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RFP-629

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
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ABSTRACT

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 $A + B \rightleftharpoons C + D$ 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

$$d[A] = P \cdot d[B] \quad (1)$$

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:

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

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

$$-\frac{d[A]}{dt} = k_2[A] \cdot [B], \quad (2)$$

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

$$k_2 t = \frac{P}{P \cdot [B]_0 - [A]_0} \ln \frac{[A]_0 \cdot [B]}{[B]_0 \cdot [A]}, \quad (3)$$

where $[A]$ = concentration of component A at any time, in moles/liter, $[A]_0$ = initial concentration of component A, in moles/liter, and similarly for $[B]$ and $[B]_0$.

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

$$-\frac{d[A]}{dt} = k_3 [A]^2 \cdot [B], \quad (4)$$

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

$$k_3 t = \frac{P}{P \cdot [B]_0 - [A]_0} \left(\frac{1}{[A]} - \frac{1}{[A]_0} \right) + \frac{P}{(P \cdot [B]_0 - [A]_0)^2} \ln \frac{[B]_0 [A]}{[A]_0 [B]}, \quad (5)$$

with the symbolic significances as before.

B. REDUCTION OF OBSERVATIONAL DATA

In dilute solution, the absorbance of a species (A) in solution for a given wave length of light (λ) is equal to the product of its molar extinction coefficient (ϵ_A^λ) and its concentration, [A], that is

$$(\text{Absorbance})_A^\lambda = \epsilon_A^\lambda [A]. \quad (6)$$

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

$$a^\lambda = \epsilon_A^\lambda [A] + \epsilon_B^\lambda [B] + \epsilon_C^\lambda [C] + \dots \quad (7)$$

This program has been written to accomodate two absorbing species, one of which is a reactant, the other a product. In the ensuing discussion it is assumed that A is a reactant, C is a product, the contribution to the absorbance at λ_1 is due primarily to A, and the contribution to the absorbance at λ_2 is due primarily to C. In addition, it is required that $-d[A] = d[C]$. The following paragraphs develop the relationships among these elements.

1. Absorbance at λ_1 : following the disappearance of A, with $\epsilon_A^{\lambda_1} > \epsilon_C^{\lambda_1}$.

The absorbance at λ_1 is equal to the sum of absorbances of the individual species present, that is, species A and C. Thus we have

$$a^{\lambda_1} = \epsilon_A^{\lambda_1} [A] + \epsilon_C^{\lambda_1} [C], \quad (8)$$

with the contribution due to A being much larger. The amount of product C, [C], present is equal to the sum

of the amount initially present plus that which was produced at the expense of A during the reaction, that is

$$[C] = [C]_0 + \{[A]_0 - [A]\}. \quad (9)$$

Equation (9) is valid only if $-d[A] = d[C]$.

Substituting (9) in (8) gives

$$a^{\lambda_1} = \epsilon_A^{\lambda_1} [A] + \epsilon_C^{\lambda_1} [C]_0 + \epsilon_C^{\lambda_1} \{[A]_0 - [A]\}. \quad (10)$$

$$\text{Now let } \theta^{\lambda_1} = a^{\lambda_1} - \epsilon_C^{\lambda_1} [C]_0. \quad (11)$$

θ^{λ_1} is, by this formulation, equal to the observed absorbance at λ_1 minus the absorbance due to any product C which was present at zero time. Upon substitution of (11), (10) becomes

$$\theta^{\lambda_1} = \epsilon_A^{\lambda_1} [A] + \epsilon_C^{\lambda_1} [A]_0 - \epsilon_C^{\lambda_1} [A]. \quad (12)$$

Rearranging (12) by solving for [A] gives

$$[A] = \frac{\theta^{\lambda_1} - \epsilon_C^{\lambda_1} [A]_0}{\epsilon_A^{\lambda_1} - \epsilon_C^{\lambda_1}}. \quad (13)$$

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 λ_2 to zero time, which is chiefly due to [C]. The ratio of the extinction coefficients for C at λ_1 and λ_2 is the scale factor necessary to compute the correction. That is,

$$\epsilon_C^{\lambda 1} [C]_o = a_{\text{initial}}^{\lambda 2} \cdot \frac{\epsilon_C^{\lambda 1}}{\epsilon_C^{\lambda 2}} \quad (14)$$

2. Absorbance at $\lambda 2$: following the growth of C, with $\epsilon_C^{\lambda 2} > \epsilon_A^{\lambda 2}$.

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:

$$a^{\lambda 2} = \epsilon_A^{\lambda 2} [A] + \epsilon_C^{\lambda 2} [C]_T, \quad (15)$$

with the contribution due to C being much the larger.

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

$$[C]_T = [C]_o + [C], \quad (16a)$$

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,

$$[C] = [A]_o - [A]. \quad (16b)$$

Let us rewrite (16b) to obtain

$$[A] = [A]_o - [C]. \quad (16c)$$

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

$$a^{\lambda 2} = \epsilon_A^{\lambda 2} [A]_o - \epsilon_A^{\lambda 2} [C] + \epsilon_C^{\lambda 2} [C]_o + \epsilon_C^{\lambda 2} [C] \quad (17)$$

$$\text{Now let } \theta^{\lambda 2} = a^{\lambda 2} - \epsilon_C^{\lambda 2} [C]_o. \quad (18)$$

$$\text{Then } \theta^{\lambda 2} = \epsilon_A^{\lambda 2} [A]_o + (\epsilon_C^{\lambda 2} - \epsilon_A^{\lambda 2}) \cdot [C]. \quad (19)$$

Rearranging (19) by solving for [C] gives

$$[C] = \frac{\epsilon_C^{\lambda_2} - \epsilon_A^{\lambda_2}[A]_0}{\epsilon_C^{\lambda_2} - \epsilon_A^{\lambda_2}} \quad (20)$$

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 $\epsilon_C^{\lambda_2}[C]_0$ is the measured or extrapolated absorbancy due to the species C at zero time, which is, exactly, $A_{\text{initial}}^{\lambda_2} - \epsilon_A^{\lambda_2}[A]_0$, barring other interferences.

3. Selection of Routines

It will be recalled from Sections 1 and 2 that $\epsilon_A^{\lambda_1} > \epsilon_C^{\lambda_1}$ and that $\epsilon_C^{\lambda_2} > \epsilon_A^{\lambda_2}$. 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 λ_1 or λ_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.

<u>Mathematical Symbol</u>	<u>FORTRAN Label</u>
$[A]_0$	A
$[B]_0$	B
$[B]_0 - [B]$	X
P	P
$e_A^{\lambda_1}$	E3
$e_C^{\lambda_1}$	E4
$e_C^{\lambda_1} [C]_0$	CORR
a^{λ_1}	ABNS
t	T
k_1	C1
k_2	C2
k_3	C3
θ^{λ_1}	BRACK
$k_1 t$	C1T
$k_2 t$	C2T
$k_3 t$	C3T
L1, L2, L3	L1, L2, L3

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). (F8.6)

L1, L2, L3 - the order selectors (vide supra Sec. B3). (3I1)

Line 3: Zero-time product absorbance - the zero time absorbance due to product C, previously defined as $\epsilon_C^{\lambda 1} [C]_0$. (F5.3)

$\epsilon^\lambda(\text{product})$ - the molar extinction coefficient of product C, previously denoted $\epsilon_C^{\lambda i}$. Note that this number will be different at different wave lengths. (F6.2)

$\epsilon^\lambda(\text{reactant})$ - the molar extinction coefficient of reactant A, previously denoted $\epsilon_A^{\lambda i}$. 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_1 and $k_1 t$, 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.

SAMPLE INPUT

9 FE 65 B/A = XEO3/PU3+ = 1/2 IN 2M HClO4 4700A TEMP = 44.9 C
 1 .0427 .00388 6.0
 .000 56.0 4.0 120
 2.0 0.195
 4.0 0.236
 6.0 0.283
 8.0 0.325
 10.0 0.364
 12.0 0.399
 14.0 0.433
 16.0 0.464
 18.0 0.497
 20.0 0.528
 22.0 0.553
 24.0 0.579
 26.0 0.608
 28.0 0.637
 30.0 0.649
 32.0 0.669
 0.0 0.0

SAMPLE OUTPUT

9 FE 65 B/A = XE03/PU3+ = 1/2 IN 2M HCL04 4700A TEMP = 44.9 C

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

T	X	K1	K1T
2.00	.000078	.060580	.1212
4.00	.000209	.083046	.3322
6.00	.000360	.097265	.5836
8.00	.000494	.102191	.8175
10.00	.000619	.104323	1.0432
12.00	.000731	.104440	1.2533
14.00	.000840	.104616	1.4646
16.00	.000940	.104002	1.6640
18.00	.001046	.104658	1.8838
20.00	.001145	.104897	2.0979
22.00	.001225	.103470	2.2763
24.00	.001308	.102820	2.4677
26.00	.001401	.103406	2.6886
28.00	.001494	.104210	2.9179
30.00	.001533	.100513	3.0154
32.00	.001597	.099423	3.1815

SAMPLE OUTPUT (Concluded)

9 FE 65 B/A = XEO3/PU3+ = 1/2 IN 2M HClO4 4700A TEMP = 44.9 C

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

T	X	K2	K2T
2.00	.000078	1.426545	2.8531
4.00	.000209	1.974271	7.8971
6.00	.000360	2.338416	14.0305
8.00	.000494	2.482409	19.8593
10.00	.000619	2.559429	25.5943
12.00	.000731	2.585806	31.0297
14.00	.000840	2.613855	36.5940
16.00	.000940	2.620736	41.9318
18.00	.001046	2.661918	47.9145
20.00	.001145	2.692043	53.8409
22.00	.001225	2.675170	58.8537
24.00	.001308	2.679392	64.3054
26.00	.001401	2.719035	70.6949
28.00	.001494	2.765622	77.4374
30.00	.001533	2.677935	80.3380
32.00	.001597	2.666421	85.3255

FORTRAN LISTING

```

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(F5.3,2F6.2,3I1)
021  FORMAT(8H RUN NO. 13, 4H  A= F8.6, 4H  B= F8.6/)
022  FORMAT(40H  T          X          K1          K1T  /)
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          K2T  /)
027  FORMAT(40H  T          X          K3          K3T  /)
041  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/P
      IF(E3-E4)141,82,241
141  LAM=2
      GO TO 42
241  LAM=1
042  I=1
142  READ 12,T(1),ABNS(1)
      IF(T(1))82,46,43
043  BRACK=ABNS(1)-CORR
      GO TO(44,45),LAM
044  X(1)=A9+(BRACK-A7)*A8
      GO TO 145
045  X(1)=(BRACK-A6)*A8
145  I=I+1
      GO TO 142
046  I=I-1
      NSP=NSP-6-1
      IF(L1)82,48,47
047  PUNCH 10,TITLE
      PUNCH 25
      PUNCH 21,NRUN,A,B
      PUNCH 22
      DO 147 J=1,I

```

FORTRAN LISTING (Concluded)

```

C1T=P*LOGF(B/(B-X(J)))
C1=C1T/T(J)
PUNCH 23,T(J),X(J),C1,C1T
147 CONTINUE
DO 247 NL=1,NSP
PUNCH 25
247 CONTINUE
048 IF(L2)82,50,49
049 PUNCH 10,TITLE
PUNCH 25
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
149 CONTINUE
DO 249 NL=1,NSP
PUNCH 25
249 CONTINUE
050 IF(L3)82,251,51
051 PUNCH 10,TITLE
PUNCH 25
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
151 CONTINUE
DO 251 NL=1,NSP
PUNCH 25
251 CONTINUE
IF(SENSE SWITCH 2)82,41
082 PUNCH 24
PAUSE
GO TO 41
END
EOF

```

PROGRAM FLOW CHART

APPENDIX A

ERLD

FORTRAN CODE: ERLF

REACTION RATE DATA SHEET

1. Title-not more than 70 characters.

---

2. Run number; $[A]_0$; $[B]_0$; P, the stoichiometry factor.

---

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

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

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