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TITLE

LSQ STERN VOLMER: LEAST SQUARES TREATMENT OF THE GENERAL STERN-VOLMER EQUATION

AUTHOR

Dr. James E. Gano and Dr. H. Bradford Thompson

COMPANY

University of Toledo
Toledo, Ohio

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SOURCE LANGUAGE

8K FOCAL ®

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LSQ STERN-VOLMER: LEAST SQUARES TREATMENT OF THE GENERAL STERN-VOLMER EQUATION

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1. ABSTRACT

LSQ STERN-VOLMER is a program designed for use by photochemists in treating data obtained from systems where the general Stern-Volmer equation must be employed.[1,2] Given trial values of the desired kinetic parameters, the program does an iterative least squares fit of the data, outputs the working parameters and plots (optional) the experimental and theoretical results on an X,Y-recorder. Details of this approach have been described.[1]

2. REQUIREMENTS

To obtain just the kinetic parameters, an 8K PDP 8 is sufficient. To employ the plotting option, an AX-08 and X,Y recorder must be included.

3. LOADING

After loading the binary FOCAL program, the AX-08 (if used) and X,Y-recorder (if used) are turned on and then the FOCAL program is started. None of the extended FOCAL functions are necessary so they can be discarded.

4. OPERATION

Operation of LSQ STERN-VOLMER is started with GO↵. After an initial descriptive commentary, ending in a colon, the following data should be entered in the order given. A,B and C are trial values for the desired parameters. Selection of the values is described in the Appendix.

$$A\ (= KQT(T) = k_q^T\ \tau_T^\circ)$$

$$B\ (= \Phi(S)/(\Phi(S) + \Phi(T))$$

$$C\ (= KQT(S) = k_q^S\ \tau_S^\circ)$$

Rø = yield of product in absence of quencher Q.

R1 = yield of product when quencher concentration is Q1.

Q1 = quencher concentration.

R2 = yield of product when quencher concentration is Q2.

Q2 = quencher concentration two.

. .

. .

. .

. .

Qn = quencher concentration n

The concentration and yield data pairs can be entered in any order but the yield must always precede the concentration. Terminate with -1↵, - 1↵ and computation will begin. After each iteration, the working values of A,B and C and the residuals (= $\sum_{i}^{n}$ [Rø/RN(Experimental) - Rø/RN(Theoretical)]^2 will be printed out. After twelve iterations, or when the residual value does not change between calculations, the computations will terminate and the calculated kinetic parameters will be printed out along with their standard deviations, SIGMA, and correlation coefficients, P. In order to have the input and output data available in a convenient form for storage, the input parameters and calculated Rø/RN values are also printed at this point.

> NOTE 1. If poor initial estimates of the parameters A,B and C were made, it should be indicated at this point by increasing rather than decreasing values for the residuals as the iterations proceed or by unrealistic final values for A,B and C.
>
> NOTE 2. If the printout of working results indicates further improvement would have been obtained if more iterations had been performed, answer NO↵ to the subsequent plotting option, answer YES↵ to the terminate question and restart the iteration by giving GO 3.12↵.

The computer then asks whether the plotting option is to be utilized.

PLOT EXPERIMENTAL?:

Plotting Option Not Desired. A NO↵ reply to the plotting option request is followed by:

TERMINATE?:

If additional sets of data are to be treated, the NO↵ reply is given. The computer reminds the operator of the pieces of data to be entered and their order and gives a colon to signal it is ready to accept the next set of values. A YES↵ reply gives an * indicating transfer of control to the FOCAL routine.

Plotting Option Desired:* ,3 A YES↵ reply gives a colon and positions the pen on the X,Y-recorder at one corner of the eventual plot. Giving F↵, F↵, etc. moves the pen from corner to corner allowing adjustment of the size and position of the plot by utilizing the zero and gain controls on the recorder. When the appropriate size and position are selected, the pen is manually lowered and F↵, F↵, F↵, F↵ is used to draw the frame of the plot. The pen is then manually raised and P↵ entered. The reply is:

MANUAL SCALING?:

A YES↵ reply to this query produces the following dialogue (with typical data inserted) wherein the coordinates of the corners of the plot are defined, following which the plot is automatically performed.

MIN. X VALUE: ϕ

MAX. X VALUE: 5

MIN. Y VALUE: ϕ.8

MAX. Y VALUE: 3

A NO↵ reply to the manual scaling question produces the plot directly with the ordinate going from 0.8 to 110% of the maximum Φ_o/Φ valve and the abscissa going from 0 to 110% of the maximum quencher concentration. Either reply above eventually results in

PLOT THEORETICAL?:

A YES↵ reply results in a plot of the theoretical curve over the experimental points. Either after the theoretical curve is plotted or if a NO↵ reply is given the following question is posed.

TERMINATE?:

If additional sets of data are to be processed, NO↵ is given and the new data is entered after the computer provides a reminder of the appropriate order. The YES↵ transfers control to the FOCAL master program.

* See comments on the plotting option in the Appendix.

5. Appendix

Plotting option. In order to utilize the plotting option described above,[3] an appropriate function for raising and lowering the pen must be available. In this case FPDN was utilized. If some other function is used locally, the program is easily modified by replacing FPDN(ø) in line 31.8ø with the local pen up function and FPDN (1) in line 31.9ø with the local pen down function. Any attempt to use the plotting option with the wrong pen control function will result in

ø7;6 @ ø5.26

Selecting trial values for A,B and C has been described in detail elsewhere.[2] If completely unrealistic values are chosen, all experience to data indicates the iteration will not converge or obviously unrealistic results are obtained. Since B, by its definition must vary between zero and one, usually 0.5 is a satisfactory choice. A and C can be usually estimated from results known for similar systems. Typical ranges are 10 - 1000 and 0-5, for A and C, respectively.

6. References

(1) J.E. Gano, submitted for publication, Mol. Photochem, (1972).
(2) J.C. Dalton and N.J. Turro, Mol. Photochem., 2, 133 (1970).
(3) The plotting routines were kindly provided by their originator, Mr. Bill Kint.

7. Program Listing

```
*W
C-8K TV5A  @1969

01.02 T !!!!!!!!!!,"        LSQ STERN-VOLMER:LEAST SQUARES TREATMENT"
01.04 T " OF THE GENERAL",!,"                              STERN-VOLMER"
01.06 T " EQUATION",!,"                  (UNIVERSITY OF TOLEDO,CHEMISTRY,"
01.07 T "J.E.GANO)"
01.08 T !!,"                    RØ/RN=(1+C*QN)(1+A*QN)/(1+A*B*QN)"
01.09 T !,"                A=KQT(T)   B=Ø(S)/(Ø(S)+Ø(T))   C=KQT(S)
01.10 T !!,"INSTRUCTIONS:",!,"TURN ON X,Y RECORDER BEFORE STARTING"
01.11 T " IF USING PLOTTING OPTION"
01.12 T !,"ORDINATE GOES FROM Ø.8 TO MAXIMUM VALUE OF RØ/RN PLUS 10%"
01.14 T !,"ABSCISSA GOES FROM ZERO .....QN PLUS 10%"
01.15 T !,"ANSWER QUESTIONS WITH YES OR NO"
01.20 S N=1;S XR=Ø;S YT=Ø

02.01 T !,"TYPE IN ESTIMATED VALUES OF KQT(T),Ø(S)/(Ø(S)+Ø(T)),KQT(S) AN
02.03 T " THEN",!,"RØ,RN,QN,ETC AND TERMINATE WITH -1,-1.",!
02.05 A AØ,BØ,CØ,RØ
02.07 A RN,QN
02.09 I (RN)2.19;I (XR-QN)2.27
02.11 S P(N)=RN
02.13 S R(N)=RØ/RN;S Q(N)=QN
02.14 I (YT-R(N))2.29
02.15 S N=N+1
02.17 G 2.07
02.19 S END=N-1
02.21 S MX=XR;S MY=YT
02.23 G 3.12
02.27 S XR=QN*1.1;G 2.11
02.29 S YT=R(N)*1.1;G 2.15

03.02 T !!!!!!!!,"  RN        RØ/RN     QN",!
03.04 S N=1
03.06 T %6.4,P(N)," ",R(N)," ",Q(N),!
03.08 S N=N+1
03.10 I (END-N)4.60,3.06,3.06
03.12 T !!,"RESIDUALS AØ        BØ        CØ"
03.14 S HOLDNO=Ø;S ITNO=12
03.15 S N=1; S ASUM=Ø;S BSUM=Ø;S CSUM=Ø;S DSUM=Ø;S ESUM=Ø;S GSUM=Ø
03.16 S YASUM=Ø;S YBSUM=Ø;S YCSUM=Ø;S SQRSUM=Ø;S AB=-10;S BC=-20;S AC=-Ø

04.01 S DNOM=(1+AØ*BØ*Q(N));S YØ=(1+AØ*Q(N))*(1+CØ*Q(N))/DNOM
04.03 S ADY=Q(N)*(1-BØ)*(1+CØ*Q(N))/DNOM↑2
04.05 S BDY=-AØ*Q(N)*(1+AØ*Q(N))*(1+CØ*Q(N))/DNOM↑2
04.06 S CDY=Q(N)*(1+AØ*Q(N))/DNOM
04.07 S ASUM=ASUM+ADY↑2;S BSUM=BSUM+BDY↑2;S CSUM=CSUM+CDY↑2
04.09 S DSUM=DSUM+ADY*BDY;S ESUM=ESUM+BDY*CDY;S GSUM=GSUM+ADY*CDY
04.13 S YASUM=YASUM+ADY*(R(N)-YØ);S YBSUM=YBSUM+BDY*(R(N)-YØ)
04.15 S YCSUM=YCSUM+CDY*(R(N)-YØ)
04.17 S SQRSUM=SQRSUM+(R(N)-YØ)↑2
04.19 S N=N+1
04.21 I (END-N)4.23,4.01,4.01
04.23 S UBC=BSUM*CSUM-ESUM↑2;S VAC=ASUM*CSUM-GSUM↑2
04.25 S WAB=ASUM*BSUM-DSUM↑2;S XFE=GSUM*ESUM-DSUM*CSUM
04.27 S YDE=DSUM*ESUM-BSUM*GSUM;S ZDF=DSUM*GSUM-ASUM*ESUM
04.30 S DETVAL=ASUM*UBC+2*DSUM*ESUM*GSUM-CSUM*(DSUM↑2)-BSUM*(GSUM↑2)
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04.32 S XXX=SQRSUM/(END-3)*DETVAL;S ARANGE=FSQT(XXX*UBC)
04.34 S BRANGE=FSQT(XXX*VAC);S CRANGE=FSQT(XXX*WAB)
04.35 I (ARANGE*BRANGE)4.36,4.80
04.36 S P(AB)=XXX*XFE/ARANGE*BRANGE;S P(BC)=XXX*ZDF/BRANGE*CRANGE
04.37 S P(AC)=XXX*YDE/ARANGE*CRANGE
04.38 S ERROR=SQRSUM-HOLDNO
04.40 T %6.4,!,SQRSUM," ",A0," ",B0," ",C0
04.41 S ITNO=ITNO-1;I (ITNO-1)4.55
04.42 I (ERROR)4.44,4.55,4.44
04.44 S A0=A0+(YASUM*UBC+YBSUM*XFE+YCSUM*YDE)/DETVAL
04.46 S B0=B0+(YASUM*XFE+YBSUM*VAC+YCSUM*ZDF)/DETVAL
04.47 S C0=C0+(YASUM*YDE+YBSUM*ZDF+YCSUM*WAB)/DETVAL
04.48 S HOLDNO=SQRSUM
04.50 G 3.15
04.55 G 3.02
04.60 T !,"KQT(T)=",A0," (SIGMA=",ARANGE,")",!!
04.62 T "0S/(0S+0T)=",B0," (SIGMA=",BRANGE,")"
04.63 T !!,"KQT(S)=",C0," (SIGMA=",CRANGE,")"
04.64 T !!,"CORRELATION COEFFICIENTS",!,"  P(AB)=",P(AB),!,"  P(BC)="
04.66 T P(BC),!,"  P(AC)=",P(AC)
04.70 A !!!!!!!!!,"PLOT EXPERIMENTAL?",REPLY
04.72 I (REPLY-155)4.74,10.26;I (0.25E+21-REPLY)4.74,5.10,4.74
04.74 T !,"YOU GOOFED. TRY AGAIN!";G 4.70
04.80 T !!,"DIVISION BY ZERO REQUESTED. IGNORE P(   ) VALUES";G 4.38

05.10 DO 31.0
05.11 A "MANUAL SCALING?",RE
05.12 I (RE-155)5.13,5.15;I (.25E+21-RE)5.13,5.14
05.13 T "WRONG ANSWER",!;G 5.11
05.14 DO 31.30;G 5.18
05.15 SET XL =0;SET YB=0;S XR=MX;S YT=MY
05.18 DO 31.4
05.20 SET N=1;SET IR=R(END)/500;SET IQ=Q(END)/500
05.22 SET X=Q(N)-IQ*4;SET Y=R(N)-IR*6
05.25 DO 31.50
05.26 DO 31.90

06.10 SET X=Q(N)+IQ*4
06.13 DO 31.5
06.15 SET Y=R(N)+IR*6
06.17 DO 31.5
06.20 SET X=Q(N)-IQ*4
06.21 DO 31.5
06.25 SET Y=R(N)-IR*6
06.27 DO 31.5
06.30 DO 31.80
06.32 S N=N+1
06.34 I (END-N)8.1,5.22,5.22

08.10 T !,"PLOT THEORETICAL?"
08.20 A PLOT
08.40 I (PL0T-155)8.42,10.26,8.42
08.42 I (PLOT-(.25E+21))8.45,9.1,8.45
08.45 T "CANNOT YOU SPEAK ENGLISH? TRY AGAIN",!
08.47 G 8.20

09.10 S X=0;S Y=(1+A0*X)*(1+C0*X)/(1+A0*B0*X)
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09.40 DO 31.5; DO 31.9
09.60 SET X=X+IQ;SET Y=(1+A0*X)*(1+C0*X)/(1+A0*B0*X)
09.80 I (X-Q(END))10.1,10.2,10.2

10.10 DO 31.5
10.15 GOTO 9.6
10.20 D0 31.8
10.26 T !,"TERMINATE?"
10.27 A TERM
10.28 I (TERM-155)10.29,10.3,10.29
10.29 I (TERM-(.25E+21))10.45,10.4,10.45
10.30 T !!!!!!!!!!
10.32 G 1.20
10.40 Q
10.45 T "YOU CANNOT SPEAK ENGLISH, CAN YOU? TRY AGAIN.",!
10.47 G 10.27

31.01 C FOCAL PLOT ROUTINES
31.10 S SI=1
31.11 S X=11;S Y=-245;D 31.16;I (SI-16)31.12,31.17,31.12
31.12 S X=511;D 31.16;I (SI)31.17
31.13 S Y=255;D 31.16;I (SI)31.17
31.14 S X=11;D 31.16;I (SI)31.17
31.15 G 31.11
31.16 S H(2040)=FDIS(X,Y);A SI
31.17 R ;Q
31.30 D 31.34;D 31.35;D 31.40
31.31 Q
31.34 A "MIN. X VALUE "XL,!,"MAX. X VALUE "XR,!
31.35 A "MIN. Y VALUE "YB,!,"MAX. Y VALUE "YT,!
31.40 S CX(2040)=500./(XR-XL);S CY(2040)=500./(YT-YB)
31.41 Q
31.50 D 31.52;D 31.53;D 31.54;S H(2040)=FDIS(XP(2040),YP(2040))
31.51 Q
31.52 S XP(2040)=11.+(X-XL)*CX(2040)
31.53 S YP(2040)=-245.+(Y-YB)*CY(2040)
31.54 I (11.-XP(2040))31.55;S XP(2040)=11.;G 31.56
31.55 I (XP(2040)-511.)31.56;S XP(2040)=511.;G 31.56
31.56 I (-245.-YP(2040))31.57;S YP(2040)=-245.;R
31.57 I (YP(2040)-255.)31.58;S YP(2040)=255.;R
31.58 R
31.80 D 31.84;S H(2040)=FPDN(0);D 31.86
31.81 Q
31.84 F ID(2040)=1,270*.5;C
31.86 F ID(2040)=1,270*.5;C
31.90 D 31.94;S H(2040)=FPDN(1);D 31.96
31.91 Q
31.94 F ID(2040)=1,270*.5;C
31.96 F ID(2040)=1,270*.5;C
*
```

8. Typical Output

```
        LSQ STERN-VOLMER:LEAST SQUARES TREATMENT OF THE GENERAL
                         STERN-VOLMER EQUATION
                (UNIVERSITY OF TOLEDO,CHEMISTRY,J.E.GANO)

                  R0/RN=(1+C*QN)(1+A*QN)/(1+A*B*QN)
               A=KQT(T)    B=0(S)/(0(S)+0(T))    C=KQT(S)

INSTRUCTIONS:
TURN ON X,Y RECORDER BEFORE STARTING IF USING PLOTTING OPTION
ORDINATE GOES FROM 0.8 TO MAXIMUM VALUE OF R0/RN PLUS 10%
ABSCISSA GOES FROM ZERO .....................QN PLUS 10%
ANSWER QUESTIONS WITH YES OR NO
TYPE IN ESTIMATED VALUES OF KQT(T),0(S)/(0(S)+0(T)),KQT(S) AND THEN
R0,RN,QN,ETC AND TERMINATE WITH -1,-1.
:13 :.8 :.1 :7.8 :6.9 :.05 :6.8 :.1 :6.8 :.15 :6.6 :.2 :6.5 :.3
:6.3 :.6 :6.1 :.8 :-1 :-1

RESIDUALS A0        B0        C0
 0.00719   13.0000   0.80000   0.10000
 0.01613   30.4008   0.91283   0.19144
 0.00059   76.8717   0.87341   0.14534
 0.00042   91.7187   0.87054   0.14243
 0.00042   94.5375   0.87063   0.14260
 0.00042   94.7840   0.87066   0.14264
 0.00042   94.7986   0.87066   0.14265
 0.00042   94.8003   0.87066   0.14265
 0.00042   94.7986   0.87066   0.14265
 0.00042   94.8022   0.87066   0.14265
 0.00042   94.8012   0.87066   0.14265
 0.00042   94.7988   0.87066   0.14265

 RN        R0/RN     QN
 6.90000   1.13043   0.05000
 6.80000   1.14706   0.10000
 6.80000   1.14706   0.15000
 6.60000   1.18182   0.20000
 6.50000   1.20000   0.30000
 6.30000   1.23810   0.60000
 6.10000   1.27869   0.80000

KQT(T)= 94.7988 (SIGMA= 75.2549)

0S/(0S+0T)= 0.87066 (SIGMA= 0.01226)

KQT(S)= 0.14265 (SIGMA= 0.02315)
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CORRELATION COEFFICIENTS
  P(AB)= 0.90146
  P(BC)= 0.92593
  P(AC)= 0.78008



PLOT EXPERIMENTAL?:NO

TERMINATE?:YES *
```