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COMPUTER PROGRAMS FOR CALCULATION OF THERMODYNAMIC FUNCTIONS OF MIXING IN CRYSTALLINE SOLUTIONS

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COMPUTER PROGRAMS FOR CALCULATION OF THERMODYNAMIC FUNCTIONS OF MIXING IN CRYSTALLINE SOLUTIONS

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July 1972

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COMPUTER PROGRAMS FOR CALCULATION OF THERMODYNAMIC FUNCTIONS OF MIXING IN CRYSTALLINE SOLUTIONS

I. INTRODUCTION

Most of the important rock-forming minerals are crystalline solutions of two or more components. Therefore, it is necessary that mineralogists and petrologists become more familiar with the thermodynamic behavior of crystalline solutions. Unfortunately the experimental data on the silicate solutions is meagre and quantitative calculations for many important minerals are not possible at present. However, a semi-quantitative study of the data available from phase-diagrams and natural mineral assemblages may often be suitably used for a better understanding of the experimental and natural assemblages. The programs described here are useful in various calculations for the thermodynamic functions of mixing and the activity-composition relations in minerals. These programs may be particularly useful to graduate students who may want to familiarize themselves with thermodynamic behavior of solutions by computing various real or hypothetical problems. The thermodynamic equations used here are taken from Guggenheim (1952, 1967), Prigogine and Defary (1954), King (1969), and Saxena (1972).

All of the programs used by Saxena (1972) are discussed below. The equation numbers used by Saxena are given in brackets, [ ].

II. PROGRAM BETA

A. Purpose

This program may be used to solve the equation

$$\ln \psi_{1A} + \frac{zq_1}{2} \ln \left[\frac{1 + \phi_{2A}(\beta - 1)}{\phi_{1A}(\beta + 1)} \right]$$

$$= \ln \psi_{1B} + \frac{zq_1}{2} \ln \left[\frac{1 + \phi_{2B}(\beta' - 1)}{\phi_{1B}(\beta' + 1)} \right] \quad [4.18] \qquad (1)$$

where ψ_{1A} and ψ_{1B} are the mole fractions of component 1 in A and B coexisting phases, ϕ_1 and ϕ_2 are constant fractions defined by

$$\phi_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad \phi_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2}; \qquad (2)$$

and β and β' are for A and B phases, respectively, and are given by the relation

$$\beta = \{1 + 4\phi_1 \phi_2 [\exp(2W/ZRT) - 1]\}^{1/2}; \qquad (3)$$

q_1 and q_2 are constant factors and for very similar components, such as Fe^{2+} and Mg^{2+} may be taken as unity. Guggenheim (1944) considered zq_1 as the number of sites which are neighbors of a molecule of type represented by component 1.

The notations ψ_{1A} and ψ_{1B} correspond to x_A^a and x_A^B and x_{2A} and ψ_{2B} correspond to ψ_B^a and x_B^B in Saxena (1972).

B. Numerical Method

Setting $y = 2W/ZRT$, let

$$f(y) = \frac{zq_1}{2} \ln \left[\frac{(\beta'(y) + 1)(\beta(y) + 1 - 2\phi_{2A})}{(\beta(y) + 1)(\beta'(y) + 1 - 2\phi_{2B})} \right]$$

$$+ \ln \left(\frac{x_{1A}}{x_{1B}} \right) + \frac{zq_1}{2} \ln \left(\frac{\phi_{1B}}{\phi_{1A}} \right) \qquad (4)$$

Then the problem of finding y^* such that (1) is satisfied becomes the problem of finding y^* such that in (4) $f(y^*) = 0$.

The method of solution is of bounding the zero, y^*, above and below by y_1 & y_2 such that after the ith iteration

$$|y_1^{(i)} - y_2^{(i)}| = (y_1^{(0)} - y_2^{(0)})/2^i$$

where $y_1^{(0)}$ and $y_2^{(0)}$ are the initial bounds input to the program. Note: the assumption,

$$y_1^{(i)} \leqslant y^* \leqslant y_2^{(i)}$$

is equivalent to

$$f(y_1^{(i)})\, f(y_2^{(i)}) \leqslant 0; y^{*(0)}$$

has initial value

$$(y_1^{(0)} + y_2^{(0)})/2.$$

At each iteration $f(y^{*(i)})$ is evaluated. If $|f(y^{*(i)})| < \epsilon$ (in this program $\epsilon = 10^{-4}$), then the zero is considered found with $y^* = y^{*(i)}$; else if

$$f(y_K^{(i)}) \quad f(y^{*(i)}) \leqslant 0$$

then

$$y_K^{(i+1)} = y_K^{(i)}, y_{\mathrm{mod}\,(K,2)+1}^{(i+1)} = y^{*(i)} \text{ and } y^{*(i+1)} = \frac{y_1^{(i+1)} + y_2^{(i+1)}}{2}$$

for $k = 1$ or 2, provided i does not exceed a predetermined maximum, in which case the search for the zero is considered a failure.

For each set $(z, q_1, q_2, \psi_{1A}, \psi_{1B})$ of data the program prints the following information: $z, q_1, q_2, \psi_{1A}, \psi_{1B}, y^{*(i)}, f(y^{*(i)}), i$, where $y^* = y^{*(i)}$ if zero found else $y^{*(i)}$ is the final estimate when the search failed.

There are two cases where failure can occur:

$$(1)\ f(y_1^{(0)})\, f(y_2^{(0)}) > 0;$$

that is, y_1 and y_2 did not bound y^*;

$$(2)\ y_2^{(0)} - y_1^{(0)}$$

was too large.

When either occurs additional information is printed as an aid:

$$(1)\ y^{*(i)}, f(y^{*(i)}), \beta(y^{*(i)}), \beta'(y^{*(i)}), e^{y^{*(i)}}$$

for each value i assumed.

C. Notation used in Program BETA

X1A	: x_{1A}	X2A	: x_{2A}		
X1B	: x_{1B}	X2B	: x_{2B}		
Z	: z				
Q1	: q_1	Q2	: q_2		
P1A	: ϕ_{1A}	P2A	: ϕ_{2A}		
P1B	: ϕ_{1B}	P2B	: ϕ_{2b}		
Y1	: $y_1^{(0)}$	Y2	: $y_2^{(0)}$	Y3	$= y^{*(0)}$
Y(1)	: $y_1^{(i)}$	Y(2)	: $y_2^{(i)}$	Y(3)	$= y^{*(i)}$
BETA	: $\beta(y)$	BETAP	: $\beta'(y)$		
F	: $f(y)$				
EY	: e^y				
X	: current value of $\beta(y)$				
XP	: current value of $\beta'(y)$				
FY	: current value of $f(y)$				
ITER	: i				

D. Input to and Output from Program BETA

Card 1 : column 1-5 (right-adjusted)
NX: number of pairs of (X_{1A}, X_{1B}) to be evaluated for a given z, q_1, q_2.

Card 2 : columns 1-5, 6-10, . . . , 76-80 (fixed point format) (X1A, X1B) up to 8 pairs per card. Card 2 format is repeated until the NX pairs of (X1A, X1B) are entered 8 to a card, except possibly the last.

Last Card : columns 1-5, 6-10, . . . , 21-25 (fixed point format) Z, Y1, Y2, Q1, Q2 respectively

This set of cards constitutes a case. Multiple cases are permitted, each case stacked one behind the other.

Figure 1 shows a sample set of input to program BETA while Figure 2 shows a sample set of output.

```
    6
.005 .995 .010 .990 .025 .975 .035 .965 .067 .933 .120 .880
4.0  0.0  6.0  .95  1.05
```

Figure 1. Sample Input to Program BETA

Z	X1A	X1B	Y	F(Y)	#	Q1	Q2
4.	0.005	0.995	0.55673E 01	0.38147E-05	15	0.950	1.050
4.	0.010	0.990	0.49726E 01	0.42915E-04	15	0.950	1.050
4.	0.025	0.975	0.42382E 01	-0.44823E-04	14	0.950	1.050
4.	0.035	0.965	0.39869E 01	-0.97275E-04	14	0.950	1.050
4.	0.067	0.933	0.35372E 01	0.87738E-04	14	0.950	1.050
4.	0.120	0.880	0.31802E 01	0.21935E-04	12	0.950	1.050

Figure 2. Sample Output from Program BETA

E. Listing of Program BETA

```
C          PROGRAM BETA
C          P.A.COMELLA
C          CODE 641.1
C          GODDARD SPACE FLIGHT CENTER
C          GREENBELT,MARYLAND 20771
      BETA(  EY)=SQRT(1.+4.*X1A*X2A*(EY-1.))                            00000100
      BETAP(  EY)=SQRT(1.+4.*X1B*X2B*(EY-1.))                           00000200
      F(X,XP)=ALOG((XP+1.)*(X+1.-2.*P2A)/((X+1.)*(XP+1.-2.*P2B)))*Z2    00000300
     1      +      ALOG(X1A/X1B)+ALOG(P1B/P1A)   *Z2                    00000400
      COMMON STACK(6,21),Y,FY,X,XP,EY,IT,ITER                           00000500
      INTEGER*4 OUT/6/,IN/5/                                            00000600
      REAL*4 A1(50),B1(50),Y(3),EY(3),X(3),XP(3),FY(3) ,FYP(3)          00000700
100   READ(IN,1,END=1500)NX,(A1(I),B1(I),I=1,NX)                        00000800
1     FORMAT(I5       /(16F5.0))                                        00000825
      READ(IN,5)Z,Y1,Y2,Q1,Q2                                           00000810
5     FORMAT(16F5.0)                                                    00000820
      Y3=.5*(Y1+Y2)                                                     00000815
      WRITE(OUT,3)                                                      00000850
3     FORMAT('1',T4,'Z',T13,'X1A',T22,'X1B',T40,'Y',T53,'F(Y)',T63,'#', 00000875
     1      T73,'Q1',T83,'Q2')                                          00000885
300   Z2=.5*Z *Q1                                                       00000950
      DO 1200 I=1,NX                                                    00001000
      X1A=A1(I)                                                         00001100
      X1B=B1(I)                                                         00001200
      X2A=1.-X1A                                                        00001300
      X2B=1.-X1B                                                        00001400
      P1A=X1A*Q1/(X1A*Q1+X2A*Q2)                                        00001410
      P2A=1.-P1A                                                        00001420
      P1B=X1B*Q1/(X1B*Q1+X2B*Q2)                                        00001430
      P2B=1.-P1B                                                        00001440
      ITER=1                                                            00001500
      IT=0                                                              00001505
      Y(1)=Y1                                                           00001525
      Y(2)=Y2                                                           00001550
      Y(3)=Y3                                                           00001575
      DO 500 J=1,2                                                      00001600
      EY(J)=EXP(Y(J)/Z2)                                                00001700
      X(J)=BETA(EY(J))                                                  00001800
      XP(J)=BETAP(EY(J))                                                00001900
      FY(J)=F(X(J),XP(J))                                               00002000
      IT=IT+1                                                           00002050
      CALL SAVE(J)                                                      00002100
      IF(ABS(FY(J)).LE..0001) GO TO 1000                                00002200
500   CONTINUE                                                          00002300
600   IF(ITER.LE.20) GO TO 625                                          00002350
      WRITE(OUT,4) Z,X1A,X1B,STACK                                      00002351
4     FORMAT(F4.0,5X,F6.3,5X,F6.3,T94,'NON-CONVERGENCE'/T94,'BETA',     00002352
     1      T105,'BETA-P',T114,'EXP(2Y/(Z*Q1))',T130,'ITER'/            00002353
     2      (31X,2E13.5,30X,3E13.5,I5))                                 00002354
      GO TO 1000                                                        00002355
      1   ' X=A-INVERSE*B :LEAST SQUARES COEFFICIENTS'/3D20.8)          00029250
6     FORMAT(T30,'K',T70,'M',T90,'N',T50,'LN(K)'/T20,D20.8,20X,         00032500
     1      2D20.8/T4,'J',T15,'XAB',T35,'XAA',T55,'Y',T75,              00032700
     2      'Y-CALC',T95,'R'/(I5,5D20.8))                               00032800
625   EY(3)=EXP(Y(3)/Z2)                                                00002360
      X(3)=BETA(EY(3))                                                  00002365
      XP(3)=BETAP(EY(3))                                                00002370
      FY(3)=F(X(3),XP(3))                                               00002380
      IT=IT+1                                                           00002383
      CALL SAVE(J)                                                      00002385
      J=3                                                               00002390
      IF(ABS(FY(J)).LE..0001) GO TO 1000                                00002395
      J2=2                                                              00002400
      DO 700 J1=1,2                                                     00002500
      SIGN=FY(J)*FY(J1)                                                 00002600
      IF(SIGN.GT.0.) GO TO 700                                          00002700
      Y(J2)=Y(J)                                                        00002710
      FY(J2)=FY(J)                                                      00002720
      Y(J)=.5*(Y(J)+Y(J1))                                              00002730
      ITER=ITER+1                                                       00002740
      GO TO 600                                                         00002750
700   J2=1                                                              00002760
1000  WRITE(OUT,2)Z,X1A,X1B,Y(J),FY(J),ITER,Q1,Q2                       00002770
2     FORMAT(F4.0,5X,F6.3,5X,F6.3,5X,2E13.5,5X,I5,2F10.3)               00003300
1200  CONTINUE                                                          00003400
      GO TO 100                                                         00003700
1500  RETURN                                                            00003800
      END                                                               00003900
      SUBROUTINE SAVE(J)                                                00003905
      COMMON STACK(5,21),ISTACK(21),YSTACK(3,5),IT,ITER                 00003910
      DO 100 I=1,5                                                      00003915
      STACK(I,IT)=YSTACK(J,I)                                           00003920
100   CONTINUE                                                          00003925
      ISTACK(IT)=ITER                                                   00003930
      RETURN                                                            00003935
      END                                                               00003940
                                                                           0086 CARDS
```

III. PROGRAM GEGIGM

A. Purpose

Program GEGIGM calculates the free energy of mixing, activity coefficients, ideal free energy of mixing and excess free energy of mixing in binary solutions.

B. Numerical Method

The program computes the various thermodynamic functions by using the following equations:

$$RT\ \ln f_A = X_B^2\ [A_0 + A_1 (3X_A - X_B) + A_2 (X_A - X_B)(5X_A - X_B)] \qquad [1.48]$$

$$RT\ \ln f_B = X_A^2\ [A_0 - A_1 (3X_B - X_A) + A_2 (X_B - X_A)(5X_B - X_A)] \qquad [1.49]$$

$$G_{EM} = X_A X_B\ [A_0 + A_1 (X_A - X_B) + A_2 (X_A - X_B)^2] \qquad [1.53]$$

$$G_{IM} = RT\ [X_A \ln X_A + X_B \ln X_B]$$

$$G_M = G_{IM} + G_{EM}$$

where f is the activity coefficient, G_{EM} excess free energy of mixing, G_{IM} ideal free energy of mixing and G_M is the total free energy of mixing.

C. Notation used in Program GEGIGM

AO	: A_0	A1	: A_1	A2	: A_2
XA	: X_A	XB	: X_B		
GAL	: $\ln f_A$	GA	: f_A	GAXA	: $f_A X_A$
GBL	: $\ln f_B$	GB	: f_B	GBXB	: $f_B X_B$
GE	: G_{EM}	GI	: G_{IM}	GM	: G_M
T	: T	R	: R		

D. Input to and Output from Program GEGIGM

Card 1 : Columns 1-7, 8-14, 15-21, 22-28, 29-35 (fixed-point format) T, A0, A1, A2, R, respectively

Card 2 : Columns 1-5
NX: number of observations of XA on which to perform the calculations. $1 \leqslant NX \leqslant 50$.

Card 3 : Columns 1-5, 6-10,. . . . , 66-70 (fixed-point format)
XA: up to 14 per card. Card 3 format is repeated until the NX observations are entered, 14 to a card, except for possibly the last card.

These cards constitute a case. Multiple case are permitted, each case stacked one behind the other.

For each case the following information is printed:

1. T, R, A0, A1, A2

2. for each observation:
   XA, XB, GA, GB, GE, GAXA, GBXB, GM

3. Plots: GAXA vs. XA
   GBXB vs. XB
   GE vs. XA
   GM vs. XA.

Figure 3 shows a sample set of input to GEGIGM while Figure 4 shows a sample set of output.

```
1273.      890.0      -2177.     0.00       1.987
   19
0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60 0.65 0.70
0.75 0.80 0.85 0.90 0.95
```

Figure 3. Sample Input Data for Program GEGIGM

T=1273. A0= 890. A1= -2177 A2= 0. R=1.9870

XA	XB	GAMMA-A	GAMMA-B	GE	GAMMA(A)*XA	GAMMA(B)*XB	GM
.050	0.950	2.557	1.007	135.342	0.128	0.957	-366.792
.100	0.900	2.020	1.026	236.844	0.202	0.924	-585.437
.150	0.850	1.654	1.056	307.772	0.248	0.898	-761.449
.200	0.800	1.398	1.094	351.392	0.280	0.875	-914.351
.250	0.750	1.219	1.138	370.969	0.305	0.854	-1051.430
.300	0.700	1.092	1.187	369.768	0.328	0.831	-1175.383
.350	0.650	1.003	1.236	351.055	0.351	0.803	-1286.628
.400	0.600	0.942	1.283	318.096	0.377	0.770	-1384.253
.450	0.550	0.903	1.324	274.156	0.406	0.728	-1466.457
.500	0.500	0.881	1.354	222.500	0.440	0.677	-1530.781
.550	0.450	0.871	1.370	166.394	0.479	0.616	-1574.218
.600	0.400	0.872	1.367	109.104	0.523	0.547	-1593.245
.650	0.350	0.882	1.342	53.895	0.573	0.470	-1583.789
.700	0.300	0.898	1.293	4.032	0.628	0.388	-1541.118
.750	0.250	0.918	1.219	-37.219	0.688	0.305	-1459.617
.800	0.200	0.940	1.122	-66.592	0.752	0.224	-1332.334
.850	0.150	0.962	1.005	-80.822	0.818	0.151	-1150.043
.900	0.100	0.981	0.875	-76.644	0.883	0.088	-898.925
.950	0.050	0.995	0.738	-50.792	0.945	0.037	-552.926

Figure 4a

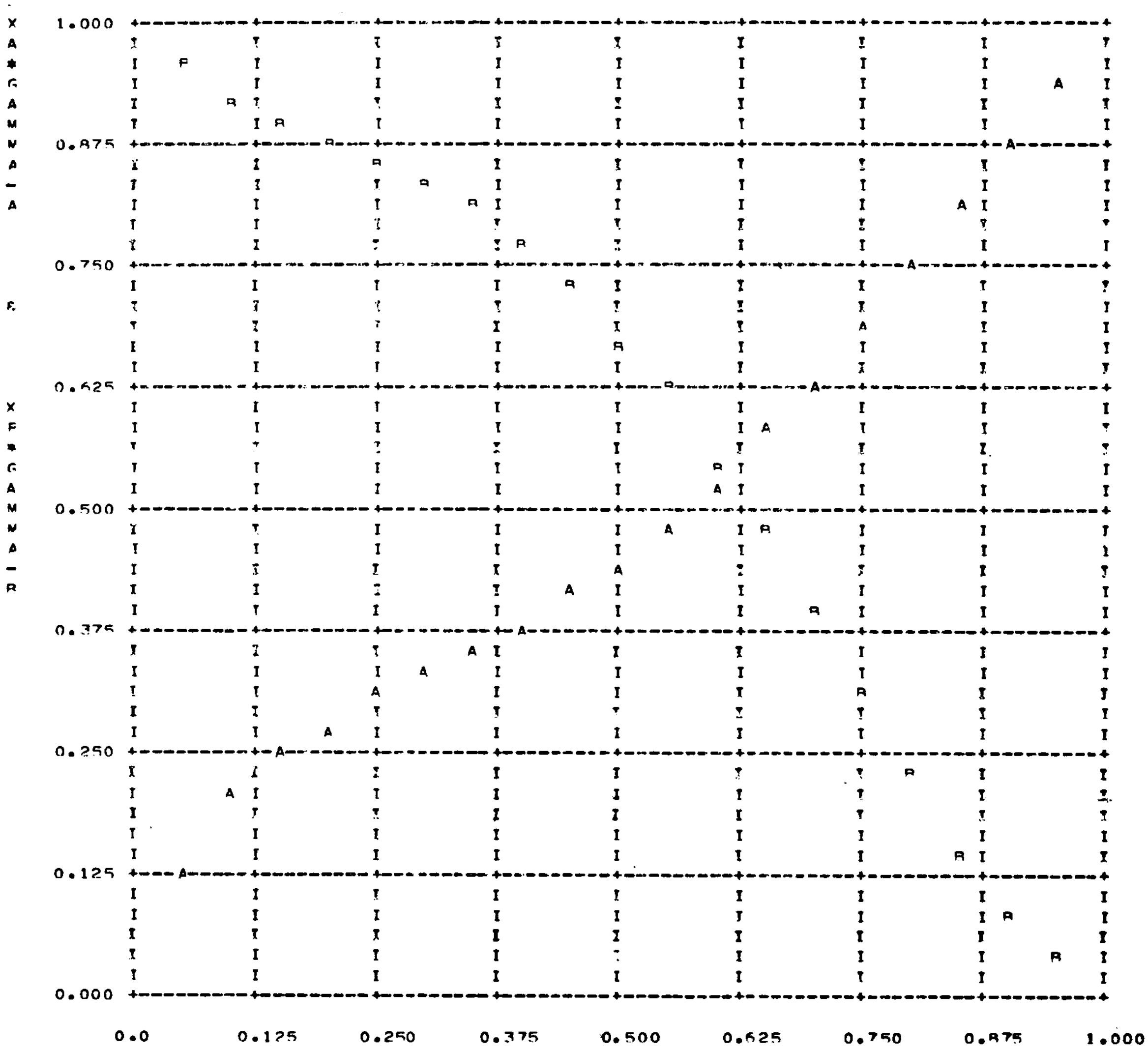

XA*GAMMA-A
&
XB*GAMMA-B
1.000
0.875
0.750
0.625
0.500
0.375
0.250
0.125
0.000
0.0
0.125
0.250
0.375
0.500
0.625
0.750
0.875
1.000

Figure 4b

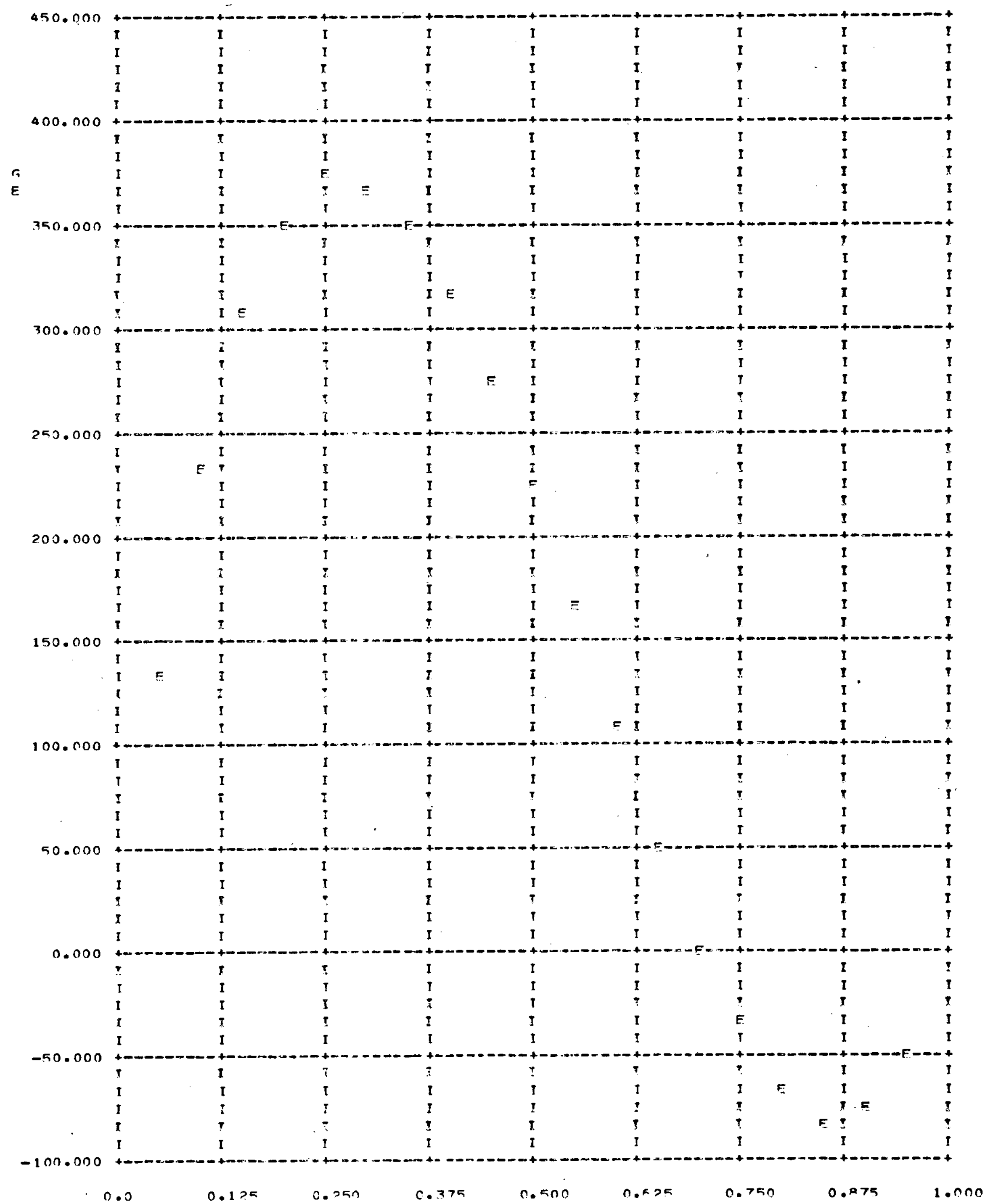

450.000
400.000
350.000
300.000
250.000
200.000
150.000
100.000
50.000
0.000
-50.000
-100.000
G
E
0.0
0.125
0.250
0.375
0.500
0.625
0.750
0.875
1.000

Figure 4c

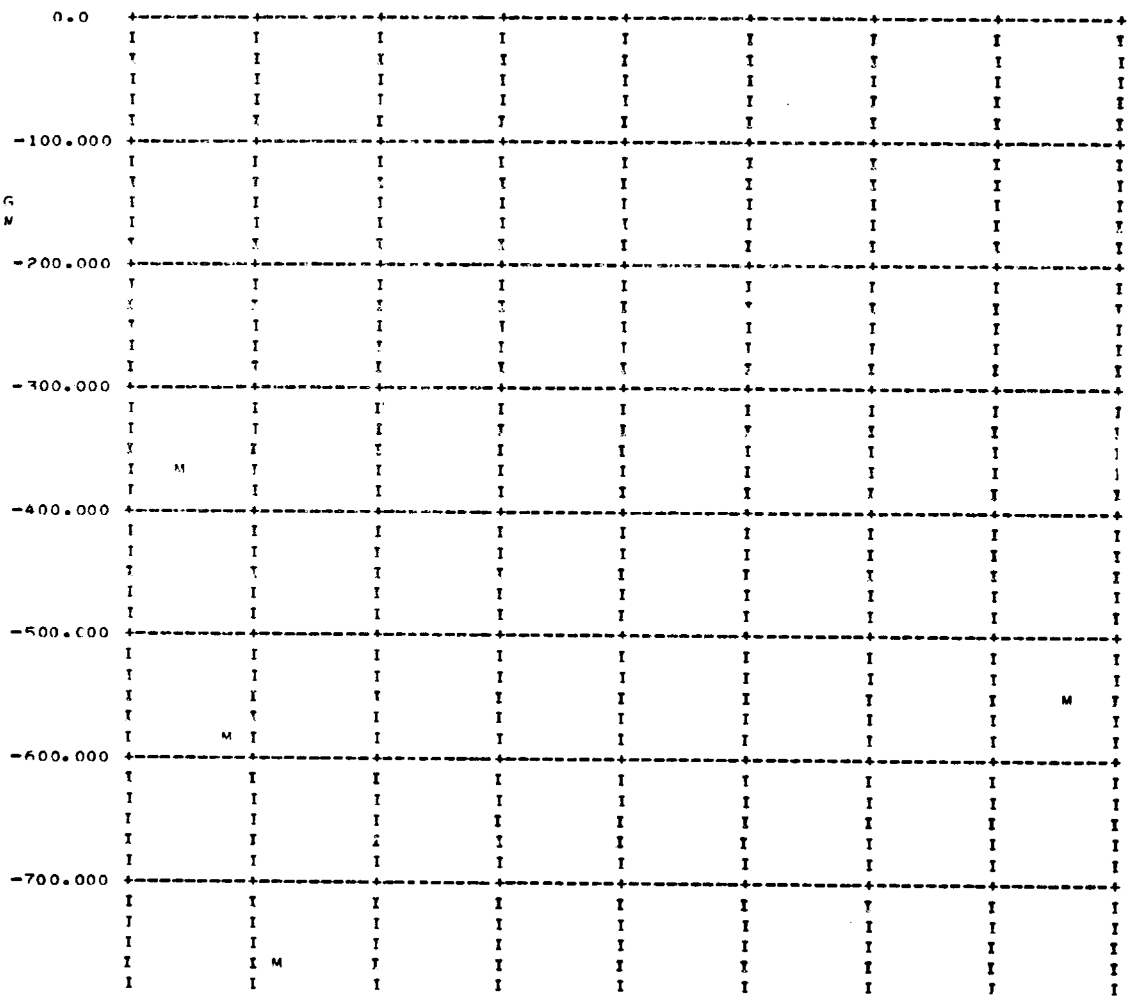


Figure 4d

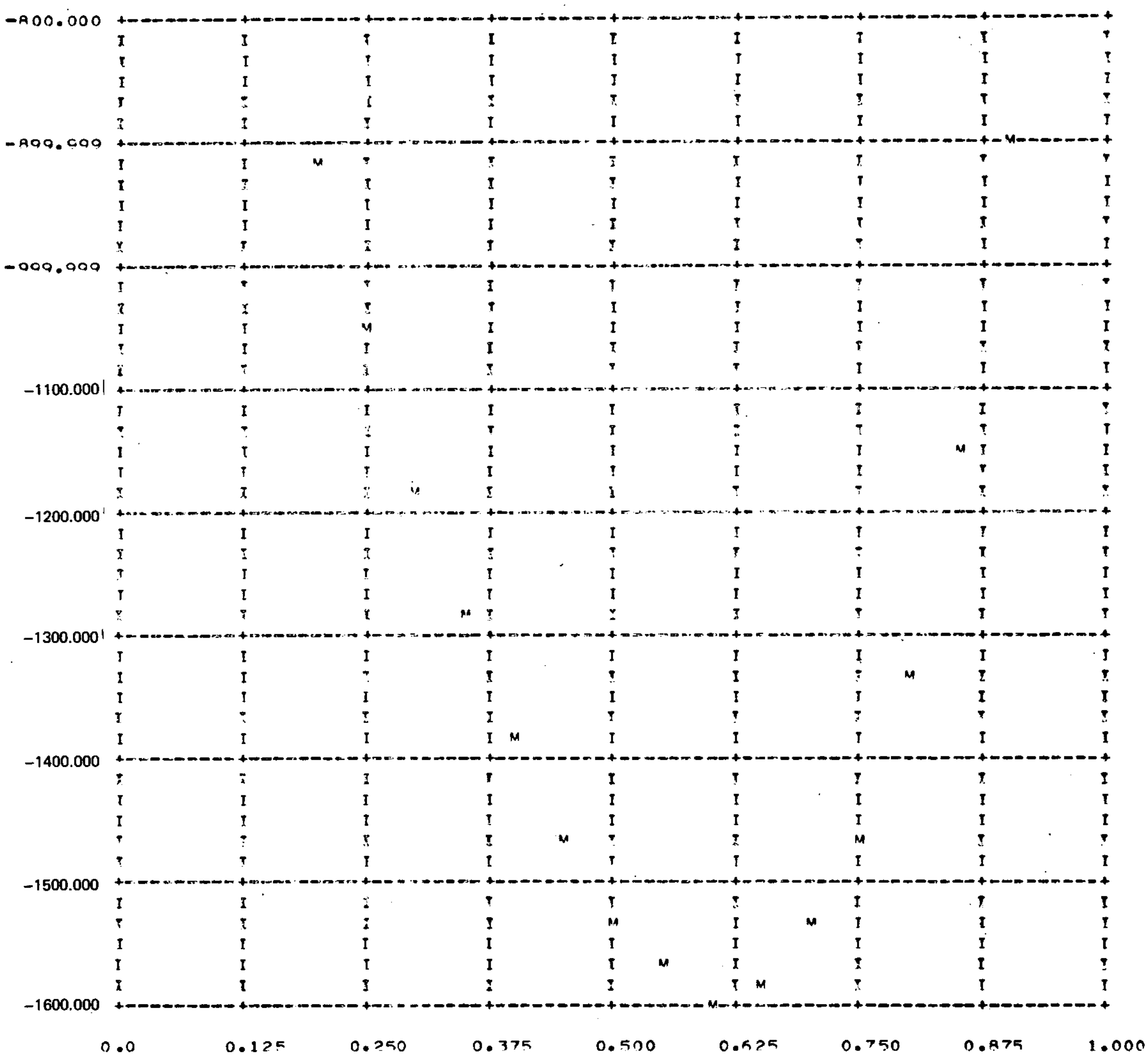


Figure 4d (Continued)

E. Listing of Program GEGIGM

```
C
C          PROGRAM GEGIGM
C          P.A.COMELLA
C          CODE 641.1
C          GODDARD SPACE FLIGHT CENTER
C          GREENBELT,MARYLAND 20771
C
      REAL*4 XA(50),XB(50),GE(50),GA(50),GB(50),GAXA(50),
     1       GBXB(50),GM(50)
      LOGICAL*1 GRID(161,101)
      INTEGER*4 NSCALE(5)/5*0/,NHL/8/,NSBH/6/,NVL/8/,NSBV/10/
     1       ,NHL1/11/,NHL2/16/
100   READ(5,1,END=1000) T,A0,A1,A2,R
1     FORMAT(7F10.3)
      RT=R*T
200   READ(5,2) NX,(XA(I),I=1,NX)
2     FORMAT(I5/(14F5.3))
      DO 300 I=1,NX
      XB(I)=1.-XA(I)
      GAL=XB(I)*XB(I)*(A0+A1*(3.*XA(I)-XB(I))+A2*(XA(I)-XB(I))
     1       *(5.*XA(I)-XB(I))))/RT
      GA(I)=EXP(GAL)
      GAXA(I)=GA(I)*XA(I)
      GBL=XA(I)*XA(I)*(A0-A1*(3.*XB(I)-XA(I))+A2*(XB(I)-XA(I))
     1       *(5.*XB(I)-XA(I))))/RT
      GE(I)=XA(I)*XB(I)*(A0+(XA(I)-XB(I))*(A1+(XA(I)-XB(I))*A2))
      GB(I)=EXP(GBL)
      GBXB(I)=GB(I)*XB(I)
      GI=RT*(XA(I)*ALOG(XA(I))+XB(I)*ALOG(XB(I)))
      GM(I)=GI+GE(I)
300   CONTINUE
      WRITE(6,3) T,A0,A1,A2,R
3     FORMAT('1T=',F5.0,5X,'A0=',F5.0,5X,'A1=',F5.0,5X,'A2=',F5.0,
     1       5X,'R=',F6.4)
      WRITE(6,4) (XA(I),XB(I),GA(I),GB(I),GE(I),GAXA(I),GBXB(I),GM(I),
     1       I=1,NX)
4     FORMAT('  XA ',5X,'  XB ',5X,'GAMMA-A',5X,'GAMMA-B',5X,'   GE ',
     1       5X,'GAMMA(A)*XA',5X,'GAMMA(B)*XB',5X,'   GM '/
     2       (F5.3,5X,F5.3,5X,F7.3,5X,F7.3,2X,F11.3,2X,F11.3,5X,F11.3,
     3       5X,F11.3))
      CALL PLOT1(NSCALE,NHL,NSBH,NVL,NSBV)
      CALL PLOT2(GRID,1.,0.,1.,0.)
      CALL PLOT3('A',XA,GAXA,NX)
      WRITE(6,5)
5     FORMAT('1')
      CALL PLOT3('B',XA,GBXB,NX)
      WRITE(6,5)
      CALL PLOT4(29,'XA*GAMMA-A      &      XB*GAMMA-B')
      CALL PLOT1(NSCALE,NHL1,NSBH,NVL,NSBV)
      CALL PLOT2(GRID,1.,0.,450.,-100.)
      CALL PLOT3('E',XA,GE,NX)
      WRITE(6,5)
      CALL PLOT4(11,'          GE')
      CALL PLOT1(NSCALE,NHL2,NSBH,NVL,NSBV)
      CALL PLOT2(GRID,1.,0.,0.,-1600.)
      CALL PLOT3('M',XA,GM,NX)
      WRITE(6,5)
      CALL PLOT4(11,'          GM')
      GO TO 100
1000  RETURN
      END
```

IV. PROGRAM REGSOL1

A. Purpose

This program may be used to analyze the distribution of a component between two binary crystalline solutions which are now assumed to be "simple mixtures" (Guggenheim, 1967).

B. Numerical Method

The relation between X_A^α, X_A^β, ω^α , ω^β , and k is given by

$$\ln \frac{X_A^\beta (1 - X_A^\alpha)}{(1 - X_A^\beta)(X_A^\alpha)} = \ln K + \frac{W^\alpha}{RT}(1 - 2X_A^\alpha) - \frac{W^\beta}{RT}(1 - 2X_A^\beta) \qquad (5)$$

[3.8]

where X's are mole fractions of A and B in α and β, W's are "interchange" energies and k, the equilibrium constant.

Given (5) and a set of NX observations $(X_{Ai}^\alpha, X_{Ai}^\beta)$, i = 1, 2, . . . , NX, the problem is to find the best estimates for

$$k, \frac{W^\alpha}{RT}, \text{and} \frac{W^\beta}{RT},$$

according to the method of least squares. Let

$$M = \frac{W^\alpha}{RT}, N = W^\beta/RT, X_1 = 1,$$

$$X_2 = 1 - 2X_A^\alpha, X_3 = 1 - 2X_A^\beta$$

$$Y = \ln\left[\frac{(1 - X_A^\alpha)}{X_A^\alpha} \cdot \frac{X_A^\beta}{(1 - X_A^\beta)}\right]$$

$$k' = \ln(k)$$

(5) can be rewritten as

$$y = k'X_1 + NX_2 - MX_3 \qquad (6)$$

The set of original observations $(X_{Ai}^\alpha, X_{Ai}^\beta)$ are now transformed into the sequence of observations $(X_{1i}, X_{2i}, X_{3i}, Y_i)$, i = 1, 2, . . . , NX which can be used in (6) to obtain the coefficients, k', N, M, in the same way as outlined in PROGRAM MATRIX.

C. Notation used in Program REGSOL1

XAA	:	X_A^α
XAB	:	X_A^β
XAA2	:	X_2
XAB2	:	X_3
K0	:	k'
M0	:	M
N0	:	N
CAY	:	k
Y	:	y
YEST	:	y as calculated using the least squares coefficients, k', M, N
R	:	y estimate - y
KCALC	:	k - calculated from (6) holding M, N constant
RK	:	R calculated - k
CHISQ	:	$\sum_{1}^{NX} R^2/Y$
KCHI	:	$\sum_{1}^{NX} RK^2/k$

D. Input to and Output from the Program REGSOL1

Card 1 : column 1-5 (right-adjusted) NX: numbers of pairs (X_A^α, X_B^α)

Card 2 : columns 1-10, 11-20, . . . , 71-80 (X_A^α, X_B^α) up to 4 pairs per card. Card 2 format is repeated until the NX pairs (X_A^α, X_B^α) are entered 4 to a card, except possibly the last.

These cards constitute a case. Multiple cases are permitted, each case stacked one behind the other.

For each case the following information is printed;

(1) The least squares matrix, A, by column,

(2) The B vector (the solution $X = A^{-1} B$).

(3) A^{-1}, X which contains the least squares coefficients.

(4) CAY, K0, M0, N0, (J, XAB(J), XAA(J), y(J), YEST(J), R(J), J = 1, NX).

(5) CHISQ.

(6) (J, CAY, KCALC(J), RK(J), J = 1, NX).

(7) KCHI.

Figure 5 shows a sample set of input to REGSOL1 while Figure 6 shows a sample set of output.

```
    9
0.021     0.341     0.070     0.692     0.094     0.815     0.136     0.864
0.258     0.902     0.341     0.899     0.533     0.907     0.033     0.475
0.029     0.539
```

Figure 5. Sample Input to Program REGSOL1

```
A-MATRIX (BY COLUMN):LEAST SQUARES MATRIX
      0.90000000D 01       0.59700000D 01      -0.38680000D 01
     -0.59700000D 01      -0.49461480D 01       0.16830920D 01
     -0.38680000D 01      -0.16830920D 01       0.31298640D 01
B-VECTOR
     -0.29237103D 02      -0.20570702D 02       0.12116246D 02

A-INVERSE (BY COLUMN)
      0.21041566D 01       0.20254862D 01       0.15111833D 01
     -0.20254862D 01      -0.21972169D 01      -0.13216109D 01
      0.15111833D 01       0.13216109D 01       0.14763786D 01
=A-INVERSE*B :LEAST SQUARES COEFFICIENTS
     -0.15408793D 01       0.19945518D 01       0.89496261D 00


Y=LN(XAB*(1-XAA)/(XAA*(1-XAB))
Y-CALC=LN(K)-M* (1-2*XAB)+N*(1-2*XAA)
R=YEST-Y
                                    K                     LN(K)                    M                      N
                            0.21419268D 00        -0.15408793D 01          0.19945518D 01         0.89496261D 00
   J          XAB                   XAA                     Y                     Y-CALC                    R
   1      0.21000000D-01       0.34100000D 00       -0.31831681D 01        -0.31570618D 01        0.16106388D-01
   2      0.70000000D-01       0.69200000D 00       -0.33961755D 01        -0.35998594D 01       -0.20368392D 00
   3      0.94000000D-01       0.81500000D 00       -0.37485768D 01        -0.37242818D 01        0.24295052D-01
   4      0.13600000D 00       0.86400000D 00       -0.36973358D 01        -0.36444457D 01        0.53390018D-01
   5      0.25800000D 00       0.90200000D 00       -0.32760367D 01        -0.32257923D 01        0.50244423D-01
   6      0.34100000D 00       0.89900000D 00       -0.28450036D 01        -0.28393269D 01       -0.44323333D-01
   7      0.53300000D 00       0.90700000D 00       -0.21453508D 01        -0.21377384D 01        0.76123585D-02
   8      0.33000000D-01       0.47500000D 00       -0.32776075D 01        -0.33590425D 01       -0.81435022D-01
   9      0.29000000D-01       0.53900000D 00       -0.36673482D 01        -0.34895541D 01        0.17779404D 00
CHISQ=SUMMATION(    R**2/Y     )=      -0.25356616D-01

K-CALC=(EXP(M0*XAB2)/EXP(N0*XAA2))*YEXP
RK=K-CALC    -    K0
   J                                                  K0                  K-CALC                                    RK
   1                                            0.21419268D 00       0.21077045D 00                          -0.34222366D-02
   2                                            0.21419268D 00       0.26258108D 00                           0.48388400D-01
   3                                            0.21419268D 00       0.20905157D 00                          -0.51411176D-02
   4                                            0.21419268D 00       0.20305685D 00                          -0.11135835D-01
   5                                            0.21419268D 00       0.20369659D 00                          -0.10496095D-01
   6                                            0.21419268D 00       0.22389996D 00                           0.97072738D-02
   7                                            0.21419268D 00       0.21256836D 00                          -0.16243212D-02
   8                                            0.21419268D 00       0.23236537D 00                           0.18172691D-01
   9                                            0.21419268D 00       0.17930387D 00                          -0.34888814D-01
CHISQ=SUMMATION(RK**2/K0)=       0.19879766D-01
```

Figure 6. Sample Output from Program REGSOL2

E. Listing of Program REGSOL1

```
C         PROGRAM:REGSOL1
C         P.A.COMELLA
C         CODE 641.1
C         GODDARD SPACE FLIGHT CENTER
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 K(10),M(10),N(10),XAA(100),XAB(100),XAA2(100),
     1     XAAQ(100),XAB2(100),XABQ(100),XABA(100),Y(100),
     2  YEST(100)    ,KO,MO,NO,R(100),A(3,3),B(3) ,YEXP(100)
     4     ,KCALC(100),RK(100),KCHI
      COMMON KO,MO,NO,XAB,XAA,XAB2,XAA2,NX
      IOUT=6
      IN=5
C         INPUT
200   READ(IN,2,END=1600) NX,(XAB(I),XAA(I),I=1,NX)
2     FORMAT( I5/(8F10.3))
      DO 300 I=1,NX
      XAA2(I)=1.D0-2.D0*XAA(I)
      XAAQ(I)=XAA2(I)*XAA2(I)
      XAB2(I)=1.D0-2.D0*XAB(I)
      XABQ(I)=XAB2(I)*XAB2(I)
      XABA(I)=XAB2(I)*XAA2(I)
      YEXP(I)= ((XAB(I)*(1.D0-XAA(I)))/(XAA(I)*(1.D0-XAB(I))))
      Y(I)=DLOG(YEXP(I))
300   CONTINUE
      JGO=1
      WRITE(IOUT,3)
3     FORMAT('1      PROGRAM REGSOL1')
      DO 600 IM=1,3
      B(IM)=0.D0
      DO 600 JM=IM,3
600   A(IM,JM)=0.D0
      DO 700 I=1,NX
      A(1,2)=A(1,2)+XAB2(I)
      A(1,3)=A(1,3)+XAA2(I)
      A(2,2)=A(2,2)+XABQ(I)
      A(2,3)=A(2,3)+XABA(I)
      A(3,3)=A(3,3)+XAAQ(I)
      B(1)=B(1)+Y(I)
      B(2)=B(2)+Y(I)*XAB2(I)
      B(3)=B(3)+XAA2(I)*Y(I)
700   CONTINUE
      A(1,1)=NX
      A(2,1)=A(1,2)
      A(1,2)=-A(1,2)
      A(2,2)=-A(2,2)
      A(3,1)=A(1,3)
      A(3,2)=-A(2,3)
      WRITE(IOUT,7) A,B
7     FORMAT('0A-MATRIX (BY COLUMN):LEAST SQUARES MATRIX'/3D20.8/3D20.8/
     1     3D20.8/' B-VECTOR'/3D20.8)
      CALL MATINV(A,3,B,1,DETERM)
      WRITE(IOUT,1) A,B
1     FORMAT('0A-INVERSE (BY COLUMN)'/3D20.8/3D20.8/3D20.8/
      KO=B(1)
      MO=B(2)
      NO=B(3)
      CAY=DEXP(KO)
      CHISQ=0.D0
      KCHI=0.D0
      DO 800 J=1,NX
```

```
      YEST(J)     = KO-MO*XAB2(J)+NO*XAA2(J)                            00030000
      R(J)=YEST(J)     -Y(J)                                            00030100
      CHISQ=    R(J)**2/    Y(J)+CHISQ                                  00030400
      KCALC(J)=DEXP(MO*XAB2(J)-NO*XAA2(J))*YEXP(J)                      00030410
      RK(J)=KCALC(J)-CAY                                                00030420
      KCHI=KCHI+RK(J)**2/CAY                                            00030430
800   CONTINUE                                                          00030500
       WRITE(IOUT,10)                                                   00030600
10     FORMAT(////' Y=LN(XAB*(1-XAA)/(XAA*(1-XAB))'/' Y-CALC=LN(K)-M*'  00030700
     1  T18,'(1-2*XAB)+N*(1-2*XAA)'/' R=YEST-Y')                        00030800
850   WRITE(IOUT,6)                        CAY,KO,MO,NO,(J,XAB(J),      00031000
     1     XAA(J),Y(J),YEST(J),R(J),J=1,NX)                             00031100
      WRITE(IOUT,9) CHISQ                                               00031900
9     FORMAT(' CHISQ=SUMMATION(    R**2/Y     )=',D20.8)                00032000
      WRITE(IOUT,11)(J,CAY,KCALC(J),RK(J),J=1,NX)                       00032010
11    FORMAT(/' K-CALC=(EXP(MO*XAB2)/EXP(NO*XAA2))*YEXP'/               00032020
     1     ' RK=K-CALC    -    KO'/                                     00032030
     2     T4,'J',T55,'KO',T75,'K-CALC',T115,'RK'/                      00032040
     3     (I5,40X,2D20.8,20X,D20.8))                                   00032050
      WRITE(IOUT,12) KCHI                                               00032060
12    FORMAT(' CHISQ=SUMMATION(RK**2/KO)=',D20.8)                       00032070
1000  CONTINUE                                                          00032300
1200  CONTINUE                                                          00032400
1500  CONTINUE                                                          00033000
      GO TO  200                                                        00033100
1600   RETURN                                                           00033200
      END                                                               00033300
      SUBROUTINE MATINV(A,N,B,M,DETERM)                                 00009700
C         MATINV IS A VERSION OF THE SHARE SUBROUTINE OF THE SAME NAME.
      IMPLICIT REAL*8 (A-H,O-Z)                                         00009800
      REAL*8 A(N,N),B(N,M),PIVOT(10)                                    00009900
      INTEGER*4 IPIVOT(10),INDEX(10,2)                                  00010000
      EQUIVALENCE (IROW,JROW),(ICOLUM,JCOLUM),(AMAX,T,SWAP)             00010100
      DETERM=1.D0                                                       00010200
      DO 20 J=1,N                                                       00010300
20    IPIVOT(J)=0                                                       00010400
      DO 550 I=1,N                                                      00010500
      AMAX=0.D0                                                         00010600
      DO 105 J=1,N                                                      00010700
      IF(IPIVOT(J).EQ.1) GO TO 105                                      00010800
      DO 100 K=1,N                                                      00010900
      IF(IPIVOT(K)-1) 80,100,740                                        00011000
80    IF(DABS(AMAX).GE.DABS(A(J,K))) GO TO 100                          00011100
      IROW=J                                                            00011200
       ICOLUM=K                                                         00011300
      AMAX=A(J,K)                                                       00011400
100   CONTINUE                                                          00011500
105   CONTINUE                                                          00011600
      IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1                                   00011700
      IF(IROW.EQ.ICOLUM) GO TO 260                                      00011800
      DETERM=-DETERM                                                    00011900
      DO 200 L=1,N                                                      00012000
      SWAP=A(IROW,L)                                                    00012100
      A(IROW,L)=A(ICOLUM,L)                                             00012200
200   A(ICOLUM,L)=SWAP                                                  00012300
      IF(M.LE.0) GO TO 260                                              00012400
      DO 250 L=1,M                                                      00012500
      SWAP=B(IROW,L)                                                    00012600
      B(IROW,L)=SWAP                                                    00012700
250   B(ICOLUM,L)=SWAP                                                  00012800
```

```
 260  INDEX(I,1)=IROW
      INDEX(I,2)=ICOLUM
      PIVOT(I)=A(ICOLUM,ICOLUM)
      DETERM=DETERM*PIVOT(I)
       A(ICOLUM,ICOLUM)=1.D0
      DO 350 L=1,N
 350  A(ICOLUM,L)=A(ICOLUM,L)/PIVOT(I)
      IF(M.LE.0) GO TO 380
      DO 370 L=1,M
      B(ICOLUM,L)=B(ICOLUM,L)/PIVOT(I)
 370  CONTINUE
 380  DO 550 L1=1,N
      IF(L1.EQ.ICOLUM) GO TO 550
      T=A(L1,ICOLUM)
      A(L1,ICOLUM)=0.D0
      DO 450 L=1,N
 450  A(L1,L)=A(L1,L)-A(ICOLUM,L)*T
      IF(M.LE.0) GO TO 550
      DO 500 L=1,M
 500  B(L1,L)=B(L1,L)-B(ICOLUM.L)*T
 550  CONTINUE
      DO 710 I=1,N
      L=N+1-I
      IF(INDEX(L,1).EQ.INDEX(L,2)) GO TO 710
      JROW=INDEX(L,1)
      JCOLUM=INDEX(L,2)
      DO 705 K=1,N
      SWAP=A(K,JROW)
      A(K,JROW)=A(K,JCOLUM)
      A(K,JCOLUM)=SWAP
 705   CONTINUE
 710  CONTINUE
 740  RETURN
      END
```

V. PROGRAM REGSOL2

A. Purpose

If the data on K, W^{α}, /RT, W^{β} /RT are available, we may calculate X_A^{α} or X_A^{β}, (given one or the other) in (5) and plot these on a Roozeboom figure. This provides us with a distribution curve or isotherm representing the distribution of a component between two binary solutions

B. Numerical Method

REGSOL2 assumes that in (5) K, W^{α}/RT, W^{β}/RT and X_A^{β} are given, the problem then being to find X_A^{α}. To accomplish this (5) is transformed as follows:

$$g(X_A^{\alpha}) = (1 - X_A^{\alpha}) \exp(-N(1 - 2X_A^{\alpha})) - f(X_A^{\beta}) X_A^{\alpha} \tag{7}$$

where

$$M = W^{\alpha}/RT, N = W^{\beta}/RT,$$

$$f(X_A^{\beta}) = \exp\left[\ln\left(k\frac{(1 - X_A^{\beta})}{X_A^{\beta}}\right) - M(1 - 2X_A^{\beta})\right]$$

The Newton-Raphson method is then applied to (7) with

$$X_A^{\alpha(0)} = X_A^{\beta}/(X_A^{\beta} + k(1 - X_A^{\beta}))$$

the zeroth estimate of X_A^{α}.

Each subsequent estimate is given by

$$X_A^{\alpha(i+1)} = X_A^{\alpha(i)} - \frac{g(X_A^{\alpha(i)})}{g'(X_A^{\alpha(i)})} \tag{8}$$

where

$$g'(X_A^{\alpha}) = (2N(1 - X_A^{\alpha}) - 1)\exp(-N(1 - 2X)) - f(X_A^{\beta})$$

Whenever $|g(X_A^{\alpha(i)})| < \epsilon$, ($\epsilon$ is set in the program at 10^{-4}), the zero is said to have been found. This method fails in that region of the X_A^{α} vs. X_A^{β} curve where the slope is parallel to the X_A^{α} axis.

C. Notation used in Program REGSOL2

XAB	:	X_A^β
XAAC	:	X_A^α
C	:	$f(X_A^\beta)$
K	:	K0
M	:	M0
N	:	N0
ALK	:	k - calc 6 using XAAC, XAB, M, N in (6)
R	:	K0 - ALK

D. Input to and Output from Program REGSOL2

Card 1 : column 1-10, 11-20, 21-30 (fixed point format) K0, M0, N0, respectively.

Card 2 : column 1-5 (right-adjusted) NX: number of observations X_A^β for which X_A^α is to be found.

Card 3 : columns 1-10, 11-20, . . . , 71-80 (fixed point format) X_A^β up to 8 observations per card. Card 2 format is repeated until the NX values of X_A^β are entered 8 to a card, except possibly the last card.

This set of cards constitutes a case. Multiple cases are permitted, each case stacked one behind the other.

For each observation the following output is provided if the zero has been found:

$$X_A^\beta, X_A^\alpha, k_o, \text{k-calculated}, R.$$

For the entire case a graph of X_A^α versus X_A^β is given.

When the Newton-Raphson method fails to find the zero the following information is given:

$$X_A^\beta, X_A^{\alpha(i)}, f(X_A^{\alpha(i)})$$

for each iteration i.

Figure 7 shows a sample set of input to program REGSOL2 while Figure 8 shows a sample set of output.

```
0.2823     2.0000     1.3390
  16
0.03       0.05       0.06       0.08       0.10       0.15       0.20       0.25
0.30       0.40       0.50       0.60       0.70       0.80       0.90       0.95
```

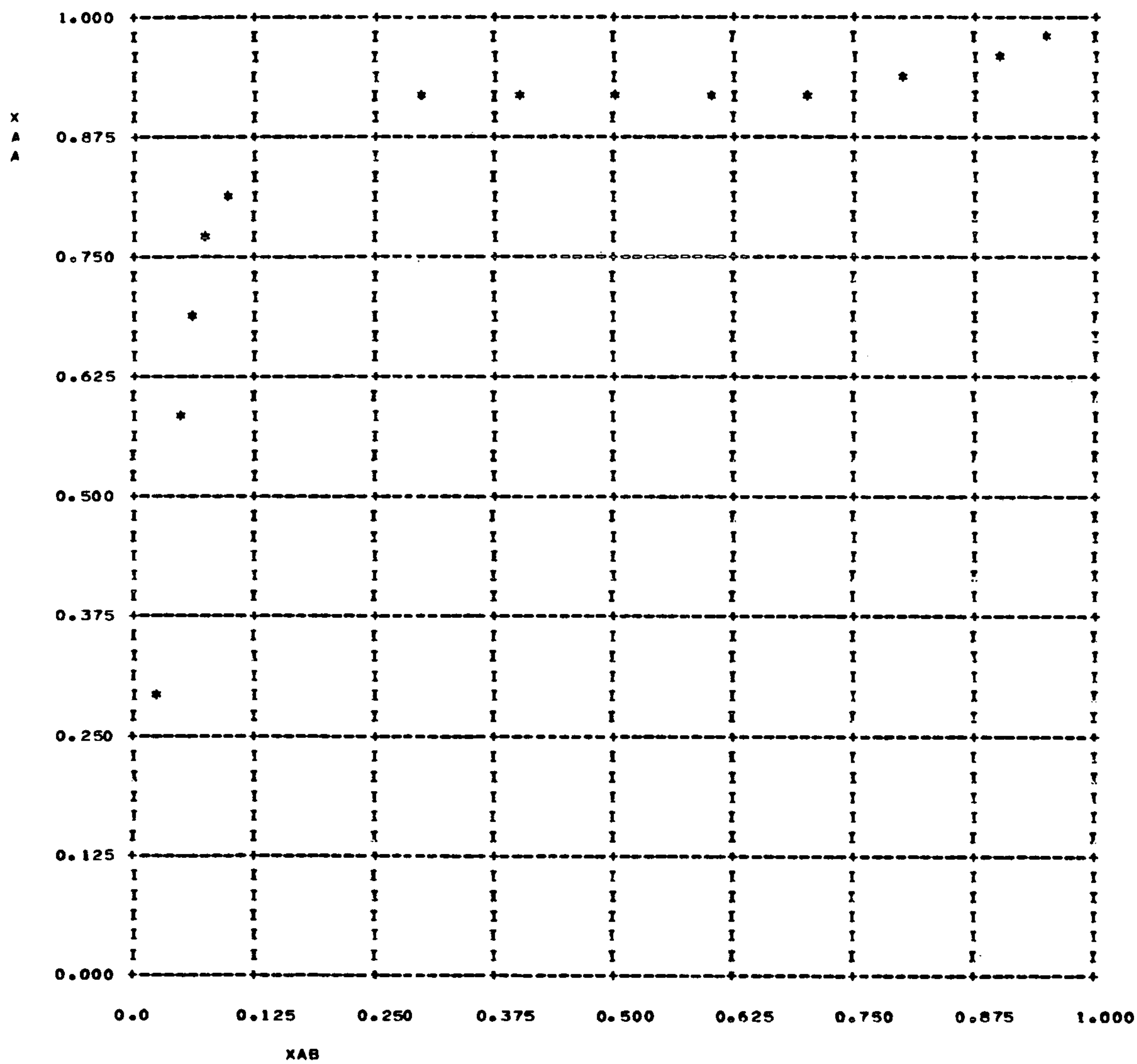
Figure 7. Sample Input to Program REGSOL2

```
FOR XAB=   0.25000E 00   ZERO WAS NOT FOUND.TRACE' OF ITERATIONS FOLLOWS:
           X                     F(X)
 0.54144782E 00   0.34369034E 00
 0.65933743E 01  -0.68313744E 08
 0.62433300E 01  -0.25080240E 08
 0.58947420E 01  -0.92051840E 07
 0.55477962E 01  -0.33774710E 07
 0.52027168E 01  -0.12387390E 07
 0.48597736E 01  -0.45410481E 06
 0.45192976E 01  -0.16636613E 06
 0.41817017E 01  -0.60902648E 05
 0.38475027E 01  -0.22272457E 05
 0.35173635E 01  -0.81342930E 04
 0.31921453E 01  -0.29654358E 04
 0.28729849E 01  -0.10783801E 04
 0.25614128E 01  -0.39076123E 03
 0.22595224E 01  -0.14085666E 03
 0.19702377E 01  -0.50367310E 02
 0.16977329E 01  -0.17775421E 02
 0.14481325E 01  -0.61282244E 01
 0.12306871E 01  -0.20158863E 01
 0.10592642E 01  -0.59501708E 00
```

Figure 8a. Sample Output from Program REGSOL2 Trace When Zero Not Found

```
        K=  0.2823E 00        M=  0.2000E 01        N=  0.1339E 01
NEWTON-RAPHSON METHOD: ITERATION #   3
   J         XAB              XAA          XAA(CALC)       K(CALC)         K(INPUT)        K-K(CALC)
   1     0.3000E-01                      0.2908E 00      0.2823E 00      0.2823E 00      0.1311E-05
   2     0.5000E-01                      0.5882E 00      0.2823E 00      0.2823E 00     -0.2980E-06
   3     0.6000E-01                      0.6809E 00      0.2822E 00      0.2823E 00      0.5084E-04
   4     0.8000E-01                      0.7757E 00      0.2823E 00      0.2823E 00      0.1848E-05
   5     0.1000E 00                      0.8220E 00      0.2823E 00      0.2823E 00      0.4292E-05
   6     0.1500E 00                      XXXX     ZERO NOT FOUND
   7     0.2000E 00                      XXXX     ZERO NOT FOUND
   8     0.2500E 00                      XXXX     ZERO NOT FOUND
   9     0.3000E 00                      0.9102E 00      0.2822E 00      0.2823E 00      0.8500E-04
  10     0.4000E 00                      0.9145E 00      0.2823E 00      0.2823E 00      0.4548E-04
  11     0.5000E 00                      0.9150E 00      0.2823E 00      0.2823E 00      0.1848E-05
  12     0.6000E 00                      0.9155E 00      0.2823E 00      0.2823E 00      0.6139E-05
  13     0.7000E 00                      0.9195E 00      0.2823E 00      0.2823E 00      0.4089E-04
  14     0.8000E 00                      0.9313E 00      0.2822E 00      0.2823E 00      0.7963E-04
  15     0.9000E 00                      0.9562E 00      0.2823E 00      0.2823E 00      0.3219E-05
  16     0.9500E 00                      0.9755E 00      0.2823E 00      0.2823E 00      0.1848E-05
```

Figure 8b. Sample Output from Program REGSOL2



KO= 0.28230E 00 MO= 0.20000E 01 NO= 0.13390E 01

Figure 8c. Sample Output from Program REGSOL2 Plot of XAA vs XAB

E. Listing of Program REGSOL2

```
C          PROGRAM REGSOL2
C          P.A.COMELLA
C          CODE 641.1
C          GODDARD SPACE FLIGHT CENTER
C          GREENBELT,MARYLAND 20771
C
      REAL*4 K,M,N
      COMMON K,M,N,X(100)    ,NX
C         INPUT
100   READ(5,2,END=1000) K,M,N
2     FORMAT(3F10.3)
      READ(5,3) NX,(X(I),I=1,NX)
3     FORMAT(I5/(8F10.3))
      CALL ESTMTE
      WRITE(6,1)
1     FORMAT('1      PROGRAM REGSOL2')
      GO TO 100
1000  RETURN
       END
      SUBROUTINE ESTMTE
      IMPLICIT REAL*4 (A-H,K-Z)
      INTEGER*4 ITER /20/,IOUT/6/,FLAG
     1  ,NSCALE(5)/5*0/,NHL/8/,NSBH/6/,NVL/8/,NSBV/10/
      REAL*4 XAAC(100),R(100),TOL/1.D-4/ ,STACK(2,20)
       COMMON KO,MO,NO ,XAB(100)     ,JX
      REAL*4 XAB2(100),RESID/0./ ,XALF/'XXXX'/
      DIMENSION XXAB(100),ALK(100)
      LOGICAL*1 GRID(5200)
      FUN(K,M,X,X2)= EXP(ALOG(K*((1.00-X)/X))-M*X2)
      GFUN(N,X)=(1.00-X)* EXP(-N*(1.00-2.00*X))-C*X
      GPF(N,X)=(2.00*N*(1.00-X)-1.00)* EXP(-N*(1.00-2.00*X))-C
      DO 500 J=1,JX
      XAB2(J)=1.00-2.00*XAB(J)
      C=FUN(KO,MO,XAB(J),XAB2(J))
      X=XAB(J)/(XAB(J)+KO*(1.-XAB(J)))
      DO 100 JTER=1,ITER
      GX=GFUN(NO,X)
      STACK(1,JTER)=X
      STACK(2,JTER)=GX
      IF(ABS(GX).LT.TOL) GO TO 200
      X=X-GX/GPF(NO,X)
100   CONTINUE
      XAAC(J)=XALF
      WRITE(IOUT,4)XAB(J),STACK
4     FORMAT('0FOR XAB=',E13.5,'  ZERO WAS NOT FOUND.TRACE'
     1     ' OF ITERATIONS FOLLOWS:'/T12,'X',T28,'F(X)'/(2E16.8))
      GO TO 500
200   XAAC(J)=X
      ALK(J)=ALOG((1.-X) *XAB(J)/((1.-XAB(J))*X))+MO*XAB2(J)
     1    -NO*(1.-2.*X)
      ALK(J)=EXP(ALK(J))
      R(J)=KO-ALK(J)
500   CONTINUE
      RESID=0.
      WRITE(IOUT,1)KO,MO,NO,JTER
1     FORMAT('1              PROGRAM REGSOL2'/
     1            T10,'K=',E12.4,T30,'M=',E12.4,T50,'N=',E12.4/
     1  ' NEWTON-RAPHSON METHOD:ITERATION #',I3/
     2          '      J',T15,'XAB',T30,'XAA',T40,'XAA(CALC)',T55,
     3'K(CALC)',T70,'K(INPUT)',T85,'K-K(CALC)')
       DO 700 J=1,JX
       IF (XAAC(J).EQ.XALF) GO TO 600
      WRITE(IOUT,7)J,XAB(J),XAAC(J),ALK(J),KO,R(J)
7     FORMAT(I5,E15.4,E30.4,3E15.4)
      GO TO 700
600   WRITE(IOUT,8)J,XAB(J),XALF
8     FORMAT(I5,E15.4,20X,A4,'     ZERO NOT FOUND')
      XAAC(J)=-1.0
700   CONTINUE
      WRITE(IOUT,3)
3     FORMAT('1')
      CALL PLOT1(NSCALE,NHL,NSBH,NVL,NSBV)
      CALL PLOT2(GRID,1.,0.,1.,0.)
      CALL PLOT3('*',XAB,XAAC,JX)
      CALL PLOT4(8,'         XAA')
      WRITE(IOUT,2)
2     FORMAT(/T25,'XAB')
      WRITE(IOUT,5) KO,MO,NO
5     FORMAT(' PROGRAM REGSOL2'/' KO=',E13.5,10X,'MO=',E13.5,10X,'NO=',
     1     E13.5)
      RETURN
      END
```

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VI. PROGRAM MATRIX

A. Purpose

This is a general program to solve an equation of the type:

$$y = a_1 x_1 + a_2 x_2 + \ldots + a_n x_n \tag{9}$$

(through the method of least squares) and, therefore, can be used for solutions of various problems. One example is in the solution of the following equation:

$$\ln K_{5a} = \ln K_D + \frac{A_o^{\alpha}}{RT}(x_A^{\alpha} - x_B^{\alpha}) + \frac{A_1^{\alpha}}{RT}(6\, x_B^{\alpha}\, x_A^{\alpha} - 1)$$

$$+ \frac{A_o^{\beta}}{RT}(x_B^{\beta} - x_A^{\beta}) + \frac{A_1^{\beta}}{RT}(6\, x_A^{\beta}\, x_B^{\beta} - 1) \qquad [5.5]$$

which is an equation representing the distribution of a component between two asymmetric binary solutions. This program may also be used in place of REGSOL1.

B. Numerical Method

To solve (9) by method of least squares for n coefficients requires m > n observations of the form ($x_{1i}, x_{2i}, \ldots, x_{ni}, y_i$) where

$$a_1 x_{1i} + \ldots + a_n x_{ni} = y_i \text{ for each } i = 1, 2, \ldots, m.$$

If A is an N x N matrix such that

$$A(i, j) = \sum_{K=1}^{m} x_{ik} x_{jk}, \quad i = 1, 2, \ldots, n, \quad y = 1, 2, \ldots, n$$

$$\text{and } B(i) = \sum_{K=1}^{m} y_k X_{ik} \quad i = 1, \ldots, n$$

then $Z = A^{-1} B$, the solution of the matrix equation $AZ = B$, is the required least squares solution of (1) with $a_i = Z_i$, $i = 1, \ldots, n$. This particular program allows $n \leqslant 10$, $m \leqslant 50$.

C. Notation used in Program MATRIX

X	:	x
Y	:	y
NCOEF	:	N
NX	:	M
A	:	A
B	:	B - before inversion of A
B	:	Z - following inversion of A
Y0	:	y - as calculated from (1)
RY	:	Y - Y0
RSUM	:	$\left(\sum_{1}^{m} RY^2\right)^{1/2}$

D. Input to and Output from Program MATRIX

Card 1 : columns 1-5, 6-10 NCOEF, NX, respectively.

Card 2 through NX + 1: columns 1-7, 8-14, . . . 71-77 X_{ki}, k = 1, . . . , NCOEF, Y_i , respectively (fixed point format).

This set of cards constitutes a case. Cases may be stacked one behind the other.

Output from each case is as follows:

(1) I, (X(K,I), K = 1, NCOEF), Y(I) I = 1, 2, . . . , N

(2) A-matrix, B-vector

(3) Determinant of A, A^{-1}, Z

(4) RSUM

(5) (Y(I), Y0(I), RY(I), I = 1, NX)

Figure 9 shows a sample set of input while Figure 10 shows a sample set of output.

3	9		
1.	0.318	0.958	-3.183
1.	-.384	.860	-3.396
1.	-.630	.812	-3.748
1.	-.728	.728	-3.697
1.	-.804	.484	-3.276
1.	-.798	.318	-2.845
1.	-.814	-.066	-2.145
1.	.050	.934	-3.278
1.	-.078	.942	-3.667

Figure 9. Sample Input to Program MATRIX


```
    X( 1,*)     X( 2,*)     X( 3,*)      Y
 1    1.000       0.318       0.958     -3.183
 2    1.000      -0.384       0.860     -3.396
 3    1.000      -0.630       0.812     -3.748
 4    1.000      -0.728       0.728     -3.697
 5    1.000      -0.804       0.484     -3.276
 6    1.000      -0.798       0.318     -2.845
 7    1.000      -0.814      -0.066     -2.145
 8    1.000       0.050       0.934     -3.278
 9    1.000      -0.078       0.942     -3.667
   A(*, 1 )    A(*, 2 )    A(*, 3 )       B
 0.9[illegible]D 01 -0.367D 01  0.597D 01 -0.292D 02
-0.337D 01  0.313D 01 -0.168D 01  0.121D 02
 0.597D 01 -0.168D 01  0.495D 01 -0.2[illegible]6D 02

A-INVERSE NOW IN A.B CONTAINS THE COEFFICIENTS AS FF:Y=B1*X1+...+B-NCOEF*X-NCOEF
DETERM=  0.6[illegible]1[illegible]9D 01
   A(*, 1 )    A(*, 2 )    A(*, 3 )       B
 0.21[illegible]D 01  0.151D 01 -0.2[illegible]3D 01 -0.154D 01
 0.151D 01  0.148D 01 -0.132D 01  0.894D 00
-0.2[illegible]3D 01 -0.132D 01  0.22[illegible]D 01 -0.199D 01

SQRT(RESIDUALS)=  0.29619D 00
     Y              YO
-0.31830D 01 -0.31671D 01 -0.15869D-01
-0.33960D 01 -0.35996D 01  0.20356D 00
-0.37480D 01 -0.37239D 01 -0.24143D-01
-0.36970D 01 -0.36440D 01 -0.52996D-01
-0.32760D 01 -0.32254D 01 -0.5[illegible]577D-01
-0.28450D 01 -0.28890D 01  0.44041D-01
-0.21450D 01 -0.21376D 01 -0.73717D-02
-0.32780D 01 -0.33596D 01  0.8[illegible]964D-01
-0.36670D 01 -0.34894D 01 -0.1776[illegible]D 00
```

Figure 10. Sample Output from Program MATRIX

E. Listing of Program MATRIX

```
C          PROGRAM MATRIX
C          P.A.COMELLA
C          CODE 641.1
C          GODDARD SPACE FLIGHT CENTER
C          GREENBELT,MARYLAND 20771
      IMPLICIT REAL*8(A-H,O-Z)
      REAL*8 A(10,10),B(10)
     1    ,X(10,50),Y(50),YO(50),RY(50)
      EQUIVALENCE (NCOEF,N)
      INTEGER*4 GAMMA(10),ALPHA(10),BETA,DELTA
      DATA GAMMA,ALPHA,BETA,DELTA/10*'  X(',10*'A(*,',' B',' Y'/
C          INPUT
100    READ(5,1,END=2000) NCOEF,NX
1     FORMAT(2I5)
      WRITE(6,8) (GAMMA(I),I,I=1,NCOEF),DELTA
8     FORMAT('1',1X,A4,I2,',*)',10(2X,A4,I2,',*)'))
      DO 200 I=1,NX
C          INPUT
      READ(5,2) (X(K,I),K=1,NCOEF),Y(I)
      WRITE(6,7)I,(X(K,I),K=1,NCOEF),Y(I)
7     FORMAT(I3,F8.3,10F11.3)
2     FORMAT(11F7.3)
200   CONTINUE
      DO 300 K=1,N
      B(K)=0.0D0
      DO 300 KP=1,N
300   A(K,KP)=0.0D0
      DO 600 K=1,N
      DO 600 I=1,NX
      DO 500 KP=1,N
500   A(KP,K)=A(KP,K)+X(KP,I)*X(K,I)
600   B(K)=B(K)+Y(I)*X(K,I)
      WRITE(6,5) (ALPHA(I),I,I=1,NCOEF),BETA
5     FORMAT(11(3X,A4,I2,' )'))
      DO 800 K=1,N
        WRITE(6,3) (A(KP,K),KP=1,N),B(K)
800   CONTINUE
3     FORMAT(11E11.3)
      CALL MATINV(A,N,B,1,DETERM)
      WRITE(6,6) DETERM
6     FORMAT('0A-INVERSE NOW IN A.B CONTAINS THE COEFFICIENTS AS FF:',
     1     'Y=B1*X1+...+B-NCOEF*X-NCOEF'/' DETERM=',E13.5)
      WRITE(6,5) (ALPHA(I),I,I=1,NCOEF),BETA
      DO 900 K=1,N
      WRITE(6,3) (A(KP,K),KP=1,N),B(K)
900   CONTINUE
      RSUM=0.0D0
      DO 1200 I=1,NX
      SUM=0.0D0
      DO 1000 K=1,N
1000  SUM=SUM+B(K)*X(K,I)
      YO(I)=SUM
      RY(I)=Y(I)-SUM
      RSUM=RSUM+RY(I)*RY(I)
1200   CONTINUE
      RSUM=DSQRT(RSUM )
      WRITE(6,4) RSUM,(Y(I),YO(I),RY(I),I=1,NX)
4     FORMAT('0SQRT(RESIDUALS)=',E13.5/'     Y           YO'/
     1     (3E13.5))
      GO TO 100
2000   RETURN
      END
      SUBROUTINE MATINV(A,N,B,M,DETERM)
C          MATINV IS A VERSION OF THE SHARE SUBROUTINE OF THE SAME NAME.
```

```
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 A(N,N),B(N,M),PIVOT(10)
      INTEGER*4 IPIVOT(10),INDEX(10,2)
      EQUIVALENCE (IROW,JROW),(ICOLUM,JCOLUM),(AMAX,T,SWAP)
      DETERM=1.D0
      DO 20 J=1,N
20    IPIVOT(J)=0
      DO 550 I=1,N
      AMAX=0.D0
      DO 105 J=1,N
      IF(IPIVOT(J).EQ.1) GO TO 105
      DO 100 K=1,N
      IF(IPIVOT(K)-1) 80,100,740
80    IF(DABS(AMAX).GE.DABS(A(J,K))) GO TO 100
      IROW=J
       ICOLUM=K
      AMAX=A(J,K)
100   CONTINUE
105   CONTINUE
      IPIVOT(ICOLUM)=IPIVOT(ICOLUM)+1
      IF(IROW.EQ.ICOLUM) GO TO 260
      DETERM=-DETERM
      DO 200 L=1,N
      SWAP=A(IROW,L)
      A(IROW,L)=A(ICOLUM,L)
200   A(ICOLUM,L)=SWAP
      IF(M.LE.0) GO TO 260
      DO 250 L=1,M
      SWAP=B(IROW,L)
      B(IROW,L)=SWAP
250   B(ICOLUM,L)=SWAP
260   INDEX(I,1)=IROW
      INDEX(I,2)=ICOLUM
      PIVOT(I)=A(ICOLUM,ICOLUM)
      DETERM=DETERM*PIVOT(I)
       A(ICOLUM,ICOLUM)=1.D0
      DO 350 L=1,N
350   A(ICOLUM,L)=A(ICOLUM,L)/PIVOT(I)
      IF(M.LE.0) GO TO 380
      DO 370 L=1,M
      B(ICOLUM,L)=B(ICOLUM,L)/PIVOT(I)
370   CONTINUE
380   DO 550 L1=1,N
      IF(L1.EQ.ICOLUM) GO TO 550
      T=A(L1,ICOLUM)
      A(L1,ICOLUM)=0.D0
      DO 450 L=1,N
450   A(L1,L)=A(L1,L)-A(ICOLUM,L)*T
      IF(M.LE.0) GO TO 550
      DO 500 L=1,M
500   B(L1,L)=B(L1,L)-B(ICOLUM,L)*T
550   CONTINUE
      DO 710 I=1,N
      L=N+1-I
      IF(INDEX(L,1).EQ.INDEX(L,2)) GO TO 710
      JROW=INDEX(L,1)
      JCOLUM=INDEX(L,2)
      DO 705 K=1,N
      SWAP=A(K,JROW)
      A(K,JROW)=A(K,JCOLUM)
      A(K,JCOLUM)=SWAP
705    CONTINUE
710   CONTINUE
740   RETURN
      END
```

VII. PROGRAM QUASI

A. Purpose

If we have data on a complete distribution isotherm, this program may be used to find 2W/ZRT for each of the two crystalline solutions assuming that they are regular solutions with the quasi-chemical approximation.

B. Numerical Method

The basic equation is

$$K = K_D \cdot \left\{\frac{1 + \phi_{1A}(\beta - 1)}{\phi_{2A}(\beta + 1)}\right\}^{\frac{Z_1 q_2}{2}} \left\{\frac{1 + \phi_{2B}(\beta' - 1)}{\phi_{1B}(\beta' + 1)}\right\}^{\frac{Z_1 q_1'}{2}} \cdot \left\{\frac{1 + \phi_{2A}(\beta - 1)}{\phi_{1A}(\beta + 1)}\right\}^{\frac{z_1 q_1}{2}} \left\{\frac{1 + \phi_{1B}(\beta' - 1)}{\phi_{2B}(\beta' + 1)}\right\}^{\frac{z_2 q_2'}{2}} \qquad (10)$$

where the symbols ϕ_{1A}, ϕ_{2A}, ϕ_{1B}, ϕ_{2B}, β, β', q_1, q_2, q_1', q_2', Z_1 and Z_2 correspond to ϕ_A^α, ϕ_B^α, ϕ_A^β, ϕ_B^β, β^α, β^β, q_A^α, q_B^α, q_A^β, q_B^β, Z^α and Z^β respectively in Saxena's equation [5.6]. Letting

$$f_{1A} = \left[\frac{1 + \phi_{2A}(\beta - 1)}{\phi_{1A}(\beta - 1)}\right]^{\frac{Zq_1}{2}}$$

$$f_{2A} = \left[\frac{1 + \phi_{1A}(\beta - 1)}{\phi_{2A}(\beta + 1)}\right]^{\frac{Zq_2}{2}}$$

$$f_{1B} = \left[\frac{1 + \phi_{2B}(\beta' - 1)}{\phi_{1B}(\beta' + 1)}\right]^{\frac{Zq_1'}{2}}$$

$$f_{2B} = \left[\frac{1 + \phi_{1B}(\beta' - 1)}{\phi_{2B}(\beta' + 1)}\right]^{\frac{Zq_2'}{2}}$$

Equation (10) may be written as

$$K = \frac{X_{1A}}{X_{2A}} \frac{X_{2B}}{X_{1B}} \frac{f_{1A}}{f_{2A}} \cdot \frac{f_{2B}}{f_{1B}}, \tag{11}$$

which is the notation used in the program. Now

$$\beta = \left\{1 + 4X_{1A} X_{2A} \left(e^{\frac{2\omega}{ZRT}} - 1\right)\right\}^{\frac{1}{2}}$$

$$\beta' = \left\{1 + 4X_{1B} X_{2B} \left(e^{\frac{2\omega'}{ZRT}} - 1\right)\right\}^{\frac{1}{2}} \tag{12}$$

The problem is to find

$$\frac{2\omega}{ZRT}, \frac{2\omega'}{ZRT}.$$

This is done by the method of non-linear least squares as outlined in the following paragraphs: Write (11)

$$f(X_{1A}, X_{1B}, k', y, y') = k' \frac{X_{2B}}{X_{1B}} \frac{f_{1A}}{f_{2A}} \cdot \frac{f_{2B}}{f_{1B}} \tag{12}$$

where

$$k' = \frac{1}{K}, y = \frac{2\omega}{ZRT}, y' = \frac{2\omega'}{ZRT}$$

Set

$$f_{obs} = X_{2A}/X_{1A},$$

$$V = f(X_{1A}, X_{1B}, k', y, y') - f_{obs} \tag{13}$$

Let

$$k' = k'_{(o)} + \Delta k'$$

$$y = y_{(o)} + \Delta y$$

$$y' = y'_{(o)} + \Delta y'$$

where $k'_{(o)}$, $y_{(o)}$, $y'_{(o)}$ are initial estimates of k', y, y'.

Then linearize (13) by doing a Taylor Series expansion about

$$(k'_{(o)}, y_{(o)}, y'_{(o)}) = (0)$$

so obtaining

$$\begin{aligned} v + f_{obs} &= f(X_{1A}, X_{1B}, k'_{(o)}, y_{(o)}, y'_{(o)}) \\ &+ \delta k' \frac{\delta f}{\delta k'}\bigg|_{(o)} + \delta y \frac{\delta f}{\delta y}\bigg|_{(o)} + \delta y' \frac{\delta f}{\delta y'}\bigg|_{(o)} \end{aligned} \tag{14}$$

and now use method of least squares to solve this equation, iterating until

$$|\delta k'|, |\delta y|, |\delta y'|$$

are less than some prescribed ϵ.

C. Notation used in Program QUASI

z_1	: Z1				
z_2	: Z2				
q_1	: Q1	q_2	: Q2		
q'_1	: Q1P	q'_2	: Q2P		
$k_{(o)}$	: KO	$y_{(o)}$	: YO	$y'_{(o)}$	: YPO

Number of observations of the pairs: (X_{1A}, X_{1B}): NX

X_{1A}	: X1A	X_{2A}	: X2A
ϕ_{1A}	: PHI1A	ϕ_{2A}	: PHI2A
ϕ_{1B}	: PHI1B	ϕ_{2B}	: PHI2B
β	: BETA	β'	: BETAP
$\frac{d\beta}{dy}$	: DBDY	$\frac{d\beta}{dy'}$	: DBDYP
f_{1A}	: F1A	f_{2A}	: F2A
f_{1B}	: F1B	f_{2B}	: F2B
$\frac{df_{1A}}{dy}$	: DF1ADY	$\frac{df_{2A}}{dy}$	: DF2ADY
$\frac{f_{1A}}{f_{2A}}$	: FA12		
$\frac{df_{1B}}{dy'}$	: DF1BDY	$\frac{df_{2B}}{dy'}$	: DF2BDY

$\frac{f_{2B}}{f_{1B}}$: FB12

$\frac{\partial f}{\partial k'}$: DFDK

$\frac{\partial f}{\partial y}$: DFDY

$\frac{\partial f}{\partial y'}$: DFDYP

$f(X_{1A}, X_{1B}, k', y, y')$: F

f_{obs} : Y

Determinant of Least Square Matrix : DET

Least square coefficients

$\delta k'$: A1 δy : A2 $\delta y'$: A3

Solution: k' : KPO
k : KP
y : YOO
y' : YPOO

D. Input to and Output from Program QUASI

Input:

Card 1 : columns 1-5, 6-10, . . . , 41-45 Z1, Z2, Q1, Q2, Q1P, Q2P, KO, YO, YPO, respectively (fixed point format).

Card 2: : columns 1-5 NX

Cards 3 & ff : columns 1-5, . . . , 76-80 $(X_{1A}^{(I)}, X_{1B}^{(I)})$, I = 1, 2, . . . , NX fixed point format, 8 pairs (X_{1A}, X_{1B}) per card until NX pairs entered with a maximum of 50 pairs.

Output from Program QUASI as follows:

(1) The input

(2) for each iteration: KP, KPO, YOO, YPOO, DET, A1, A2, A3

(3) for the final iteration

X_{1A} (input), X_{1A} (calculated), f_{1A}, f_{2A}, β (y)
X_{1B} (input), X_{1B} (calculated), f_{1B}, f_{2B}, β' (y)
RESID : Y-F

Figure 11 shows a sample set of input while Figure 12 shows a sampling of output.

```
2.0   2.0   1.0   1.0   1.0   1.0   0.15 1.5   1.0
   6
0.0210.3410.0700.6920.1110.7990.1500.8500.2620.8970.3370.902
```

Figure 11. Sample Input Data for Program QUASI

```
CONSTANTS AND INITIAL VALUES
Z1=  0.20000E 01     Z2=  0.20000E 01     Q1=  0.10000E 01     Q2=  0.10000E 01     Q1P=  0.10000E 01     Q2P=  0.10000E 01
K0=  0.15000E 00     Y0=  0.15000E 01    YP0=  0.10000E 01
```

I	X1A	X1B
1	0.021	0.341
2	0.070	0.692
3	0.111	0.799
4	0.150	0.850
5	0.262	0.897
6	0.337	0.902

```
ITERATION:  0     K0=  0.15000E 00     1/K0=  0.66667E 01      Y=  0.15000E 01      YP=  0.10000E 01
                 DET=
ITERATION:  1     K0=  0.10841E 00     1/K0=  0.92241E 01      Y=  0.11791E 01      YP=  0.61774E 00
                 DET=  0.11663E 04       A1=  0.25574E 01     A2= -0.32086E 00      A3= -0.38226E 00
ITERATION:  2     K0=  0.10761E 00     1/K0=  0.92928E 01      Y=  0.12412E 01      YP=  0.70080E 00
                 DET=  0.19199E 04       A1=  0.68787E-01     A2=  0.62034E-01      A3=  0.83056E-01
ITERATION:  3     K0=  0.10806E 00     1/K0=  0.92537E 01      Y=  0.12450E 01      YP=  0.70117E 00
                 DET=  0.23756E 04       A1= -0.39152E-01     A2=  0.37947E-02      A3=  0.37367E-03
ITERATION:  4     K0=  0.10803E 00     1/K0=  0.92563E 01      Y=  0.12446E 01      YP=  0.70100E 00
                 DET=  0.23633E 04       A1=  0.25766E-02     A2= -0.35054E-03      A3= -0.17069E-03
ITERATION:  5     K0=  0.10804E 00     1/K0=  0.92561E 01      Y=  0.12446E 01      YP=  0.70101E 00
                 DET=  0.23615E 04       A1= -0.12327E-03     A2=  0.17373E-04      A3=  0.77288E-05
ITERATION:  6     K0=  0.10804E 00     1/K0=  0.92562E 01      Y=  0.12446E 01      YP=  0.70101E 00
                 DET=  0.23569E 04       A1=  0.81758E-05     A2=  0.65433E-06      A3= -0.25030E-05
```

FINAL RESULTS

X1A-INPUT	X1A-CALC	F1A	F2A	BETA(Y)	X1B-INPUT	F1B	F2B	BETAP(YP)	RESID
0.21000E-01	0.21011E-01	0.31550E 01	0.10010E 01	0.10969E 01	0.34100E 00	0.13107E 01	0.10832E 01	0.13831E 01	-0.10975E-04
0.70000E-01	0.68511E-01	0.26420E 01	0.10093E 01	0.12820E 01	0.69200E 00	0.10689E 01	0.13476E 01	0.13660E 01	0.14887E-02
0.11100E 00	0.11393E 00	0.23503E 01	0.10210E 01	0.14056E 01	0.79900E 00	0.10314E 01	0.14966E 01	0.12855E 01	-0.29345E-02
0.15000E 00	0.15956E 00	0.21397E 01	0.10355E 01	0.15035E 01	0.85000E 00	0.10183E 01	0.15892E 01	0.12321E 01	-0.95568E-02
0.26200E 00	0.26104E 00	0.17352E 01	0.10927E 01	0.17064E 01	0.89700E 00	0.10091E 01	0.16925E 01	0.11728E 01	0.96017E-03
0.33700E 00	0.30166E 00	0.15578E 01	0.11441E 01	0.17914E 01	0.90200E 00	0.10083E 01	0.17047E 01	0.11658E 01	0.35336E-01

Figure 12. Quasi-Chemical Approximation: Equation (5.6)

E. Listing of Program QUASI

```
C
C        PROGRAM QUASI
C        QUASI CHEMICAL APPROXIMATION
C        P.A. COMELLA
C        CODE 641.1
C        GODDARD SPACE FLIGHT CENTER
C        GREENBELT,MARYLAND 20771
C
      REAL*4 K0,KP,KP0,X1A(50),X1B(50),PHI1B(50),PHI2B(50),X2B(50),
     1       X21B(50),X1AC(50),FA1(50),FA2(50),FB1(50),FB2(50),BET(50),
     2       BETP(50),FUN(50),DIFF(50),RESID(50)
     3       ,XB12(50)
      LOGICAL*1 TEST
      INTEGER*4 IN/5/,OUT/6/
      COMMON SUM1,SUM2,SUM3,SUM4,SUM5,SUM6,SUM7,SUM8,SUM9
50    READ(IN,1,END=2000)Z1,Z2,Q1,Q2,Q1P,Q2P,K0,Y0,YP0,NX,(X1A(I),X1B(I)
     1    ,I=1,NX)
1     FORMAT( 9F5.0/I5/(16F5.0))
      WRITE(OUT,3) Z1,Z2,Q1,Q2,Q1P,Q2P,K0,Y0,YP0,(I,X1A(I),
     1       X1B(I),I=1,NX)
3     FORMAT('1',10X,'QUASI-CHEMICAL APPROXIMATION:EQUATION(5.6)'/
     1       '0CONSTANTS AND INITIAL VALUES'/
     2       ' Z1=',E13.5,5X,'Z2=',E13.5,5X,'Q1=',E13.5,5X,'Q2=',
     3       E13.5,5X,'Q1P=',E13.5,5X,'Q2P=',E13.5/' K0=',E13.5,5X,'Y0=',
     3       E13.5,4X,'YP0=',E13.5/'0    I',15X,
     4       'X1A',17X,'X1B'/(I5,10X,F10.3,10X,F10.3))
      Z12=0.5*Z1
      Z22=0.5*Z2
      ZQ1=Z12*Q1
      ZQ2=Z22*Q2
      ZQP1=Z12*Q1P
      ZQP2=Z22*Q2P
      ZQ11=ZQ1-1.0
      ZQ21=ZQ2-1.0
      ZQP11=ZQP1-1.0
      ZQP21=ZQP2-1.0
      KP=1.0/K0
      KP0=KP
      Y00=Y0
      YP00=YP0
      RSUM=0.0
      TEST=.FALSE.
      INDEX=0
      WRITE(OUT,5)
5     FORMAT('-')
      WRITE(OUT,4) INDEX,K0,KP0,Y00,YP00
      INDEX=1
      DO 200 I=1,NX
      X2B(I)=1.0-X1B(I)
      PHI1B(I)=X1B(I)*Q1P/(X1B(I)*Q1P+X2B(I)*Q2P)
      PHI2B(I)=1.0-PHI1B(I)
      X21B(I)=X2B(I)/X1B(I)
      X1AC(I)=X1A(I)
      XB12(I)=2.0*X1B(I)*X2B(I)
200   CONTINUE
900   SUM1=0.0
      SUM2=0.0
      SUM3=0.0
      SUM4=0.0
      SUM5=0.0
      SUM6=0.0
      SUM7=0.0
      SUM8=0.0
      SUM9=0.0
      EY=EXP(Y00)
```

```
      EYP=EXP(YP00)
      EY1=EY-1.0
      EYP1=EYP-1.0
      DO 1000 I=1,NX
      XA1=X1A(I)
      XA2=1.0-XA1
      XA12=2.0*XA1*XA2
      BETA=SQRT(1.0+2.0*XA12*EY1)
      BP1=BETA+1.0
      BM1=BETA-1.0
      BETAP=SQRT(1.0+2.0*XB12(I)*EYP1)
      PHI1A=XA1*Q1/(XA1*Q1+XA2*Q2)
      PHI2A=1.0-PHI1A
      BPP1=BETAP+1.0
      BPM1=BETAP-1.0
      BPP1Q=BPP1*BPP1
      BP1Q=BP1*BP1
      DBDY=XA12*EY/BETA
      DBDYP=XB12(I)*EYP/BETAP
      F1A=1.0+PHI2A*BM1/(PHI1A*BP1)
      F2A=1.0+PHI1A*BM1/(PHI2A*BP1)
      F1B=1.0+PHI2B(I)*BPM1/(PHI1B(I)*BPP1)
      F2B=1.0+PHI1B(I)*BPM1/(PHI2B(I)*BPP1)
      DF1ADY=ZQ1*F1A**ZQ11*2.0*PHI2A/(PHI1A*BP1Q)*DBDY
      DF2ADY=ZQ2*F2A**ZQ21*2.0*PHI1A/(PHI2A*BP1Q)*DBDY
      F1A=F1A**ZQ1
      F2A=F2A**ZQ1
      FA12=F1A/F2A
      DF1BDY=ZQP1*F1B**ZQP11*PHI2B(I)/(PHI1B(I)*BPP1Q)*DBDYP
     1*2.0
      DF2BDY=ZQP2*F2B**ZQP21*PHI1B(I)/(PHI2B(I)*BPP1Q)*DBDYP
     1*2.0
      F1B=F1B**ZQP1
      F2B=F2B**ZQP2
      FB12=F2B/F1B
      DFDK=X21B(I)*FA12*FB12
      DFDY=KP0*X21B(I)*FB12*(F2A*DF1ADY-F1A*DF2ADY)/(F2A*F2A)
      DFDYP=KP0*X21B(I)*FA12*(F1B*DF2BDY-F2B*DF1BDY)/(F1B*F1B)
      F=KP0*DFDK
      Y=XA2/X1A (I)
      YF=Y-F
      X1AC(I)=1.0/(1.0+F)
      IF (TEST .EQ. .FALSE.) GO TO 950
      FA1(I)=F1A
      FA2(I)=F2A
      FB1(I)=F1B
      FB2(I)=F12B
      FB2(I)=F2B
      BET(I)=BETA
      BETP(I)=BETAP
      FUN(I)=F
      DIFF(I)=YF
      RESID(I)=X1A(I)-X1AC(I)
      RSUM=RSUM+RESID(I)*RESID(I)
C     GO TO 1000
950   CONTINUE
      SUM1=SUM1+DFDK*DFDK
      SUM2=SUM2+DFDK*DFDY
      SUM3=SUM3+DFDK*DFDYP
      SUM4=SUM4+DFDK*YF
      SUM5=SUM5+DFDY*DFDY
      SUM6=SUM6+DFDY*DFDYP
      SUM7=SUM7+DFDY*YF
      SUM8=SUM8+DFDYP*DFDYP
      SUM9=SUM9+DFDYP*YF
```

```
1000  CONTINUE
      IF (TEST .EQ. .TRUE.) GO TO 1100
      DET=DETERM(1,5,8,6,6)+DETERM(2,6,3,2,8)+DETERM(3,2,6,5,3)
      A1=(DETERM(4,5,8,6,6)+DETERM(7,6,3,2,8)+DETERM(9,2,6,5,3))/DET
      A2=(DETERM(1,7,8,6,9)+DETERM(2,9,3,4,8)+DETERM(3,4,6,7,3))/DET
      A3=(DETERM(1,5,9,6,7)+DETERM(2,4,6,2,9)+DETERM(3,2,7,5,4))/DET
      TEST=(ABS(A1/KPO).LT.1.E-05).AND.(ABS(A2/YOO).LT.1.E-05).AND.
     1     (ABS(A3/YPOO).LT.1.E-05).OR.INDEX.GT.10
      KPO=KPO+A1
      YOO=YOO+A2
      YPOO=YPOO+A3
      KP=1.0/KPO
      WRITE(OUT,4) INDEX,KP,KPO,
     1     YOO,YPOO,DET,A1,A2,A3
      IF(TEST.EQ..TRUE.) GO TO 900
      INDEX=INDEX+1
4     FORMAT(' ITERATION:',I3,5X,'KO=',E13.5,5X,'1/KO=',E13.5,
     1     5X,'Y=',E13.5,5X,'YP=',E13.5/18X,'DET=',E13.5,5X,
     2     '  A1=',E13.5,4X,'A2=',E13.5,5X,'A3=',E13.5)
      GO TO 900
1100  KP=1.0/KPO
      WRITE(OUT,6) (X1A(I),X1AC(I),FA1(I),FA2(I),BET(I),
     1     X1B(I),FB1(I),FB2(I),BETP(I),RESID(I),I=1,NX)
6     FORMAT('-FINAL RESULTS'/'  X1A-INPUT',4X,'X1A-CALC',8X,
     1     'F1A',8X,'F2A',6X,'BETA(Y)',3X,'X1B-INPUT',7X,
     2     'F1B',8X,'F2B',5X,'BETAP(YP)',2X,'RESID'/
     3     (10E13.5))
      GO TO 50
2000  RETURN
      END
      REAL FUNCTION DETERM*4(I,J,K,L,M)
      COMMON SUM(20)
      DETERM=SUM(I)*(SUM(J)*SUM(K)-SUM(L)*SUM(M))
      RETURN
      END
```

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