COMPUTER PROGRAMS TO DETERMINE CHEMICAL DIFFUSIVITIES USING THE BOLTZMAN-MATANO ANALYSIS

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COMPUTER PROGRAMS TO DETERMINE CHEMICAL DIFFUSIVITIES USING THE BOLTZMAN-MATANO ANALYSIS

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Abstract. A BASIC language computer technique has been developed to determine chemical diffusivities, using the Boltzman-Matano analysis. The computer programs with printout examples and a sample run are discussed in detail.

INTRODUCTION

The Boltzman-Matano analysis has been used for several years to determine chemical diffusivities. The technique is generally used where the diffusivity varies as a function of concentration for a given diffusion couple.

Described also is a computer technique for the Boltzman-Matano analysis. The computer programs were written in the BASIC language for use on a time-sharing computer.

Data obtained in a study to be later published (RFP-1546, Harvey) on the determination of chemical diffusivity of plutonium-gallium alloys in the epsilon phase were used to demonstrate the program.

DISCUSSION

Technique:

To determine chemical diffusivities at various concentrations using the Boltzman-Matano analysis, the following computations must be made:

1. The Matano interface is located where Area A = Area B in Figure 1.

FIGURE 1. The Matano Interface Is Positioned to Show Area A Equals Area B.
2. At a given weight percent concentration \( (c_3) \), the chemical diffusivity is determined using the slope of the tangent and Area E in Figure 2.

The Boltzman equation is:

\[
\frac{D_c}{2t} = \frac{1}{dc} \int_{c_1}^{c_2} x(dc), \quad \text{or} \quad \frac{\text{Area} \ (E)}{2t} \left( \frac{dc}{dx} \right)
\]

Where area = Area E, in Figure 2 in weight percent per centimeter

\[ x = \text{distance in centimeters} \]

\[ \frac{dc}{dx} = \text{tangent in weight percent per centimeter} \]

\[ t = \text{diffusion time in seconds} \]

The concentrations were used as weight percent (wt \%) for these calculations since only a small concentration difference needed to be examined. Atomic percents should be used in these calculations for larger concentration differences since the atomic percent-to-weight percent conversion is linear only for small differences. The concentration units drop out in the diffusion calculations.

The data were obtained with a microprobe analyzer and tabulated as wt \% gallium versus microns. Then the data were plotted on probability paper as concentrations \( (c - c_1/c_2 - c_1) \) versus distance (microns). Completing the best-fit curve through the data, then the curve in Figure 3 was plotted. A polynomial equation, describing concentration as a function of distance in microns for Figure 3, was then determined:

\[
\text{Concentration} = A + Bx + Cx^2 + Dx^3 + Ex^4 + Fx^5
\]

Generally, Figure 3 should be divided into three sections and three polynomial equations determined so that a better fit of the data could be obtained.

The General Electric Time-Share Basic Language library program, POLFIT***, was used to determine the best-fit polynomial equation to fifth order for each
section of Figure 3. The program uses a least-square technique to fit a polynomial equation to a set of data.

Once the equations describing the data in the three sections of Figure 3 have been determined, then the areas above the curve in Section 1 and below the curve in Section 3 are determined using the INTEG program (see Appendix A, Page 9).

The location of the Matano interface and diffusivities at various concentrations in Section 2 of Figure 3 are determined using the MATANO program (see Appendix B, Page 11). Since this program will solve only for diffusivities at concentrations within Section 2, limits of the program should be selected to include the concentrations of interest.

Sample Run:

A typical gallium concentration versus distance profile for the epsilon-phase, plutonium-gallium study is shown in Figure 4. The line describing the data in the figure was taken from the probability plot in Figure 5. The location of the three sections in Figure 4 are decided upon. Then from the best-fit curve, a tabulation of concentration versus distance is made for every 50 microns. These data are then entered into POLFIT*** to determine the three polynomial equations. A typical printout from POLFIT*** for Section 1 of Figure 4 is given in Figure 6.

The polynomial equations for the three sections of Figure 4 as determined by POLFIT*** are:

Section 1 —

Integral Limits 0 to 450 microns,

\[
C = 2.1162895104 - (8.4448951956E-5)X - (2.6655009924E-7)X^2 - (4.2951050056E-9)X^3 + (2.8251751146E-12)X^4 + (4.1025614771E-16)X^5
\]

Section 2 —

Integral Limits 450 to 1350 microns,

\[
C = 1.9379688524 + (9.9024518312E-4)X -(2.8476917195E-6)X^2 - (2.2328494909E-9)X^3 + (4.3223728579E-12)X^4 - (1.4744020852E-15)X^5
\]
FIGURE 4. A Typical Plot of Concentration versus Microns for the Epsilon-Phase, Plutonium-Gallium Study.

FIGURE 5. Data from Probability Plot Was Used in Figure 4.
Section 3 –

Integral Limits 1350 to 2250 microns,

\[ C = 10.154622027 - (2.4947225047 \times 10^{-2})X \\
+ (2.6442678606 \times 10^{-5})X^2 - (1.4579842495 \times 10^{-8})X^3 \\
+ (4.1041451624 \times 10^{-12})X^4 - (4.6574232299 \times 10^{-16})X^5 \]

The program INTEG (Appendix A) is used to determine the upper and lower areas in Sections 1 and 3 of Figure 4. Figure 7 gives the printout from this program for Section 1 of Figure 4.

The INTEG program was used to determine the lower area of Section 3 of Figure 4. The lower area was 53.315 microns per weight percent.

The MATANO program (see Appendix B) was used to determine the location of the Matano interface and diffusivities at various concentrations in Section 2 of Figure 4. A typical printout from this program is given in Figure 8.

SUMMARY

The computer technique for determining diffusion coefficients by the Boltzman-Matano analysis is much faster than doing the calculations by hand. The polynomial equation must describe the concentration-distance profile accurately or the equation will be a source of computation error using the computer technique. The major errors for the hand-calculation method occur in locating the Matano interface and determining the slope of the concentration-distance line at specific concentrations.

A listing of the programs INTEG and MATANO are given as Appendix A and B, respectively with an explanation of the variables.
RFP-1544

10 DATA 2.1162895104,-8.4448951956E-5,-2.6654009924E-7
20 DATA -4.2951050056E-9,2.8251751146E-12,4.1025614771E-16

RUN

INTEG 09:53 CSS B FRI.05/01/70

THIS PROGRAM INTEGRATES THE FOLLOWING EQUATION

\[ Y = A + B \times X + C \times X^2 + D \times X^3 + E \times X^4 + F \times X^5 \]

ENTER A-F ON DATA LINES 0-40

A = 2.11629  B = -8.4449E-5  C = -2.6654E-7
D = -4.29511E-9  E = 2.82518E-12  F = 4.10256E-16

FØR LØWER AREA ENTER ZERØ  FØR UPPER AREA ENTER 1 ? 1

ENTER UPPER CONCENTRATION ? 2.12

ENTER UPPER AND LØWER INTEGRAL LIMITS ? 450,0

UPPER AREA = 51.3536 MICRØN*W/A

FIGURE 7. A Typical Printout from the Program INTEG. The Data Inputed by the User are Underlined.

10 DATA 1.9379688524,9.9024518312E-4,-2.8476917195E-6
20 DATA -2.2328494999E-9,4.3223725799E-12,-1.474402852E-15

RUN

MATANO 10:16 CSS B FRI.05/01/70

THIS PROGRAM INTEGRATES THE FOLLOWING EQUATION AND SOLVES
FØR THE MATANO INTERFACE AND DIFFUSION COEFFICIENTS

\[ Y = A + B \times X + C \times X^2 + D \times X^3 + E \times X^4 + F \times X^5 \]

ENTER A-F ON DATA LINES 0-40

A = 1.93797  B = 9.90245E-4  C = -2.84769E-6
D = -2.23285E-9  E = 4.32237E-12  F = -1.4744E-15

FIGURE 8. A Typical Printout from the Program MATANO. The Data Inputed by the User are Underlined.
ENTER INITIAL LOWER AND UPPER AREAS? 53.315, 51.3536
ENTER LOWER AND UPPER CONCENTRATION VALUES? .14, 2.12
ENTER LOWER AND UPPER INTEGRAL LIMITS? 450, 1350

<table>
<thead>
<tr>
<th>MICRONS</th>
<th>LOWER AREA</th>
<th>UPPER AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>370.849</td>
<td>247.911</td>
</tr>
<tr>
<td>810</td>
<td>313.689</td>
<td>309.551</td>
</tr>
<tr>
<td>812.08</td>
<td>311.909</td>
<td>311.732</td>
</tr>
<tr>
<td>812.089</td>
<td>311.838</td>
<td>311.819</td>
</tr>
<tr>
<td>1200</td>
<td>311.83</td>
<td>311.829</td>
</tr>
</tbody>
</table>

MATANO INTERFACE AT 812.09 MICRONS

ENTER DIFFUSION TIME IN SECONDS? 2700
TO STOP PROGRAM LET C = 999
ENTER CONCENTRATION? .45
CONCENTRATION = .44994 MICRONS = 1212.8
AREA UNDER CURVE = 88.0306 MICRON*WT %
SLOPE = -8.76727 WT %/CM
TOTAL AREA = 2.12227E-2 CM*WT %

DIFFUSION COEF = 4.48273E-7 AT .44994 WT %

ENTER CONCENTRATION? 1.64
CONCENTRATION = 1.63982 MICRONS = 514.2
AREA ABOVE CURVE = 78.4573 MICRON*WT %
SLOPE = -18.7419 WT %/CM
TOTAL AREA = 2.21498E-2 CM*WT %

DIFFUSION COEF = 2.18857E-7 AT 1.63982 WT %

--- Figure 8. (continued) ---
Appendix A. Computer Program INTEG.

INTEG  10:02  CSS B  FRI. 05/01/70

50  PRINT" THIS PROGRAM INTEGRATES THE FOLLOWING EQUATION"
60  PRINT
65  PRINT
70  PRINT"   Y = A+B*X+C*X^2+D*X^3+E*X^4+F*X^5"
75  PRINT
76  PRINT
81  PRINT
83  PRINT" ENTER A-F ON DATA LINES 0-40"
84  PRINT
100  READ A,B,C,D,E,F
102  PRINT
104  PRINT" A = " A " B = " B " C = " C
106  PRINT" D = " D " E = " E " F = " F
107  PRINT
108  PRINT
110  PRINT" FOR LOWER AREA ENTER ZERO FOR UPPER AREA ENTER 1"
111  INPUT W
112  PRINT
115  IF W = 1 THEN 140

(continued) ———

Key for INTEG

A to F are polynomial equation constants used to describe concentration (Y) as a function of microns (X).

When Z = 0 the area (A1) below the Y(X) curve is calculated from X = 0 to X = X1.

Y1 and Y2 are the lower and upper concentration values.

When Z = 1 the area (A2) below the Y(X) curve is calculated from X = 0 to X = X2.

X1 and X2 are the upper and lower integral limits.

A3 — is the area below the Y(X) curve, above the Y1 concentration, and between X1 and X2.

A4 — is the area above the Y(X) curve, below the Y2 concentration, and between X1 and X2.
120 PRINT"ENTER LOWER CONCENTRATION";
125 INPUT Y1
130 PRINT
135 G0 T0 200
140 PRINT"ENTER UPPER CONCENTRATION";
145 INPUT Y2
150 PRINT
200 LET Z = 0
210 PRINT"ENTER UPPER AND LOWER INTEGRAL LIMITS";
215 INPUT X1,X2
220 PRINT
290 LET X = X1
300 LET A2 = A*X+R/P*X+2+C/3+X+3+D/4*X+4+E/5*X+5+F/6*X+6
310 IF Z = 1 THEN 400
320 LET A1 = A2
330 LET Z = 1
340 LET X = X2
350 G0 T0 300
400 IF W = 1 THEN 500
410 LET A3 = A1-A2-Y1*(X1-X2)
430 PRINT" LOWER AREA = " A3 " MICRON*W/0"
440 G0 T0 540
490 PRINT
500 LET A4 = Y2*(X1-X2)-A1+A2
530 PRINT" UPPER AREA = " A4 " MICRON*W/0"
540 PRINT
541 PRINT
542 PRINT
999 END

Key for INTEG

A to F are polynomial equation constants used to describe concentration (Y) as a function of microns (X).

When Z = 0 the area (A1) below the Y(X) curve is calculated from X = 0 to X = X1.

Y1 and Y2 are the lower and upper concentration values.

When Z = 1 the area (A2) below the Y(X) curve is calculated from X = 0 to X = X2.

X1 and X2 are the upper and lower integral limits.

A3 — is the area below the Y(X) curve, above the Y1 concentration, and between X1 and X2.

A4 — is the area above the Y(X) curve, below the Y2 concentration, and between X1 and X2.
Appendix B. Computer Program MATANO.

MATANO  10:30 CSS B  FRI.05/01/70

50 PRINT" THIS PROGRAM INTEGRATES THE FOLLOWING EQUATION AND"
52 PRINT" SOLVES"
55 PRINT" FOR THE MATANO INTERFACE AND DIFFUSION COEFFICIENTS"
60 PRINT
65 PRINT
70 PRINT" Y = A+B*X+C*X^2+D*X^3+E*X^4+F*X^5"
75 PRINT
83 PRINT" ENTER A-F ON DATA LINES 0-40"
84 PRINT
91 PRINT
100 READ A,B,C,D,E,F
102 PRINT
104 PRINT" A = " A " B = " B " C = " C
106 PRINT" D = " D " E = " E " F = " F
107 PRINT
108 PRINT
110 PRINT" ENTER INITIAL LOWER AND UPPER AREAS";
111 INPUT A4,A5
112 PRINT
120 PRINT" ENTER LOWER AND UPPER CONCENTRATION VALUES";
125 INPUT Y1,Y2
130 PRINT
200 LET Z = 0
210 PRINT" ENTER LOWER AND UPPER INTEGRAL LIMITS";
215 INPUT X2,X1
220 LET X3 = X1
221 PRINT
222 LET I = 100
229 PRINT
230 PRINT" MICRONS LOWER AREA UPPER AREA"
231 PRINT
240 LET X = X2
250 GO TO 300
290 FOR X = X3 TO X2 STEP -1
300 LET A2 = A*X+8/2*X^2+C/3*X^3+D/4*X^4+E/5*X^5+F/6*X^6
310 IF Z = 0 THEN 340
320 IF Z = 1 THEN 360
330 IF Z = 2 THEN 400
340 LET A1 = A2
345 LET Z = 1
350 GO TO 290
360 LET A3 = A2
365 LET Z = 2
370 GO TO 290
400 LET A6 = A4+A3-A2-Y1*(X1-X)
410 LET A7 = A5+Y2*(X-X2)+A1-A2
420 IF A6>A7 THEN 510
500 NEXT X
510 IF I < .0001 THEN 600
512 PRINT X,A6,A7
(continued)
515 LET X = X + I
520 LET X3 = X
530 LET I = .1 * I
540 G0 TO 290
600 PRINT
605 LET X4 = X
610 PRINT
620 PRINT
630 PRINT "MATANO INTERFACE AT " X4 " MICRONS"
632 PRINT "-------------------"
640 PRINT
650 PRINT
670 PRINT
705 PRINT "ENTER DIFFUSION TIME IN SECONDS"
710 INPUT T
712 PRINT" ENTER CONCENTRATION"
715 INPUT C1
720 PRINT
730 IF C1 = 999 THEN 999
740 FOR X = X2 TO X1 STEP .2
745 LET C2 = A + B * X + C * X^2 + D * X^3 + E * X^4 + F * X^5
750 IF C1 > C2 THEN 760
755 NEXT X
760 LET S = B + 2 * C * X + 3 * D * X^2 + 4 * E * X^3 + 5 * F * X^4
761 IF S1 = S * 10000
780 LET A2 = A * X + B / 2 * X^2 + C / 3 * X^3 + D / 4 * X^4 + E / 5 * X^5 + F / 6 * X^6
810 LET A6 = A4 + A3 - A2 - Y1 * (X1 - X)
820 LET A7 = A5 + Y2 * (X - X2) + A1 - A2
830 PRINT" CONCENTRATION = " C2 " MICRONS = " X
840 PRINT
850 IF X < X4 THEN 890
860 PRINT" AREA UNDER CURVE = " A6 " MICRON*WT %"
870 PRINT
880 LET A8 = (A6 + (X - X4) * (C2 - Y1)) / 1E4
885 G0 TO 910
890 PRINT" AREA ABOVE CURVE = " A7 " MICRON*WT %"
900 PRINT
905 LET A8 = (A7 + (X4 - X) * (Y2 - C2)) / 1E4
910 PRINT" SLIPPE = " S1 " WT %/CM"
915 PRINT
920 PRINT" TOTAL AREA = " A8 " CM*WT %"
925 PRINT
930 LET D1 = -A8 / (S1 * 2 * T)
940 PRINT" DIFFUSION COEF = " D1 " AT " C2 " WT %"
942 PRINT" ==============="
950 PRINT
951 PRINT
960 G0 TO 910
990 PRINT" CONCENTRATION VALUE TOO LOW"
991 G0 TO 910
999 END
Key for MATANO

A to F are polynomial equation constants used to describe concentration (Y) as a function of microns (X).

A4 and A5 are the initial lower and upper areas determined from the INTEG program.

Y1 and Y2 are the lower and upper concentration values.

X1 and X2 are the upper and lower integral limits.

When Z = 0 the area (A1) below the Y(X) curve is calculated from X = 0 to X = X2.

When Z = 1 the area (A3) below the Y(X) curve is calculated from X = 0 to X = X1.

When Z = 2 the area (A2) below the Y(X) curve is calculated from X = 0 to X.

A6 is the area below the Y(X) curve, above the Y1 concentration, between X1 and X, and plus the initial lower area.

A7 is the area above the Y(X) curve, below the Y2 concentration, between X2 and X, and plus the initial upper area.

X4 is the location of the Matano interface where A6 = A7 and calculated to 0.001 microns.

C1 is the concentration at which the diffusion coefficient is of interest.

C2 is the actual concentration where the diffusion coefficient is calculated.

S is the tangent at C2 expressed in weight percent per micron.

S1 is the tangent at C2 expressed in weight percent per centimeter.

A8 is the total area shown in Figure 2 (Page 2) used in the diffusion coefficient calculation.

D1 is the diffusion coefficient.