^l \{[A]_o - [A]\}.
\] (10)
Now let \( \alpha_{\lambda l} = \alpha_{\lambda l}^0 - e_{\lambda C}^l [C]_o \). 
(11)
\( \alpha_{\lambda l} \) is, by this formulation, equal to the observed absorbance at \( \lambda l \) minus the absorbance due to any product C which was present at zero time. Upon substitution of (11), (10) becomes
\[
\alpha_{\lambda l} = e_{\lambda A}^l [A] + e_{\lambda C}^l [C]_o - e_{\lambda C}^l [A].
\] (12)
Rearranging (12) by solving for \([A]\) gives
\[
[A] = \frac{\lambda l}{e_{\lambda A}^l - e_{\lambda C}^l} [A]_o.
\] (13)
Equation (13) is the programmed formula. The concentration of reactant B, \([B]\), is determined by the stoichiometric relationship of Equation (1). Note that in Equation (11) the correction to be applied must derive from some independent source. Usually, the most convenient way to do this is to extrapolate the absorbance at \( \lambda 2 \) to zero time, which is chiefly due to \([C]\). The ratio of the extinction coefficients for C at \( \lambda 1 \) and \( \lambda 2 \) is the scale factor necessary to compute the correction. That is,
2. **Absorbance at $\lambda_2$:** following the growth of C, with $\varepsilon^\lambda_2_C > \varepsilon^\lambda_A$.

The absorbance at $\lambda_2$ is equal to the sum of absorbances of the individual species present, A and C. Using the formulation of Equation (8), we have the following expression:

$$A^{\lambda_2} = \varepsilon^{\lambda_2}_A [A] + \varepsilon^{\lambda_2}_C [C]_T,$$

(15)

with the contribution due to C being much the larger.

$[C]_T$ is the total amount of product C present.

$$[C]_T = [C]_0 + [C],$$

(16a)

where $[C]$ is the amount of product C which has been produced at the expense of A during the studied portion of the reaction, that is,

$$[C] = [A]_0 - [A].$$

(16b)

Let us rewrite (16b) to obtain

$$[A] = [A]_0 - [C].$$

(16c)

Upon substituting (16a) and (16c) in (15) we obtain

$$A^{\lambda_2} = \varepsilon^{\lambda_2}_A [A]_0 - \varepsilon^{\lambda_2}_A [C] + \varepsilon^{\lambda_2}_C [C]_0 + \varepsilon^{\lambda_2}_C [C]$$

(17)

Now let

$$\vartheta^{\lambda_2} = A^{\lambda_2} - \varepsilon^{\lambda_2}_C [C]_0.$$

(18)

Then

$$\vartheta^{\lambda_2} = \varepsilon^{\lambda_2}_A [A]_0 + (\varepsilon^{\lambda_2}_C - \varepsilon^{\lambda_2}_A) [C].$$

(19)
Rearranging (19) by solving for $[C]$ gives

$$[C] = \frac{\epsilon^\lambda_2 - \epsilon^\lambda_2[A]_0}{\epsilon^\lambda_2 - \epsilon^\lambda_2}$$  \hspace{1cm} (20)

Equation (20) is the programmed formula, and is in the same form as Equation (13). Note that all dependence on the variability of $[A]$ has been removed. The quantity $\epsilon^\lambda_2[C]_0$ is the measured or extrapolated absorbancy due to the species $C$ at zero time, which is, exactly, $\alpha^\lambda_2 - \epsilon^\lambda_2[A]_0$, barring other interferences.

3. Selection of Routines

It will be recalled from Sections 1 and 2 that $\epsilon^\lambda_1 > \epsilon^\lambda_1$ and that $\epsilon^\lambda_2 > \epsilon^\lambda_2$. This difference in the magnitudes of the molar extinction coefficients is tested by the program to determine which of the above routines (data taken at $\lambda 1$ or $\lambda 2$) to use.

The rate order calculation routines are selected by the program user. The input calls three characters called $L1$, $L2$, and $L3$ for this purpose. These are one-digit numbers which are tested in sequence for a zero or positive value. The results of the test are tabulated below:

- If $L1 = 0$, go on to test $L2$, do not calculate first-order rate constants;
  - $> 0$, compute and output first-order rate constants, then test $L2$.
- If $L2 = 0$, go on to test $L3$, do not calculate second-order rate constants;
> 0, compute and output second-order rate constants, then test L3.

If L3: = 0, go on to termination routine, do not calculate third-order rate constants;

> 0, compute and output third-order rate constants, then go to termination routine.

C. FORTRAN NOTATION

The mathematical symbols used in the above discussion are represented in the FORTRAN source program by the labels indicated in the right column.

<table>
<thead>
<tr>
<th>Mathematical Symbol</th>
<th>FORTRAN Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A]₀</td>
<td>A</td>
</tr>
<tr>
<td>[B]₀</td>
<td>B</td>
</tr>
<tr>
<td>[B]₀-[B]</td>
<td>X</td>
</tr>
<tr>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>e^{λ₁} A</td>
<td>E3</td>
</tr>
<tr>
<td>e^{λ₁} C</td>
<td>E4</td>
</tr>
<tr>
<td>e^{λ₁} C [C]₀</td>
<td>CORR</td>
</tr>
<tr>
<td>A^{λ₁} t</td>
<td>ABNS</td>
</tr>
<tr>
<td>k₁</td>
<td>C₁</td>
</tr>
<tr>
<td>k₂</td>
<td>C₂</td>
</tr>
<tr>
<td>k₃</td>
<td>C₃</td>
</tr>
<tr>
<td>A^{λ₁} k₁t</td>
<td>BRACK</td>
</tr>
<tr>
<td>k₂t</td>
<td>C₂T</td>
</tr>
<tr>
<td>k₃t</td>
<td>C₃T</td>
</tr>
<tr>
<td>L₁, L₂, L₃</td>
<td>L₁, L₂, L₃</td>
</tr>
</tbody>
</table>
D. RUNNING TIME

The time required to process a set of data is dependent on the amount of data and on the computer configuration. Data for twenty measurements are processed in about one minute by an ASI-210 machine with paper tape I/O.

E. INPUT

This section describes the contents of each datum field. The datum field format (in parentheses) follows the datum description. For an experiment yielding n absorbance measurements, there will be $3 + n$ lines of input. A data coding form is included with this write-up as Appendix A. This form clearly shows all numerical formats, with field lengths and decimal points indicated on the sheet.

Line 1: Title - not more than 70 alpha numeric characters (10A7).

Line 2: Run Number - any integer number, but no more than three digits (I3).

$[A]_0$ - the initial (starting) concentration in moles/liter of reactant A. (F8.6)

$[B]_0$ - the initial (starting) concentration in moles/liter of reactant B. (F8.6)

P - the stoichiometry factor (vide supra Sec. A). (P8.6)

$L_1,L_2,L_3$ - the order selectors (vide supra Sec. B3). (3Il)

Line 3: Zero-time product absorbance - the zero time absorbance due to product C, previously defined as $e_C [C]_0$. (F5.3)
\( \varepsilon^\lambda(\text{product}) \) - the molar extinction coefficient of product C, previously denoted \( \varepsilon^\lambda_C \). Note that this number will be different at different wave lengths. (F6.2)

\( \varepsilon^\lambda(\text{reactant}) \) - the molar extinction coefficient of reactant A, previously denoted \( \varepsilon^\lambda_A \). Note that this number will be different at different wave lengths. (F6.2)

Line 4: Time (elapsed minutes) - the number of minutes elapsed from the beginning of the reaction to the first measurement. (F6.2)

Absorbance - the spectrophotometer reading at the time entered in the first field of Line 4. (F5.3)

The remaining lines contain all subsequent observational data, one observation to a line, in the same format as Line 4. The last data line must be followed by a zero field to signal the end of computation. A sample input is presented on page 11.

F. OUTPUT

The computer generates a table containing \( t \) and the computed values of \( X = [B]_0 - [B] \), \( k_t \) and \( k_1t \), for each of the order routines selected. The "Title", Run number, \( [A]_0 \), and \( [B]_0 \) data are reproduced at the top of the output page. Table columns are appropriately headed. Output is terminated by the message "END OF JOB" which is printed at the top of a new page. A sample output is presented on page 12.
G. OPERATING PROCEDURE

The ASI-210 FORTRAN II compiler features a "load-and-go" operating system. The data may be loaded immediately after the program. The program is automatically executed upon being compiled.

Sense Switch* 2 - Sense switch 2 is referenced by the program at the end of the job. If sense switch 2 is OFF, the program branches to the beginning to reinitialize for a new job. If sense switch 2 is ON, the program branches to a pause condition. Depressing the RUN button will cause the program to return to the beginning to reinitialize for a new job. No exit to monitor has been programmed. One may call the monitor during the pause condition.

The program, as written, references the paper tape I/O devices.

The FORTRAN II code is presented on page 14. The program flow chart is shown on page 16.

---

* Sense switches are located on the computer console and provide the operator with a means of altering the program sequence.
9 FE 65  B/A = XE03/Pu3+ = 1/2 IN 2M HClO4  4700A TEMP = 44.9 C

<table>
<thead>
<tr>
<th></th>
<th>1.0427</th>
<th>.00388</th>
<th>6.0</th>
<th>4.0</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>56.0</td>
<td>4.0</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.195</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>0.236</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>0.283</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.0</td>
<td>0.325</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>0.364</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.0</td>
<td>0.399</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>0.433</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.0</td>
<td>0.464</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18.0</td>
<td>0.497</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.0</td>
<td>0.528</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.0</td>
<td>0.553</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24.0</td>
<td>0.579</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.0</td>
<td>0.608</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28.0</td>
<td>0.637</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.0</td>
<td>0.649</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.0</td>
<td>0.669</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Sample Output**

9 FE 65  \( \text{B/A = } xe_{03}/pu_{3+} = 1/2 \) in 2M HClO4  \( 4700A \) TEMP = 44.9 C

**Run No. 1**  \( A = 0.042700 \)  \( B = 0.003880 \)

<table>
<thead>
<tr>
<th>T</th>
<th>X</th>
<th>K1</th>
<th>K1T</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0.000078</td>
<td>0.060580</td>
<td>1.212</td>
</tr>
<tr>
<td>4.00</td>
<td>0.000205</td>
<td>0.083046</td>
<td>3.332</td>
</tr>
<tr>
<td>6.00</td>
<td>0.000360</td>
<td>0.097265</td>
<td>5.836</td>
</tr>
<tr>
<td>8.00</td>
<td>0.000494</td>
<td>1.02191</td>
<td>8.175</td>
</tr>
<tr>
<td>10.00</td>
<td>0.000619</td>
<td>1.04323</td>
<td>1.0432</td>
</tr>
<tr>
<td>12.00</td>
<td>0.000731</td>
<td>1.04440</td>
<td>1.2533</td>
</tr>
<tr>
<td>14.00</td>
<td>0.000840</td>
<td>1.04616</td>
<td>1.4646</td>
</tr>
<tr>
<td>16.00</td>
<td>0.000940</td>
<td>1.04002</td>
<td>1.6640</td>
</tr>
<tr>
<td>18.00</td>
<td>0.001046</td>
<td>1.04658</td>
<td>1.8638</td>
</tr>
<tr>
<td>20.00</td>
<td>0.001145</td>
<td>1.04897</td>
<td>2.0979</td>
</tr>
<tr>
<td>22.00</td>
<td>0.001225</td>
<td>1.03470</td>
<td>2.2763</td>
</tr>
<tr>
<td>24.00</td>
<td>0.001308</td>
<td>1.02820</td>
<td>2.4677</td>
</tr>
<tr>
<td>26.00</td>
<td>0.001401</td>
<td>1.03406</td>
<td>2.6886</td>
</tr>
<tr>
<td>28.00</td>
<td>0.001494</td>
<td>1.04210</td>
<td>2.9179</td>
</tr>
<tr>
<td>30.00</td>
<td>0.001533</td>
<td>1.00513</td>
<td>3.0154</td>
</tr>
<tr>
<td>32.00</td>
<td>0.001597</td>
<td>0.99423</td>
<td>3.1815</td>
</tr>
</tbody>
</table>
SAMPLE OUTPUT (Concluded)

9FE65  B/A = XE03/PU3+ = 1/2  IN 2M HClO4  4700A TEMP = 44.9 C

RUN NO.  1  A= .042700  B= .003880

<table>
<thead>
<tr>
<th>T</th>
<th>X</th>
<th>K2</th>
<th>K2T</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>.000078</td>
<td>1.426545</td>
<td>2.8531</td>
</tr>
<tr>
<td>4.00</td>
<td>.000209</td>
<td>1.974271</td>
<td>7.8971</td>
</tr>
<tr>
<td>6.00</td>
<td>.000360</td>
<td>2.338416</td>
<td>14.0305</td>
</tr>
<tr>
<td>8.00</td>
<td>.000494</td>
<td>2.482409</td>
<td>19.8593</td>
</tr>
<tr>
<td>10.00</td>
<td>.000619</td>
<td>2.559429</td>
<td>25.5943</td>
</tr>
<tr>
<td>12.00</td>
<td>.000731</td>
<td>2.585806</td>
<td>31.0297</td>
</tr>
<tr>
<td>14.00</td>
<td>.000840</td>
<td>2.613855</td>
<td>36.5940</td>
</tr>
<tr>
<td>16.00</td>
<td>.000940</td>
<td>2.620736</td>
<td>41.9318</td>
</tr>
<tr>
<td>18.00</td>
<td>.001046</td>
<td>2.661918</td>
<td>47.9145</td>
</tr>
<tr>
<td>20.00</td>
<td>.001145</td>
<td>2.692043</td>
<td>53.8409</td>
</tr>
<tr>
<td>22.00</td>
<td>.001225</td>
<td>2.675170</td>
<td>58.8537</td>
</tr>
<tr>
<td>24.00</td>
<td>.001308</td>
<td>2.679392</td>
<td>64.3054</td>
</tr>
<tr>
<td>26.00</td>
<td>.001401</td>
<td>2.719035</td>
<td>70.6949</td>
</tr>
<tr>
<td>28.00</td>
<td>.001494</td>
<td>2.765622</td>
<td>77.4374</td>
</tr>
<tr>
<td>30.00</td>
<td>.001533</td>
<td>2.67935</td>
<td>86.3380</td>
</tr>
<tr>
<td>32.00</td>
<td>.001597</td>
<td>2.666421</td>
<td>85.3255</td>
</tr>
</tbody>
</table>
C ERLF 27MY65
C REACTION RATE CONSTANT
C G.J.WERKEMA X752

DIMENSION T(60),ABNS(60),X(60)
DIMENSION TITLE(10)

010 FORMAT(10A7)
011 FORMAT(13,3F8.6)
012 FORMAT(F6.2,F5.3)
013 FORMAT(F5.3,2F6.2,311)
021 FORMAT(8H RUN NO. 13, 4H A= F8.6, 4H B= F8.6/)
022 FORMAT(40H T , X K1 )
023 FORMAT(F6.2,2X,F8.6,2X,F10.6,2X,F10.4)
024 FORMAT(19H END OF JOB )
025 FORMAT(1H )
026 FORMAT(40H T X K2 )
027 FORMAT(40H T X K3 )

NSP=66
READ 10,TITLE
READ 11,NRUN,A,B,P
READ 13,CORR,E4,E3,L1,L2,L3.
A1=P*B-A
A2=P/A1
A3=A2/A1
A4=A/B
A5=1.0/A
A6=E3*A
A7=E4*A
A8=1.0/(P*(E4-E3))
A9=A/A1
141 LAM=2
241 LAM=1
042 I=1
142 READ 12,T(I),ABNS(I)
143 IF(T(I))82,46,43
043 BRACK=ABNS(I)-CORR
044 GO TO(44,45),LAM
045 X(I)=A9+(BRACK-A1)*A8
046 GO TO 145
047 X(I)=(BRACK-A6)*A8
145 I=I+1
046 I=I-1
NSP=NSP-6-1
147 IF(L1)82,48,47
047 PUNCH 10,TITLE
PUNCH 25
PUNCH 21,NRUN,A,B
PUNCH 22
DO 147 J=1,1
C1T=P*LOGF(B/(B-X(J)))
C1=C1T/T(J)
PUNCH 23,T(J),X(J),C1,C1T
CONTINUE
DO 247 NL=1,NSP
PUNCH 25
CONTINUE
IF(L2)82,50,49
PUNCH 10,TITLE
PUNCH 21,NRUN,A,B
PUNCH 26
DO 149 J=1,I
C2T=A2*LOGF((A*(B-X(J)))/(B*(A-P*X(J))))
C2=C2T/T(J)
PUNCH 23,T(J),X(J),C2,C2T
CONTINUE
DO 249 NL=1,NSP
PUNCH 25
CONTINUE
IF(L3)82,251,51
PUNCH 10,TITLE
PUNCH 21,NRUN,A,B
PUNCH 27
DO 151 J=1,I
FIR=LOGF((A*(B-X(J)))/(B*(A-P*X(J))))
C3T=A2/(A-P*X(J))-A2*A5-A3*FIR
C3=C3T/T(J)
PUNCH 23,T(J),X(J),C3,C3T
CONTINUE
DO 251 NL=1,NSP
PUNCH 25
CONTINUE
IF(SENSE SWITCH 2)82,41
PUNCH 24
PAUSE
GO TO 41
END
EOF
## APPENDIX A

**ERLD REACTION RATE DATA SHEET**

**FORTRAN CODE: ERLF**

1. Title—not more than 70 characters.

2. Run number; \([A]_0; [B]_0; P\), the stoichiometry factor.

3. Zero-time product absorbance; \(c\lambda(\text{product}); c\lambda(\text{reactant}); L1, L2, L3\).

4. Time (elapsed minutes); Absorbance. Fill last line with zeroes.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**17**