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Research and Development Report

APPLICATION OF GIBBS-DUHEM EQUATION
TO BINARY VAPOR-LIQUID EQUILIBRIUM
DATA OF METAL SYSTEMS USING
NEWTON'S INTERPOLATION FORMULAE

by

V. E. Sater and F. D. Stevenson

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August, 1965

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APPLICATION OF GIBBS-DUHEM EQUATION TO BINARY VAPOR-
LIQUID EQUILIBRIUM DATA OF METAL SYSTEMS USING
NEWTON'S INTERPOLATION FORMULAE

V. E. Sater[†] and F. D. Stevenson

ABSTRACT

Integration of the Gibbs-Duhem equation using Newton's interpolation formulae has been programmed in Fortran for both smoothed and unsmoothed activity coefficient data of binary systems, giving values of the second activity coefficient as a function of concentration. The conventional area test has also been programmed to test the thermodynamic consistency when both activity coefficients have been independently determined. The Gibbs-Duhem equation is additionally used with numerically differentiated values of the log activity coefficient-concentration curves to indicate local consistency of the data. The programs and examples of their application are included.

[†]Present address: Arizona State University, Tempe, Arizona.

INTRODUCTION

Vapor-liquid equilibrium of binary liquid metal systems is currently under study at the Ames Laboratory by the Langmuir vaporization technique. Often the vapor pressure difference between components of metal systems is sufficiently great that one component may be considered non-volatile compared to the other. Thus the activity of the volatile metal may readily be obtained from measured vaporization rates¹ while the activity of the nonvolatile metal must be evaluated from the Gibbs-Duhem equation.

In cases where vaporization of both metal components is significant, the vaporization rate of each may be obtained by using radioactive tracers or other analytical techniques. The activities of both components may then be calculated directly, and the Gibbs-Duhem equation used as a check on the thermodynamic consistency of the data. An alternative approach used by Hansen and Miller² uses the Gibbs-Duhem Equation to generate self consistent activity-concentration curves based on data for both components; the deviation of the data points from the self-consistent curves being an estimate of the reliability of the data.

The usual approach to a computer solution of the Gibbs-Duhem equation for the activity coefficient of the second component is to obtain an analytical expression relating the measured activity coefficients to composition. This technique is sometimes difficult to apply; especially, if the data are few in number, scattered, incomplete, or are otherwise not well behaved. Unfortunately, much of the activity coefficient data of liquid metal systems and particularly those resulting from vaporization studies are

somewhat scattered. Nevertheless, it is desirable to utilize the data obtained as fully as possible and to have some estimate of the thermodynamic consistency.

Three computer programs for the IBM 7074 have been prepared, to facilitate the analysis of activity coefficient data, viz.: (1) a program for calculating the activity coefficient of the second component of a binary system from smoothed data of the first, (2) a program for performing the same function for raw activity coefficient data using a segmented curve fitting technique, and (3) a program for testing the thermodynamic consistency of the data where both activity coefficients are experimentally measured and smoothed. The latter program tests the consistency by the conventional "area test" method.

GIBBS-DUHEM EQUATION

The unrestricted Gibbs-Duhem equation as expressed by Van Ness³ viz.,

$$\frac{\Delta v}{RT} dp - \frac{\Delta H}{RT^2} dT = \sum x_i d \ln \gamma_i \quad (1)$$

may be simplified for isothermal data to the following :

$$x_1 \frac{\partial \ln \gamma_1}{\partial x_1} + x_2 \frac{\partial \ln \gamma_2}{\partial x_1} = 0 \quad (2)$$

provided the volume change on mixing is small or the pressure change is small over the range of measurements. This equation is used in various forms to determine γ_2 from γ_1 vs x_1 data and also for checking the

thermodynamic consistency when both coefficients have been determined experimentally.

If the activity coefficient of one component in a binary solution is known as a function of composition, the activity coefficient of the second component can be found by integrating the Gibbs-Duhem equation as follows:

$$\begin{array}{cc} \ln \gamma_2 & \ln \gamma_1 \\ \text{at } x_1 & \text{at } x_1 \\ \int d \ln \gamma_2 & \int (x_1/x_2) d \ln \gamma_1 \\ \ln \gamma_2 & \ln \gamma_1 \\ \text{at } x_1 = 0 & \text{at } x_1 = 0 \end{array} \quad (3)$$

Two choices of reference (standard) states are in common use. The one frequently used for liquid metal systems sets the activity equal to unity for the pure component. The second is to let the ratio of the activity to mole fraction approach unity at infinite dilution. The preceding standard state is used in the computer programs described in this report. It is therefore apparent that at $x_1 = 0$ ($\ln \gamma_2 = 0$), Equation (2) becomes

$$\ln \gamma_2 = - \int \begin{array}{c} \ln \gamma_1 \\ \text{at } x_1 \\ (x_1/x_2) d \ln \gamma_1 \\ \ln \gamma_1 \\ \text{at } x_1 = 0 \end{array} \quad (4)$$

With the equation in this form, the integrand increases without limit as x_1 approaches unity making the calculation of γ_2 difficult in the dilute region.

To circumvent this problem, a new function, α , is defined⁴ by the following :

$$\alpha_1 = \ln \gamma_1 / x_2^2$$

Substitution of this function into Equation (2) and integrating by parts leads to:

$$\ln \gamma_2 = -\alpha_1 x_1 x_2 + \int_0^{x_1} \alpha_1 dx_1 \quad (5)$$

The advantage of the alpha function is that it remains finite over the entire composition range for most systems. Given smoothed values of γ_1 as a function of x_1 and values of α_1 at $x_1 = 1.0$ and 0, γ_2 may be obtained as a function of composition from Equation (5). A subprogram was prepared to calculate and plot the value of alpha as a function of concentration for the raw data. This facilitated the extrapolation and smoothing of the data.

A common method of testing the thermodynamic consistency is to integrate Equation (1) by parts between the limits of $x_1 = 0$ and $x_1 = 1.0$. This gives the conventional area test, viz.,

$$\int_0^1 \ln (\gamma_1 / \gamma_2) dx_1 = 0 \quad (6)$$

One disadvantage encountered in applying the area test is that extrapolated values of γ_1 and γ_2 are necessary, requiring in some cases questionable extrapolations. If the data are thermodynamically consistent, Equation (6) should be satisfied within the limits of experimental error associated with the measurements.

NUMERICAL ANALYSIS

The calculation of γ_2 from Equation (5), using tabulated values of α_1 at equally spaced concentration intervals, was accomplished by analytically integrating Newton's Interpolation Formulae over the range of their respective application. Since the formula used for a particular interval depends on the location of the interval, three forms of the integrated function are necessary: viz.,

First Interval

$$\int_0^h y(x)dx = (5y_1 + 8y_2 - y_3)h/12 \quad (7a)$$

Central Intervals

$$\int_{x_{i+1}}^{x_{i+1} + h} y(x)dx = (-y_i + 13y_{i+1} + 13y_{i+2} - y_{i+3})h/24 \quad (7b)$$

Final Interval

$$\int_{x_n - h}^{x_n} y(x)dx = (5y_n + 8y_{n-1} - y_{n-2})h/12 \quad (7c)$$

where

h = uniform concentration increment

y_i = alpha at concentration x_i ; $y_i (x_1 = 0) = y_1$

x_n = upper limit of integration, usually 1.0

(note: In the above equation, the subscripts refer to the location of the point and not to the component involved.)

The test for thermodynamic consistency, using Equation (6) follows the same integration procedure except the function $y(x)$ now represents $\log(\gamma_1/\gamma_2)$ instead of α . Even with perfectly consistent data, the chances of the integral over the entire composition being exactly equal to zero are small due to experimental errors, round-off errors, and the numerical method. The residue generated is meaningless without a basis of comparison. The residual area is, therefore, recorded as the fraction of the total area.

As a supplementary test of consistency, the first derivatives of $\log \gamma$ vs x_1 are evaluated at each increment of x_1 using the differentiated Newton Interpolation Formulae.

These derivatives, for the indicated values of x are:

$$\left. \frac{dy}{dx} \right|_{x=0} = (-3y_1 + 4y_2 - y_3)/2h \quad (8a)$$

$$\left. \frac{dy}{dx} \right|_{h \leq x_i < x_n - h} = (-2y_{i-1} - 3y_i + 6y_{i+1} - y_{i+2})/6h \quad (8b)$$

$$\left. \frac{dy}{dx} \right|_{x=x_n - h} = (2y_n + 3y_{n-1} - 6y_{n-2} + y_{n-3})/6h \quad (8c)$$

$$\left. \frac{dy}{dx} \right|_{x=x_n} = (3y_n - 4y_{n-1} + y_{n-2})/2h \quad (8d)$$

These values are then substituted into the Gibbs-Duhem equation for a null test. Due to the inherent instability of numerical differentiation, these results must be used as a measure of inconsistency with discretion. The

area test alone as currently used is not a sufficient proof of consistent data as pointed out by Bourne⁵, although, a low value of the residual area coupled with a close comparison between the terms of the Gibbs-Duhem equation as obtained from the differentiation of the smoothed data should indicate relative thermodynamic consistency.

COMPUTER PROGRAMS

The programs subsequently described were written in Fortran for use with the IBM 7074 computer. However, adoption to other computers using Fortran language should require only minor changes. A listing of each program and sample outputs are included in the Appendix: "PRINT" statements are used for output; however, if a high-speed printer is not available, the output statements and format must be modified for punched card or tape output.

Program 1 This program, written to calculate values of the activity coefficient of the second component from activity coefficients of the first, essentially solves Equation (5) for γ_2 using Equation (7) to evaluate the integral (i. e., the integrated form of Newton's second order interpolation formula in the first and last panel and the third order formula for center panels). Input requires values of either $(\log \gamma_1)/x_2^2$ or $(\ln \gamma_1)/x_2^2$ at equidistant intervals of x_1 . A value for α_1 at $x_1 = 0$ must be included which means that an extrapolation of the raw data must be made. If it is desired to integrate all the way to $x_1 = 1$, an extrapolation of a curve of α_1 vs x_1 must be made since α_1 is indeterminate at $x_1 = 1$. The program is written so that it will only integrate up to the highest value of x_1 put in as data.

The printed output identifies the system and tabulates values of x_1 , α_1 , γ_1 , $\log \gamma_1$, and α_2 , γ_2 , $\log \gamma_2$, x_2 for each data point used as input.

Program 2 This program fits an equation in x_1 to experimental values of $\log \gamma_1$; the resulting equation is used in Equation (5) to obtain an expression for $\log \gamma_2$ in terms of x_1 . Three separate equations are used to describe $\log \gamma_1$ over the entire composition range. One, based on a least squares analysis of the data between $x_1 = 0$ and 0.5, is used to describe the region $x_1 = 0$ to 0.3. The second, based on data between 0.5 and 1, is used in the region, .7 to 1. Using these two equations to obtain values of γ_1 at $x_1 = 0.3$ and $x_1 = 0.7$, the data between these values of x_1 are fitted to an equation which is forced to satisfy these values of $\log \gamma_1$ at $x_1 = 0.3$ and 0.7.

In the dilute region some systems yield a linear plot if $\log \gamma_1$ is plotted vs x_1 and other systems are better described by a plot of $\log \gamma_1$ vs x_2^2 . To determine which plot gives the straighter line the data points from $x_1 = 0$ to $x_1 = 0.5$ are used in a least squares analysis with the following equations:

$$\log \gamma_1 = a x_1 + b \quad (9)$$

and

$$\log \gamma_1 = a x_2^2 + b \quad (10)$$

The sum of the squares of the deviations is also calculated for each fitting equation and the form giving the smallest sum is chosen to represent the data. Thus, if it is decided that Equation (9) gives the better fit, the

final form used in the dilute region is:

$$\log \gamma_1 = a x_1^2 + b x_1 + c \quad (11)$$

If, on the other hand, Equation (11) gives a better fit, then:

$$\log \gamma_1 = x_2^2 (a x_2^2 + b x_2 + c) \quad (12)$$

is used. Equation (12) is a rearrangement of the Margules equation.

Equation (12) is also used to describe the data in the middle and concentrated ranges.

Once the equations for $\log \gamma_1$ are established, the integral of Equation (5) can be used to represent the $\log \gamma_2$ vs x_1 relationship. If Equation (11) is used in the dilute region ($x_1 = 0$ to 0.3), then

$$\log \gamma_2 = a x_1^2 + (2a + b) (x_1 + \ln x_2) \quad (13)$$

is used in that region to represent $\log \gamma_2$. If Equation (12) is used, then

$$\log \gamma_2 = x_1^2 \left[a x_1^2 + \left(b - \frac{2a}{3} \right) x_1 + \left(c - \frac{b}{2} \right) \right] \quad (14)$$

is used in the dilute region.

In the middle ($x_1 = 0.3$ to 0.7) and concentrated ($x_1 = 0.7$ to 1) ranges, the integration of Equation (5) involves an integration constant. For the middle range:

$$\begin{aligned} \log \gamma_2 &= x_1^2 \left[a x_1^2 + \left(b - \frac{2a}{3} \right) x_1 + \left(c - \frac{b}{2} \right) \right] \\ &- (.3)^2 \left[a (.3)^2 + \left(b - \frac{2a}{3} \right) (.3) + \left(c - \frac{b}{2} \right) \right] \\ &- \log \gamma_2 (x_1 = 0.3) \end{aligned} \quad (15)$$

Note that the set of constants (a, b, c) in Equation (15) are based on a fit of the data of the middle range while the set in Equations (13) or (14) are based on data in the dilute range. Also note that the value of $\log \gamma_2$ at $x_1 = 0.3$, needed in Equation (15) is evaluated using Equation (13) or (14).

A similar equation is used in the concentrated region.

As these equations and constants are developed, the program uses this information to calculate values of $\log \gamma_1$ and $\log \gamma_2$ for x_1 incremented from 0 to 1 by an arbitrary increment size.

This program requires at least three points in the region $x_1 \leq .5$, three in the region $x_1 > 0.5$, and at least one in the region $0.3 < x_1 < 0.7$. Of course, the desired input would be at least ten points equally spaced over the entire composition range. With few data or bunched points, the program may work but the results would be of dubious value.

The printed output identifies the system and prints out a table of the input data. Tables of x_1 , a_1 , γ_1 , a_2 , γ_2 , $\log \gamma_2$, and x_2 for values of x_1 incremented by Δx from 0 to 1 are also produced. The least squares equations including the constants are printed for each composition range and for each component along with the number of data points used in the least-squares determination.

Program 3 This program is designed to test the thermodynamic consistency of a set of activity coefficients which have been independently measured for both components. The program requires as input data smoothed values of both $\log \gamma_1$ and $\log \gamma_2$ (or $\ln \gamma_1$ and $\ln \gamma_2$) for equidistant values of x_1 . The program covers the entire range of composition and requires

preliminary graphical extrapolations to determine the activity coefficients at infinite dilution.

Derivatives of $\log \gamma$ with respect to x_1 are evaluated using Equation (9) for substitution into the Gibbs-Duhem equation. This provides an additional check on thermodynamic consistency.

The area test, as expressed by Equation (6), is performed using Equation (7) as in Program 1, except $y(x)$ is used to represent $\log (\gamma_1/\gamma_2)$ in this case. The residue generated can be compared to the maximum area calculated to allow interpretation of the results. If the residue is small compared to the maximum area, this test is satisfied. See Fig. 4. (The value of the maximum area occurs when the $\log (\gamma_1/\gamma_2)$ is equal to zero. This null point is found by determining in which interval the function changes sign and then using the Newton-Raphson numerical method to determine the root.)

Although the area test alone is not a sufficient proof of consistency, a low value of the residual area coupled with a close comparison between the terms of the Gibbs-Duhem equation should indicate thermodynamically consistent data.

The printed output identifies the system and tabulates value of x_1 , $\log \gamma_2$, $\int_0^{x_1} \log \frac{\gamma_1}{\gamma_2} dx$, $x_1 \frac{d(\log \gamma_1)}{dx_1}$, $x_2 \frac{d(\log \gamma_2)}{dx_1}$, and the sum of the last two terms for each value of x_1 used as input.

Examples

Fig. 1 illustrates the results of using Program 1 with smoothed values of $\log \gamma_{Cd}$ to calculate the activity coefficients of tin in a

Fig. 1. Example of Results of Program 1. (System: Cadmium-Tin at 483°C, Taylor⁶)

⊙ Input data (smoothed)

□ Output data (calculated from Eq. 5).

cadmium-tin alloy. The results coincide with those obtained by Taylor⁶ using graphical integration of the Gibbs-Duhem equation. Note that the plot does not extend beyond $x_{\text{Cd}} = .9$ since a value of α_1 at $x_{\text{Cd}} = 1.0$ was not included in the input data and the program does not have the capability of extrapolating the data.

Fig. 2 shows the results of applying Program 2 to the same system using raw input data. The results calculated by Taylor are also shown. For this particular set of data, the program gives a poor fit in the range $x_{\text{Cd}} > .7$ and this directly affects the values of $\log \gamma_{\text{Sn}}$ as shown in the figure. This is the result of round-off error in the computations and points out that any least-squares results should be plotted versus the original data to check the authenticity.

The results of using Program 2 on the zinc-tin system data⁶ are shown in Fig. 3. In this case, a good fit of the data was obtained resulting in a close comparison between the values of $\log \gamma_{\text{Sn}}$ generated by the program and those calculated graphically by Taylor.

Table I shows the output of Program 3 testing the consistency of smoothed data for the cadmium-tin system reported by Taylor. The residual area is 0.00153 compared with a 'maximum area' of 0.0733, indicating reasonable satisfaction of the area test (see Fig. 4). Values for the left hand side of Equation (2) are also given (indicated by SUM) along with values for both terms of the equation. The low values of SUM compared with the values of these terms also tend to indicate local consistency. This information coupled with reasonable satisfaction of the area test supports the conclusion that the data are thermodynamically consistent.

Fig. 2. Example of Results of Program 2. (System: Cadmium-Tin
at 483°C, Taylor⁶)
Input data (Raw)
Least Squares Curves
Calculated by Taylor.

Fig. 3. Example of Results of Program 2. (System: Zinc-Tin at 467°C., Taylor⁶)
 Input data (Raw)
 Least squares curves
 Calc. by Taylor.

Fig. 4. Results of the Area Test, Program 3. (System: Cadmium-Tin at 483°C, Taylor⁶)

SUMMARY

It is apparent from the examples given that Program 1 (for smoothed data) represents a reliable method of integrating the Gibbs-Duhem equation. The accuracy of the method depends primarily on the accuracy with which the data can be smoothed.

The curve fitting technique of Program 2 gives satisfactory results for sufficient and well behaved data as is illustrated by the zinc-tin system (Figure 3). However, such a curve fitting technique can lead to erroneous results if it is not used with discretion. Best results, for example, are usually obtained when data are numerous and not clustered. An inherent weakness of the fitting polynomial is that little weight is given in the least squares fit to the points near $x_1 = 1$. This is illustrated by the cadmium-tin system (Figure 2). Consequently, it is always advisable to plot the computer output along with the original data as a check.

Thermodynamic consistency as established by the area test in Program 3 is dependent on the accuracy with which extrapolated values of the alpha function are obtained. Other limitations of the area test are similarly limitations of this analysis. Also, caution must be exercised when applying the differential test due to its inherent sensitivity to small errors in the data, especially if the data have much curvature.

In spite of the foregoing limitations, the indicated tests for thermodynamic consistency serve as significant guides to the internal consistency of vapor-liquid equilibrium data when used judiciously.

TABLE I
THERMODYNAMIC CONSISTENCY TEST FOR THE SYSTEM
CADMIUM(1)-TIN(2)

CALCULATED USING THE GIBBS-DUHEM EQUATION
PROGRAM SATER NO. 3

ATOM FRACT. x(1)	LOG ACT. COEFF. COMP. 1	LOG ACT. COEFF. COMP. 2	INTEGRAL FROM 0 TO x $\int_0^{x_1} \ln(\gamma_1/\gamma_2) dx_1$	COMP. 1 $x_1 \frac{d \log \gamma_1}{dx_1}$	COMP. 2 $x_2 \frac{d \log \gamma_2}{dx_1}$	SUM
0.000	0.279C	0.0000	0.00000E 00	0.00000E 00	0.15000E-02	0.15000E-02
0.100	0.229C	0.0027	0.25266E-01	-0.47500E-01	0.46350E-01	-0.11500E-02
0.200	0.184C	0.0105	0.45259E-01	-0.85000E-01	0.85467E-01	0.46667E-03
0.300	0.1440	0.0240	0.59939E-01	-0.11250E 00	0.11433E 00	0.18333E-02
0.400	0.1090	0.0430	0.69241E-01	-0.13000E 00	0.12700E 00	-0.30000E-02
0.500	0.0790	0.0670	0.73150E-01	-0.13667E 00	0.13667E 00	0.00000E 00
0.600	0.0540	0.0980	0.71575E-01	-0.13900E 00	0.14000E 00	0.10000E-02
0.700	0.0330	0.1370	0.64204E-01	-0.12950E 00	0.12350E 00	-0.60000E-02
0.800	0.0170	0.1840	0.50725E-01	-0.10800E 00	0.11367E 00	0.56667E-02
0.900	0.0060	0.2500	0.30283E-01	-0.76500E-01	0.74833E-01	-0.16667E-02
1.000	0.0000	0.3330	0.15329E-02	-0.35000E-01	0.00000E 00	-0.35000E-01

"MAXIMUM AREA" IS 0.73281E-01 AT x = 0.522

NOMENCLATURE

- a - activity
- h - composition increment
- H - enthalpy
- R - gas law constant
- T - absolute temperature
- v - molal volume
- x - mole fraction

Greek Letters

- α - function defined in text
- γ - activity coefficient

Subscripts

- i - denotes component (except in section on Numerical Analysis)
- n - denotes last data point

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A P P E N D I X

INPUT FORMAT AND PROGRAM LISTINGS

Input for Program 1

This program calculates values of γ_2 based on smoothed values of α_1 at uniformly spaced values of x_1 . The data must be in the following form:

Card 1, Cols. 1-3, Number of data points, no decimal point
 Col. 6, 1 if "ln" is used.
 2 if "log" is used.

Card 2, Cols. 31-75, Names of the components of the system, component 1 first.

Card 3, Cols. 30-40, Name of component 1.
 Cols. 70-80, Name of component 2.

Cards 4 to N + 3, (where N = number of data points.)
 Cols. 1-6, x , written with a decimal point.
 Cols. 7-14, α , written with a decimal point.

The data points should be in the order of increasing x , starting with $x_1 = 0$.

If more than one set of data is to be processed, the above sequence is repeated. To indicate that all data have been processed, the last card in the data deck should have a zero in Cols. 3 and 6. All numbers should be right-justified in their fields.

PROGRAM NO. 1

C SATER PROGRAM NO.1 CALC.OF ACT.COEFF.USING THE GIBBS-DUHEM EQUAT.
 DIMENSION X(101),A(101)

1 READ 101,N,L
 IF(L)2,2,3

N = number data points

L = distinguishes ln and log₁₀

2 STOP

3 READ 103

READ 104

DO 4 I=1,N

4 READ 102,X(I),A(I)

X = mole fraction of component 1

A = alpha function $\equiv \ln \gamma_1/x_2^2$

PRINT 105

PRINT 103

PRINT 107

PRINT 108

PRINT 106

PRINT 104

GO TO (15,16),L

15 PRINT 109

GO TO 17

16 PRINT 110

17 PRINT 111

PN= N-1

DX=X(N)/PN

I=1

XX=0.0

Z=0.0

Y=A(1)

YA=0.0

YL=1.

ZA=1.

GO TO (9,10),L

9 YL=EXP(Y)

GO TO 11

10 YL=EXP(XF(Y))

11 PRINT 112,X(I),YA,YL,Y,ZA,ZL,Z,XX

I=I+1

IF (I-2)2,21,22

21 AREA =DX*(5.*A(1)+8.*A(2)-A(3))/12.

I=2, First panel

8 XX=1.-X(I)

Z=AREA-X(I)*XX*A(I)

Y=XX*XX*A(I)

GO TO (12,13),L

12 YL=EXP(Y)

ZL=EXP(Z)

GO TO 14

13 YL=EXP(XF(Y))

ZL=EXP(XF(Z))

14 YA=YL*X(I)

ZA=ZL*XX

GO TO 11

22 IF(I-N)5,6,1

5 AREA=AREA+DX*(-A(I-2)+13.*A(I-1)+13.*A(I)-A(I+1))/24.

GO TO 8

Example: if N=11, X(N)=1.0

PN = number of panels = 11-1=10

DX = $\Delta x = 1.0/10 = 0.1$

XX = x_2

Z = $\ln \gamma_2$

Y = $\ln \gamma_1$

YA = a_1

ZA = a_2

YL = γ_1

ZL = γ_2

$$\text{AREA} = \int_0^{x_1} \alpha_1 dx_1 = \frac{\Delta x}{12} (5\alpha_1 + 8\alpha_2 - \alpha_3)$$

$$\ln \gamma_2 = \int_0^{x_1} \alpha_1 dx_1 - \alpha_1 x_1 x_2$$

$$\ln \gamma_1 = \alpha_1 x_2^2$$

$$\gamma_1 = e^{\ln \gamma_1} \quad \gamma_2 = e^{\ln \gamma_2}$$

$$a_1 = \gamma_1 x_1, \quad a_2 = \gamma_2 x_2$$

Center Panels

$$\int_0^{x_i} \alpha_1 dx_1 = \int_0^{x_{i-1}} \alpha_1 dx_1 + \frac{\Delta x}{24}$$

$$(-\alpha_i - 2 + 13(\alpha_{i-1} + \alpha_i) - \alpha_{i+1})$$

```

6 AREA=AREA+DX*(5.*A(I)+8.*A(I-1)-A(I-2))/12.
GO TO 8

```

Last panel

$$\int_0^{x_N} \alpha_1 dx_1 = \int_0^{x_{N-1}} \alpha_1 dx_1 + \frac{\Delta x}{12} (5\alpha_N + 8\alpha_{N-1} - \alpha_{N-2})$$

```

101 FORMAT(I3,I3)
102 FORMAT(F6.0,F8.0)
103 FORMAT(1H,29X45H COMPONENTS OF THE SYSTEM )
104 FORMAT(1H,28X11HCOMPONENT 1,29X11HCOMPONENT 2)
105 FORMAT(1H4,37X35HACTIVITY COEFFICIENTS OF THE SYSTEM)
106 FORMAT(1HJ)
107 FORMAT(1HJ,34X41HCALCULATED USING THE GIBBS-DUHEM EQUATION)
108 FORMAT(1H,43X21HPROGRAM SATER NO.1)
109 FORMAT(1HJ,17X4HATOM,5X4HACT.,4X4HACT.,7X2HLN,12X4HACT.,4X4HACT.,6
1X2HLN,7X4HATOM)
110 FORMAT(1H,17X4HATOM,5X4HACT.,4X4HACT.,7X3HLOG,11X4HACT.,4X4HACT.,
16X3HLOG,6X4HATOM)
111 FORMAT(1H/,16X6HFRACT.,11X19HCOEFF. ACT.COEFF.,14X25HCOEFF. ACT
1.COEFF. FRACT.)
112 FORMAT(1H,15X,F6.3,3XF6.3,2XF6.3,4XF7.4,8XF6.3,2XF6.3,3XF7.4,4XF6
1.3)
END

```

Input for Program 2

The input data must be in the following form:

- Card 1, Cols. 1-3, Numbers of data points, no decimal point
 Cols. 6, 1 if "ln" is used
 2 if "log" is used
 Cols. 7-11, Output increment size, Δx , with decimal point
- Card 2, Cols. 31-74, Names of the components of the system, component 1 first
- Card 3, Cols. 47-66, Name of component 1
- Card 4, Cols. 30-40, Name of component 1
 Cols. 70-80, Name of component 2
- Cards 5 to (N + 4), (where N = number of data points)
 Cols. 1-6, x_1 written with a decimal point
 Cols. 7-14, $\log \gamma_1$ or $\ln \gamma_1$ written with a decimal point

The data points should be in the order of increasing x_1 . (The program requires at least three points in the region $x_1 \leq .5$, three in the region $x_1 > 0.5$, and at least one in the region $0.3 \leq x_1 \leq 0.7$. Of course, the desired input would be at least ten points equally spaced over the entire composition range. With few data and/or bunched points, the program may work but the results would be of dubious value.)

If more than one set of data is to be processed, the above sequence is repeated. To indicate that all data have been processed, the last card in the data deck should have a zero in Cols 3, 6 and 11 and a decimal point in Column 10. All numbers should be right justified in their fields.

PROGRAM NO. 2

C SATER PROGRAM NO.2 CALC. OF ACTIVITY COEFFICIENTS USING RAW DATA
C AND THE GIBBS-DUHEM EQUATION
C DIMENSION X(101),Y(101)

```

1 READ 101,N,L,DX
  IF(L)2,2,3
2 STOP
3 READ 103
  READ 114
  READ 104
  PRINT 105
  PRINT 103
  PRINT 107
  PRINT 108
  PRINT 113
  PRINT 114
  GO TO (8,9),L
8 PRINT 115
  GO TO 10
9 PRINT 116
10 PRINT 117
  DO 4 I=1,N
    READ 102,X(I),Y(I)
4 PRINT 118,X(I),Y(I)
  PRINT 119
  PRINT 104
  GO TO (5,6),L
5 PRINT 109
  GO TO 7
6 PRINT 110
7 PRINT 111

```

N = number of data points
L = distinguishes in 8 $\log_{10}$
DX = desired Δx spacing of output

X = mole fraction of component 1
Y = $\ln \gamma_1$

```

M=1
ZB=0.0
16 S1 =0.
  S2=0.
  S3=0.
  S4=0.
  S6=0.
  S7=0.
  S8=0.
  S9=0.
  S10 =0.
  S11 =0.
  S12 =0.
  S13 =0.
  S14 =0.
  S15=0.

```

M refers to the range of the data being fitted.

M = 1 "dilute" region
2 "conc."
3 "middle "

Sums initially set equal to zero.

```

S16 =0.
S17 =0.
S18 =0.
GO TO (13,14,39),M
13 I=1
20 IF(X(I)-.5)11,11,12
12 SN= I-1
   N1= I-1
   IF(SN-3.)15,17,17
11 Y1=Y(I)
   X1=X(I)
   X2= 1.-X1
   X12=X1*X1
   X13=X1*X12
   X14=X12*X12
   X22=X2*X2
   X24=X22*X22
   S1= S1 + X14*X24
   S2= S2 + X13*X24
   S3= S3 + X12*X24
   S4= S4 + X12*X22*Y1
   S5= S5 + X12*X24
   S6= S6 + X1*X24
   S7= S7 + X1*X22*Y1
   S8= S8 + X24
   S9= S9+X22*Y1
   GO TO (18,19,18),M
18 S10 = S10 + X14
   S11 = S11 + X13
   S12 = S12 + X12
   S13 = S13 + X12*Y1
   S14 = S14 + X1
   S15 = S15 + X1*Y1
   S16 = S16 + Y1
   S17 = S17 + X22
   S18 = S18 + Y1*Y1
19 I=I+1
   GO TO (20,14,41),M
17 D=SN*S8-S17*S17
   T=S9*SN-S16*S17
   A1= T/D
   T=S8*S16-S9*S17
   B1=T/D
   D=S12*SN-S14*S14
   T=S15*SN-S14*S16
   A2= T/D
   T=S12*S16-S14*S15
   B2= T/D
   SDS2 =S18-2.*A2*S15-2.*B2*S16+A2*A2*S12+2.*A2*B2*S14+SN*B2*B2
   SDS1 =S18-2.*A1*S9 -2.*B1*S16+A1*A1*S8 +2.*A1*B1*S17+SN*B1*B1
   IF(SDS2-SDS1)21,22,23
23 MM=1
27 D=S1*S3*S8+S2*S6*S3*2.-S3*S3*S3-S1*S6*S6-S2*S2*S8
   T=S3*S4*S8+S2*S6*S9+S3*S7*S6-S6*S6*S4-S2*S7*S8-S3*S3*S9
   AA1=T/D
   T=S1*S7*S8+S3*S4*S6+S2*S3*S9-S3*S3*S7-S2*S4*S8-S1*S6*S9
   BB1=T/D
   T=S1*S3*S9+S2*S3*S7+S2*S4*S6-S3*S3*S4-S1*S6*S7-S2*S2*S9
   CC1=T/D
   BB2=(3.*BB1-2.*AA1)/3.
   CC2= CC1-.5*BB1
   GO TO (22,28),M

```

Region: $x_1 \leq .5$

SN=N1 =number of points for $x_1 \leq 5$

Check to see if at least 3 points
in range.

$$\begin{aligned}
 S1 &= \sum (x_1 x_2)^4, & S2 &= \sum x_1^3 x_2^4 \\
 S3 &= \sum x_1^2 x_2^4, & S4 &= \sum (x_1 x_2)^2 \ln \gamma_1 \\
 S5 &= \sum x_1^2 x_2^4, & S6 &= \sum x_1 x_2^4 \\
 S7 &= \sum x_1 x_2^2 \ln \gamma_1, & S8 &= \sum x_2^4 \\
 S9 &= \sum x_2^2 \ln \gamma_1 \\
 S10 &= \sum x_1^4, & S11 &= \sum x_1^3 \\
 S12 &= \sum x_1^2, & S13 &= \sum x_1^2 \ln \gamma_1 \\
 S14 &= \sum x_1, & S15 &= \sum x_1 \ln \gamma_1 \\
 S16 &= \sum \ln \gamma_1, & S17 &= \sum x_2^2 \\
 S18 &= \sum (\ln \gamma_1)^2
 \end{aligned}$$

Does $\ln \gamma_1 = a x_1 + b$

or $\ln \gamma_2^2 = a x_2^2 + b$ give

better fit in region $x_1 \leq .5$?

Calc. coeff. for
 $\ln \gamma_1 = x_2^2 (a x_1^2 + b x_1 + c)$

```

22 A1=AA1
   B1=BB1
   C1=CC1
   B2=BB2
   C2=CC2
   W=0.
26 YC=(1.-W)*(1.-W)*(AA1*W*W +BB1*W +CC1)
   Z=W*W*(AA1*W*W+BB2*W+CC2)+ZB
47 GO TO (30,31),L
30 G1= EXPF(YC)
   G2= EXPF(Z)
   GO TO 32
31 G1= EXPXF(YC)
   G2= EXPXF(Z)
32 AC1=G1*W
   AC2=G2*(1.-W)
   WW=1.-W
   PRINT 112,W,AC1,G1,YC,AC2,G2,Z,WW
   GO TO (45,2,46),M
45 IF (W-.3)24,52,52
24 W=W+DX
   GO TO 26
21 MM=2
   D=S10*S12*SN +2.*S11*S12*S14-S12*S12*S12-S10*S14*S14-SN*S11*S11
   T=S11*S14*S16+S12*S14*S15+SN*S12*S13-S13*S14*S14-SN*S11*S15-S16*
1S12*S12
   A2=T/D
   T=SN*S10*S15+S12*S13*S14+S11*S12*S16-S12*S12*S15-S10*S14*S16-SN*
1S11*S13
   B2=T/D
   T=S10*S12*S16+S11*S12*S15+S11*S13*S14-S12*S12*S13-S10*S14*S15-S16*
1S11*S11
   C2=T/D
   A1=2.*A2+B2
   W=0.
29 YC=A2*W*W+B2*W +C2
   Z=A1*(W+ LOGF(1.-W))+A2*W*W
   GO TO(33,34),L
33 G1= EXPF(YC)
   G2=EXPF(Z)
   GO TO 35
34 G1=EXPXF(YC)
   G2=EXPXF(Z)
35 AC1=G1*W
   AC2=G2*(1.-W)
   WW= 1.-W
   PRINT 112,W,AC1,G1,YC,AC2,G2,Z,WW
   IF(W-.3)36,52,52
36 W=W+DX
   GO TO 29
52 M=2
   GO TO 16
14 IF(I-N)11,11,38
38 N2=N-N1
   IF(N2-3)25,27,27
28 V=.7
   YD=(1.-V)*(1.-V)*(AA1*V*V+BB1*V+CC1)
   M=3
   GO TO 16

```

Calc. values of $\ln \gamma_1$ and
 $\ln \gamma_2$ for $x_1 \leq .3$ and $x_1 \geq .7$
 using $\ln \gamma_1 = x_2^2 (a x_1^2 + b x_1 + c)$.

Calc. coeff. for $\ln \gamma_1 = a x_1^2 +$
 $b x_1 + c$ in region $x_1 \leq .5$

Calc. values of $\ln \gamma_1$ and $\ln \gamma_2$
 for $x \leq .3$ based on

$$\ln \gamma_1 = a x_1^2 + b x_1 + c$$

$$W = x_1, AC1 = a_1, G1 = \gamma_1, YC = \ln \gamma_1$$

$$WW = x_2, AC2 = a_2, G2 = \gamma_2, Z = \ln \gamma_2$$

Go to conc. region.

N2 = number of data points $> .5$.

Check to see if at least 3 points
 in range. Set $x_1 = .7$

Calc. $\ln \gamma_1$ at $x_1 = .7$.

Go to middle region.

```

39 I=1
   J=0
42 IF(X(I)-.3)40,41,41
40 I=I+1
   GO TO 42
41 IF(X(I)-.7)43,44,44
43 J=J+1
   GO TO 11
44 T1= YC/((W-V)*(1.-W)*(1.-W))
   T2= YD/((W-V)*(1.-V)*(1.-V))
   T3= T1-T2
   T4= T2*W -V*T1
   SQX=S1-2.*(V+W)*S2+(2.*V*W+(V+W)*(V+W))*S3-2.*V*W*(V+W)*S6+V*V*W*W
1  *S8
   SGQX= -S4 +(V+W)*S7 -V*W*S9
   ST3 = T3*(-S2+(V+W)*S3-V*W*S6)
   ST4 = T4*(-S3+(V+W)*S6-V*W*S8)
   A=(ST3+ST4-SGQX)/SQX
   B=T3- A*(V+W)
   C= T1*(W-V)-A*W*W-B*W
   D= B-2.*A/3.
   E= C-.5*B
   ZA=Z-W*W*(E+W*(D+A*W))
   ZB=V*V*((A-AA1)*V*V+(D-BB2)*V+(E-CC2))+ZA
48 W=W+DX
   YC=(1.-W)*(1.-W)*(A*W*W +B*W +C)
   Z=W*W*(A*W*W+D*W+E)+ZA
   GO TO 47
46 IF(W-.7) 48,49,49
49 IF(W-1.) 50,51,2
50 W=W+DX
   IF(W-1.)26,26,53
53 W=1.
   GO TO 26
15 PRINT 120
   GO TO 1
25 PRINT 121
   GO TO 1
51 PRINT 122,N1
   GO TO (60,61),L
60 GO TO (62,63),MM
62 PRINT 123
   PRINT 124,A1,B1,C1
   PRINT 125,B2,C2
   GO TO 64
63 PRINT 126
   PRINT 127,A2,B2,C2,A1
64 PRINT 128,J
   PRINT 133
   PRINT 124,A,B,C
   PRINT 132,D,E,ZA
   PRINT 129,N2
   PRINT 133
   PRINT 124,AA1,BB1,CC1
   PRINT 132,BB2,CC2,ZB
   GO TO 1
61 GO TO (65,66),MM
65 PRINT 130
   PRINT 124,A1,B1,C1
   PRINT 125,B2,C2
   GO TO 67

```

Sums terms for $.3 \leq x_1 \leq .7$.

J = no. of points, $.3 \leq x_1 \leq .7$

Calc. constants for

$$\ln \gamma_1 = x_1^2 (a x_1^2 + b x_1 + c)$$

in region $.3 \leq x_1 \leq .7$.

Calc. $\ln \gamma_1$ and $\ln \gamma_2$

for $.3 < x_1 < .7$

```

66 PRINT 131
   PRINT 127,A2,B2,C2,A1
67 PRINT 128,J
   PRINT 134
   PRINT 124,A,B,C
   PRINT 132,D,E,ZA
   PRINT 129,N2
   PRINT 134
   PRINT 124,AA1,BB1,CC1
   PRINT 132,BB2,CC2,ZB
   GO TO 1

101 FORMAT(I3,I3,F5.0)
102 FORMAT(F6.0,F8.0)
103 FORMAT(1H ,29X45H  COMPONENTS OF THE SYSTEM
104 FORMAT(1H ,28X11HCOMPONENT 1,29X11HCOMPONENT 2)
105 FORMAT(1H1,37X35HACTIVITY COEFFICIENTS OF THE SYSTEM)
106 FORMAT(1HJ)
107 FORMAT(1HJ,34X41HCALCULATED USING THE GIBBS-DUHEM EQUATION)
108 FORMAT(1H ,43X21HPROGRAM      SATER NO.2)
109 FORMAT(1HJ,17X4HATOM,5X4HACT.,4X4HACT.,7X2HLN,12X4HACT.,4X4HACT.,6
   1X2HLN,7X4HATOM)
110 FORMAT(1HJ,17X4HATOM,5X4HACT.,4X4HACT.,7X3HLOG,11X4HACT.,4X4HACT.,
   16X3HLOG,6X4HATOM)
111 FORMAT(1HS,16X6HFRACT.,11X19HCOEFF.   ACT.COEFF.,14X25HCOEFF.   ACT
   1.COEFF. FRACT.)
112 FORMAT(1H/,15X,F6.3,3XF6.3,2XF6.3,4XF7.4,8XF6.3,2XF6.3,3XF7.4,4XF6
   1.3)
113 FORMAT(1HK,35X40HRAW INPUT DATA IN TERMS OF THE COMPONENT)
114 FORMAT(1H ,45X20H  COMPONENT 1
115 FORMAT(1HJ,44X4HATOM,14X2HLN)
116 FORMAT(1HJ,44X4HATOM,13X3HLOG)
117 FORMAT(1HS,43X6HFRACT.,9X10HACT.COEFF.)
118 FORMAT(42XF6.3,9XF7.4)
119 FORMAT(1HK,44X18HCALCULATED RESULTS)
120 FORMAT(1H ,34X40HNOT ENOUGH DATA IN THE RANGE X= 0 TO .5 )
121 FORMAT(1H ,34X40HNOT ENOUGH DATA IN THE RANGE X= .5 TO 1 )
122 FORMAT(1HK,6X29HFROM X1 = 0 TO .3  (BASED ON ,I3,13H DATA POINTS))
123 FORMAT(1H ,10X86H LN(GAMMA 1)= X2*X2*(A*X1*X1 + B*X1 + C)  AND  LN
   1(GAMMA 2)= X1*X1*(A*X1*X1 + D*X1 + F))
124 FORMAT(1H ,14X10HWHERE A = ,E12.5,2H ,4X4HB = ,E12.5,2H ,4X4HC =
   1 ,E12.5)
125 FORMAT(1H ,14X10H  AND D = ,E12.5,2H ,4X4HE = ,E12.5)
126 FORMAT(1H ,10X81H LN(GAMMA 1)= A*X1*X1 + B*X1 + C      AND  LN(GAM
   1MA 2)= A*X1*X1 + D*(X1 + LN(X2)))
127 FORMAT(1H ,14X10HWHERE A = ,E12.5,2H ,4X4HB = ,E12.5,2H ,4X4HC =
   1 ,E12.5,11H  AND  D = ,E12.5)
128 FORMAT(1HK,6X29HFROM X1 =.3 TO .7  (BASED ON ,I3,13H DATA POINTS))
129 FORMAT(1HK,6X29HFROM X1 =.7 TO 1.  (BASED ON ,I3,13H DATA POINTS))
130 FORMAT(1H ,10X86HLOG(GAMMA 1)= X2*X2*(A*X1*X1 + B*X1 + C)  AND LOG
   1(GAMMA 2)= X1*X1*(A*X1*X1 + D*X1 + E))
131 FORMAT(1H ,10X81HLOG(GAMMA 1)= A*X1*X1 + B*X1 + C      AND  LOG(GAM
   1MA 2)= A*X1*X1 + D*(X1 + LN(X2)))
132 FORMAT(1H ,14X10H  AND D = ,E12.5,2H ,4X4HE = ,E12.5,2H ,4X4HF =
   1 ,E12.5)
133 FORMAT(1H ,10X90H LN(GAMMA 1)= X2*X2*(A*X1*X1 + B*X1 + C)  AND  LN
   1(GAMMA 2)= X1*X1*(A*X1*X1 + D*X1 + E) + F)
134 FORMAT(1H ,10X90HLOG(GAMMA 1)= X2*X2*(A*X1*X1 + B*X1 + C)  AND LOG
   1(GAMMA 2)= X1*X1*(A*X1*X1 + D*X1 + E) + F)
   END

```


Input for Program 3

The input data must be in the following form:

Card 1, Cols. 1-3, Number of data points, no decimal point

Col. 6 1 if "ln" is used.
 2 if "log" is used

Card 2, Cols. 26-70, Identification of the system, such as "Cadmium (1) - Tin (2)"

Cards 3 to N+2, (where N = number of data points)

Cols. 1-6, x_1 written with a decimal point

Cols. 7-14, $\log \gamma_1$ or $\ln \gamma_1$ written with a decimal point

Cols. 15-22, $\log \gamma_2$ or $\ln \gamma_2$ written with a decimal point

The data should be in the order of increasing x_1 starting with $x_1 = 0$ and ending with $x_1 = 1$. If more than one set of data is to be processed, the above sequence is repeated. To indicate that all data have been processed, the last card in the data deck should have a zero in Cols. 3 and 6. All numbers should be right-justified in their fields.

PROGRAM NO. 3

C SATER PROGRAM NO.3 CONSISTENCY CHECK USING THE GIBBS-DUHEM EQUATION
DIMENSION X(101),Y(101),Z(101),YZ(101)

1 READ 101,N,L

IF(L)2,2,3

2 STOP

3 READ 103

DO 4 I=1,N

READ 102,X(I),Y(I),Z(I)

4 YZ(I)= Y(I)-Z(I)

PRINT 105

PRINT 103

PRINT 107

PRINT 108

GO TO (5,6),L

5 PRINT 109

GO TO 7

6 PRINT 110

7 PRINT 111

PRINT 106

PN= N-1

DX=X(N)/PN

K=1

N=number of data points

L=distinguishes ln & log₁₀

X=mole fraction of comp. 1

Y=ln γ_1

Z=ln γ_2

YZ=ln (γ_1/γ_2)

PN= no. of panels
DX= Δx AREA= $\int_0^{x_1} \ln(\gamma_1/\gamma_2) dx_1$

```

I=1
AREA=0.0
GD1=.5*(-3.*Y(1)+4.*Y(2)-Y(3))*X(1)/DX
GD2=.5*(-3.*Z(1)+4.*Z(2)-Z(3))*(1.-X(1))/DX
EGD= GD1 +GD2
10 PRINT 112,X(I),Y(I),Z(I),AREA,GD1,GD2,EGD
I=I+1
IF(I-N)11,11,19
11 IF(YZ(I))12,13,12
13 K=2
XC=X(I)
IF(I-2)2,15,18
12 IF((YZ(I-1))/YZ(I))14,16,16
16 IF(I-2)2,15,17
14 K=3
IF(I-2)2,25,26
25 A=.25*(-3.*YZ(1)+4.*YZ(2)-YZ(3))
B=(YZ(1)-2.*YZ(2)+YZ(3))/6.
ROOT=SQRTF(A*A-3.*B*YZ(1))
XC=DX*(ROOT-A)/(3.*B)
IF(XC)29,29,30
30 IF(XC-X(2))31,29,29
29 XC=-DX*(ROOT+A)/(3.*B)
31 U=XC/DX
DAM=DX*(YZ(1)*U+A*U*U+B*U*U*U)
15 DA=DX*(5.*YZ(1)+8.*YZ(2)-YZ(3))/12.
GO TO (22,23,24),K
24 AREAM=AREA+DAM
K=1
GO TO 22
23 AREAM=AREA+DA
K=1
22 AREA=AREA+DA
47 GD1=(-2.*Y(I-1)-3.*Y(I)+6.*Y(I+1)-Y(I+2))*X(I)/(6.*DX)
GD2=(-2.*Z(I-1)-3.*Z(I)+6.*Z(I+1)-Z(I+2))*(1.-X(I))/(6.*DX)
EGD=GD1+GD2
GO TO 10
18 IF(I-N)37,20,2
17 IF(I-N)37,20,2
26 IF(I-N)27,28,2
28 A=.25*(3.*YZ(N)-4.*YZ(N-1)+YZ(N-2))
B=(YZ(N)-2.*YZ(N-1)+YZ(N-2))/6.
ROOT=SQRTF(A*A-3.*B*YZ(N))
XC=X(N)+DX*(ROOT-A)/(3.*B)
IF(XC-X(N-1))41,41,42
42 IF(XC-X(N))43,41,41
41 XC=X(N)-DX*(ROOT+A)/(3.*B)
43 U=(XC-X(N))/DX
DAM=DX*(YZ(N)*(U+1.)+A*(U*U-1.)+B*(U*U*U+1.))
20 DA=DX*(5.*YZ(N)+8.*YZ(N-1)-YZ(N-2))/12.
GO TO (44,45,46),K
46 AREAM=AREA+DAM
K=1
GO TO 44
45 AREAM=AREA+DA
K=1

```

First point, $x_1=0$

$$GD1 = x_1 \frac{d \ln \gamma_1}{d x_1}$$

$$GD2 = x_2 \frac{d \ln \gamma_2}{d x_1}$$

$XC = \text{root of } \ln(\gamma_1/\gamma_2) = 0.$

First Panel

U= dimensionless increment

DA= area of single panel.

AREAM= Max. area

DAM = Area between x_{i-1} and XC

Center points

Last panel

```

44 AREA=AREA+DA
   GD1=(1.5*Y(N)-2.*Y(N-1)+.5*Y(N-2))*X(N)/DX
   GD2=(1.5*Z(N)-2.*Z(N-1)+.5*Z(N-2))*(1.-X(N))/DX
   EGD=GD1+GD2
   GO TO 10
27 A=(-11.*YZ(I-2)+18.*YZ(I-1)-9.*YZ(I)+2.*YZ(I+1))/6.
   B= YZ(I-2)-2.5*YZ(I-1)+2.*YZ(I)-.5*YZ(I+1)
   C=(YZ(I+1)-3.*YZ(I)+3.*YZ(I-1)-YZ(I-2))/6.
   X1=X(I-1)
   U1=1.
21 U2=U1*U1
   U3=U1*U2
   G=YZ(I-2)+A*U1+B*U2+C*U3
   DG=A+2.*B*U1+3.*U2*C
   U=U1-G/DG
   XC=U*DX+X(I-2)
   DDX=XC-X1
   IF(DDX)32,33,34
32 DDX=-DDX
34 IF(DDX-.00001)33,33,35
35 U1=U
   X1=XC
   GO TO 21
33 DAM=DX*(YZ(I-2)*(U-1.)+.5*A*(U2-1.)+B*(U3-1.)/3.+.25*C*(U*U3-1.))
37 DA=DX*(-YZ(I-2)+13.*(YZ(I-1)+YZ(I))-YZ(I+1))/24.
   GO TO (38,39,40),K
40 AREAM=AREA+DAM
   K=1
   GO TO 38
39 AREAM=AREA+DA
   K=1
38 AREA=AREA+DA
   IF(I-N+1)47,48,2
48 GD1=(2.*Y(N)+3.*Y(N-1)-6.*Y(N-2)+Y(N-3))*X(N-1)/(DX*6.)
   GD2=(2.*Z(N)+3.*Z(N-1)-6.*Z(N-2)+Z(N-3))*(1.-X(N-1))/(6.*DX)
   EGD=GD1+GD2
   GO TO 10
19 PRINT 104,AREAM,XC
   GO TO 1

```

Last point,
 $x_1 = 1.0$

Newton-Raphson
search for
root, XC

Center
Panels

Next to last point,
 $x_1 = 1.-\Delta x$

```

102 FORMAT(F6.0,F8.0,F8.0)
101 FORMAT(I3,I3)
105 FORMAT(1H1,26X,45HTHERMODYNAMIC CONSISTENCY TEST FOR THE SYSTEM)
103 FORMAT(1H ,24X,45H          COMPONENTS OF THE SYSTEM          )
107 FORMAT(1HJ,29X41HCALCULATED USING THE GIBBS-DUHEM EQUATION)
108 FORMAT(1H ,38X21HPROGRAM      SATER NO.3)
109 FORMAT(1HK,16X4HATOM,7X2HLN,11X2HLN,8X8HINTEGRAL,13X20HGIBBS-DUHEM
1 EQUATION)
110 FORMAT(1HK,16X4HATOM,6X3HLOG,10X3HLOG,9X8HINTEGRAL,13X20HGIBBS-DUH
1EM EQUATION)
111 FORMAT(1H ,15X6HFRACT.,2X10HACT.COEFF.,3X10HACT.COEFF.,7X4HFROM,11
1X6HCOMP.1,9X6HCOMP.2,11X3HSUM)
106 FORMAT(1HS,16X4HX(1),5X6HCOMP.1,7X6HCOMP.2,8X6HO TO X)
104 FORMAT(1HJ,26X16HMAXIMUM AREA IS ,E12.5,7H  AT X=,F6.3)
112 FORMAT(1H ,15XF6.3,2XF7.4,6XF7.4,6XE12.5,3XE12.5,3XE12.5,3XE12.5)
END

```