THE UNIVERSITY OF MICHIGAN

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THE CORRELATION OF BINARY AND TERNARY LIQUID-LIQUID EQUILIBRIA

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NOMENCLATURE

a_i	activity of component i
b_{12} , c_{12} , d_{12}	coefficients in Equation (2.97)
B_{ij} , C_{ij} , D_{ij}	Redlich-Kister binary coefficients
c_ℓ	equation coefficients or parameters. When the Redlich-Kister equations are referred to, c_1 , c_2 , --- c_6 is B_{12} , B_{23} , B_{31} , C_{12} , C_{23} , C_{31} respectively
C	number of components or first Redlich-Kister ternary interaction coefficients
C_v	constant volume heat capacity
D, D'	critical phase determinants defined in Equations (2.88a), (2.95a)
D_1 , D_2	second Redlich-Kister ternary interaction coefficients
D_ℓ	meterized steepest descent correction factor
e_1 , e_2	coefficients in Equation (4.23)
F_i	the ternary Redlich-Kister expressions for log γ_i retaining only B_{ij} and C_{ij}
$\mathcal{F}$	the function defined in Equation (3.10)
f_i	fugacity of component i
f_L , g_L , h_L	(L = 1, 2, -- 6), terms in (Eqtn.(3.10)), (eqtn.(3.11)), (eqtn.(3.12)) multiplying c_1 ... c_6
G	Gibbs' free energy equal H - TS
$\mathcal{G}$	the function defined in Equation (3.11)
ΔG_M , ΔH_M	free energy, enthalpy of mixing
ΔG^E	excess free energy of mixing
ΔG^i_M	ideal free energy of mixing
H	enthalpy

NOMENCLATURE (CONT'D)

$\mathcal{H}$	the function defined in Equation (3.12)
L_1, L_2	$\log x_1'/x_1''$, $\log x_2'/x_2''$ respectively
n	number of moles
P	number of phases or total pressure
P_i°	vapor pressure of the pure component i
p_i	partial pressure of component i
Q	the Q function equal $\frac{\Delta G^E}{2.303\,RT}$
q_i , a_{ij} , a_{ijk} ...	coefficients in Wohl's equations, see Equation (2.50)
R	any extensive property or the gas constant
S	entropy
$\mathcal{S}$	any arbritary function or system of functions
T	absolute temperature, °K
t	temperature, °C
U	internal energy
V	variance or volume
V_i	coefficients appearing in Scatchard's equations (see Table I)
w	a weight factor, wee Equation (4.13)
x_i', x_i'' , ...	mol fraction of component i in liquid phase one, two, etc.
X_1, X_2, X_3, X_4	terms in Equations (3.8) and (3.9)
y_i	mol fraction of component i in the vapor phase
Y_{1i} , Y_{2i} ---, Z_{1i} , Z_{2i} --	experimentally determined values for the dependent variables y_1 , y_2 ---, and the independent variables z_1 , z_2 ---, ith data point; see Equation (4.12)

NOMENCLATURE (CONT'D)

z_i	the effective volumetric fractions in Wohl's equations defined in Equation (2.51)

Greek Letters:

α	magnitude of the steepest descent correction in the direction given by D_ℓ.
β_i	population parameters in equations to be fitted by least squares
γ_i	activity coefficient of component i in solution
$\delta, \delta^2, \delta^3 \ldots$	operators indicating the first, second, third, etc. order terms in Taylor series expansion
Δ	used alone: represents the sum of the squares of deviations to be minimized by least squares; used with another variable: means change from state one to state two
$\epsilon_1, \epsilon_2, \mathcal{E}_1, \mathcal{E}_2$	arbitrary values to determine the degree of accuracy of iterative processes (see Appendix B)
ϕ_i	equal $F_i'' - F_i'$ see Equations (3.10a), (3.11b), (3.12c)
θ	the angle between the meterized steepest descent directions at the (n-1)th and nth trials

Subscripts*:

i, j, k, ---	the ith, jth, kth --- components
A, B, C, ---	component A, B, C
1, 2, 3, ---	component 1, 2, 3

* Subscripts having other meanings will be obvious from context.

Sub Bars:

$\underline{R}_i$	equal $\dfrac{R_i}{\sum_{i=1}^{k} n_i}$ the value of any extensive property R per mole of solution

NOMENCLATURE (CONT'D)

Superscripts:

$*$	refers to mathetically predicted values of dependent variables, no * refers to actual experimentally measured value of variables
c	means critical value pertaining to a critical phase
E	means excess, as excess free energy
i	means ideal, as ideal free energy of mixing
$[N]$	refers to the Nth iteration, in a trial and error solution
o	refers to the standard state, here taken to be the pure component in the liquid state at T

Superbars:

$\bar{R}_i$	equal $\frac{\partial R}{\partial n_i}$ where R is any extensive property

I. INTRODUCTION

The prediction of equilibria in liquid phases is of greatest importance in the chemical and metallurgical industries. Although there has been a long continued effort in this field, accurate prediction of the phase equilibria in liquid phases is impossible, except in cases of mixtures which follow or deviate only slightly from Raoult's Law.

This problem will ultimately be solved only through a thorough understanding of the interactions of molecules and molecular forces in solutions. Such understanding unfortunately may be many years away, and the demand of the process industries for accurate prediction methods continues to grow as more complex separation problems are undertaken and higher product purities are desired.

Because of the increased importance of solvent extraction processes, this thesis is devoted to the prediction of equilibrium in two phase liquid systems. No attempt has been made to solve the long range problem of understanding solution behavior from a molecular view point. Rather, a means of extending our existing experimental data on liquid systems is investigated in this thesis which has the possibility of providing an immediate answer to the demand for accurate phase equilibrium prediction.

A. Purpose of the Investigation

This research is an attempt to develope a correlation which will permit the prediction of parameters in equations suitable for the representation of phase equilibria. Attention is focused on the case of two phase liquid equilibria in three component systems, but the ideas evolved hopefully may be extrapolated to systems having any number of components.

B. Formulation of the Problem

Assume that a function or system of functions exist

$$\mathscr{S}(c_1, c_2 \cdots c_{2n}, x_1', x_2' \cdots x_m', x_1'', x_2'' \cdots x_m'') = 0$$

where the c's are parameters, the x''s are the compositions of phase one, the x'''s are the compositions of phase two, and n is the number of pairs of components. The questions that may be raised are:

1. Do Equations(s) (1.1) satisfactorily represent the desired equilibrium? or are more coefficients or better equations required?

2. Can the parameters in (1.1) be determined from systems containing fewer components than the case for which (1.1) is written?

3. Consider a series of systems containing components A, B, C_1, D ...; A, B, C_2, D ...; A, B, C_3, D... etc. where C_1, C_2, C_3 ... are homologs. Are the parameters in (1.1) simple functions of some monotonic property of component C_1, C_2, C_3 ... such as molecular weight?

Question two suggests a correlation in the form of tabulated parameters determined from simple systems which can be used in Equation (1.1) to predict the equilibria for more complex systems. Question three suggests a correlation in the form of graphs of the parameters in (1.1) plotted against some property of the variable component, C_i.

Such a correlation has been demonstrated by White(53) who used the Redlich-Kister equations to represent the binary vapor-liquid equilibria of hydrocarbon-mercaptan systems and found for mercaptan homologs, that equation parameters were nearly straight line functions of the number of carbon atoms in the mercaptan.

The system of functions (1.1) which have been proposed for the present work are the Redlich-Kister equations(33) which have been successfully used to represent vapor-liquid equilibrium data. The questions stated above will be restated more specifically for the case of the Redlich-Kister equations to represent ternary liquid-liquid equilibria.

Many equations of the Redlich-Kister type such as Wohl's, Margules', and Van Laar's equations and others(54,20,47,39) have been used to represent phase equilibria. However because of their complexity they have not been used extensively to represent ternary liquid-liquid equilibria. Scheibel has recently discussed the use of the Redlich-Kister equations in representing ternary liquid-liquid equilibria.(40) Other authors have used the Van-Laar equations(18) and modified versions of the Van-Laar(4) to represent ternary liquid-liquid equilibria. Because of the complexity of the equations the methods used were approximate and usually graphical. By using high-speed digital computers in the present research more rigorous solution of the equations and more exact determination of the equation parameters from experimental data was possible.

The subject of the effect of temperature on equilibria was not studied in this research.

C. Summary

Section II of this dissertation is a review of liquid-liquid equilibria from a thermodynamic viewpoint. In part A is a review of equilibrium diagrams. Part B gives the thermodynamic foundations of the equations for representing phase equilibria, and gives examples of the equations. The interrelation of the molar free energy of mixing and equilibrium diagrams is discussed in Section C. Those interested in the prediction of critical mixing points (i.e. plait points) will find Section II., D. especially useful. Part E. is a brief review of methods to predict the variation of activity coefficients with temperature.

The application of the Redlich-Kister equations to the cases of binary and ternary two phase liquid equilibria is taken up in Section III. The equations are presented and their ability to represent ternary liquid equilibria is demonstrated. Part C. presents relations enabling one to tell if a given set of Redlich-Kister equation parameters will represent a system having one or more than one liquid-phase. Equations enabling prediction of critical points from equation parameters are given.

Section IV deals with the problems of determining equation parameters from experimental data. Methods of determination of the parameters for the cases of binary liquid-liquid and vapor-liquid equilibria are discussed in Section A. The ternary liquid-liquid case is taken up in Section B. Methods of visual curve fitting are discussed. The problems of the use of least squares in the case of the Redlich-Kister equations are surveyed; approximate and exact methods of least squares curve fitting are applied. Those interested in fitting equations that are non-linear in equation parameters will find this section useful.

The feasibility of the Redlich-Kister equations to represent and correlate ternary liquid-liquid equilibria is determined in Section V. The questions of the preceeding section have been set down as research hypotheses for the specific case of the Redlich-Kister equations. Part A tests the hypothesis that equation parameters determined from binary data can be used to predict ternary liquid-liquid equilibria. Parts B and C attempt to answer question 3 of the preceeding section pertaining to the usefulness of homologous series of systems in predicting liquid-liquid equilibria. The conclusions as to the feasibility of the Redlich-Kister equations in representing phase equilibria are presented in Section VI as well as recommendations for future work.

II. REVIEW OF THE LITERATURE RELATED TO LIQUID-LIQUID EQUILIBRIA

A. Review of Binary and Ternary Liquid-Liquid Phase Diagrams:(7,13,22)

Figure 1 is a plot of composition versus temperature for a two component system in which there is limited liquid phase miscibility. Below the temperature T_c, components A and B are only partially miscible in the range shown. Specification of a temperature T_1, requires for this system that when there are two phases they must have a composition of x_{B_1} and x_{B_2} respectively. This fact is given by the phase rule:

$$V = C + 2 - P = 2 + 2 - 2 = 2$$

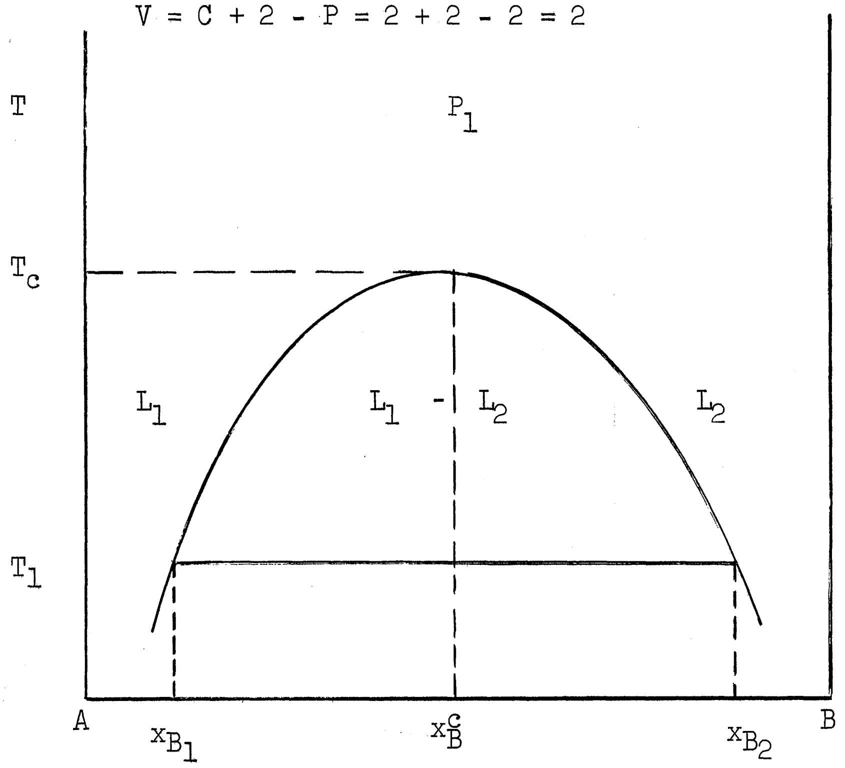


Figure 1. Partially Miscible Binary System.

Specification of pressure and temperature, P_1 and T_1 therefore defines the system as seen from the diagram. Actually T-x diagrams for systems consisting only of condensed phases are little affected by pressure and little error is introduced by not counting pressure as a phase rule variable for such systems.

Addition of a third component, C, to the binary AB now causes the temperature composition diagram to become three dimensional. For the case where there are two condensed phases in equilibrium in a ternary the variance becomes:

$$V_c = 3 + 1 - 2 = 2$$

This means that in addition to specifying the temperature we must specify one composition variable, say x_A, the mole fraction of A in phase one, to specify the system.

Figures 2 and 3 are two possibilities of the temperature-composition diagram for a system ABC where A and B are partially miscible and C is completely miscible with both A and B. The familiar trangular composition diagram has been used.

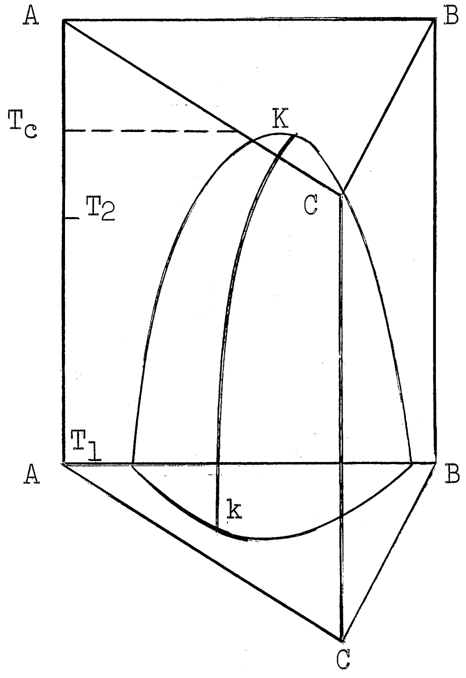


Figure 2. $T-x_A-x_B$ Diagram Type I.

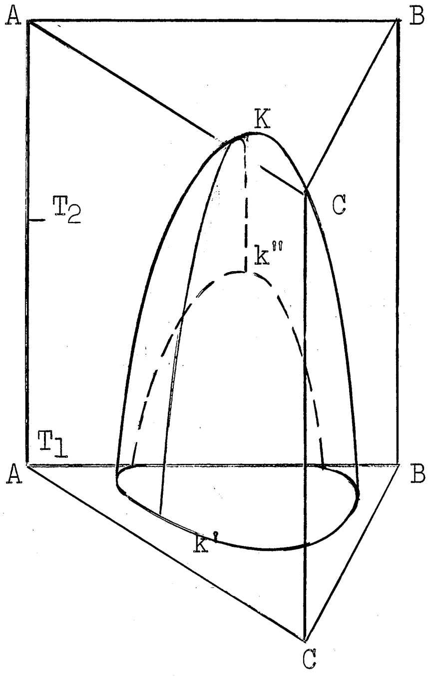


Figure 3. $T-x_A-x_B$ Diagram Type II.

In Figure 2 there is no ternary critical point. The point K lies in the T-A-B plane and is the point (T_c, a) in Figure 1, the critical point of the binary solution. Figure 3 shows the case where there is a ternary critical point K, in addition to the binary critical point k.

Isothermal cuts of the solid figures shown in Figure 2 and 3 are shown below:

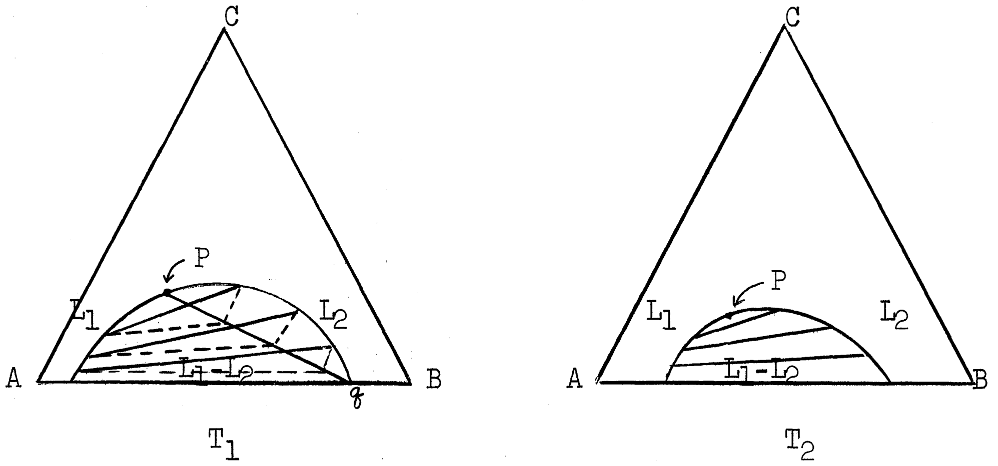


Figure 4. Isothermal Cuts of Figure 2.

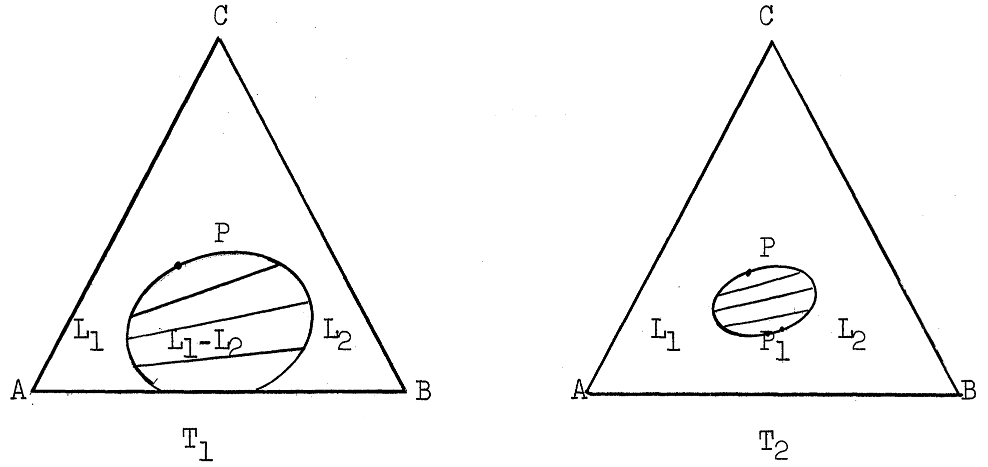


Figure 5. Isothermal Cuts of Figure 3.

Each of these isothermal cuts has at least one critical point or plait point, P where the two liquid phases become identical. At T_2 in Figure 5 the two phase region lies entirely within the ternary region and there are two plait points P and P'. The curves in Figures 4 and 5 are known as binodal curves and the straight lines connecting points on the binodal curves are known as tie lines. The tie lines connect the compositions of liquid phase one (L_1) in equilibrium with liquid phase two (L_2). In Figures 2 and 3 the lines kK and k'Kk" are the loci of the plait points shown in the isothermal cuts. Since the tie lines in the ternary case are usually not parallel to the AB edge of trangular diagram P does not have to occur at the maximum point of the binodal curve. In the binary case the tie lines in the T-x figure parallel to the AB edge and the critical point does occur at the maximum of the temperature composition curve.

The line Pq in Figure 4 (T_1) is known as a convolute line and is useful in correlating the tie lines. It is simply the locus of points which are the intersections of the dashed lines drawn from the end points of the tie lines parallel to the A-C and A-B edges of the triangular diagram.

Figure 6 shows isothermal cuts of some of the cases of systems consisting of liquid phases where there is more than one pair of partially miscible constituents.

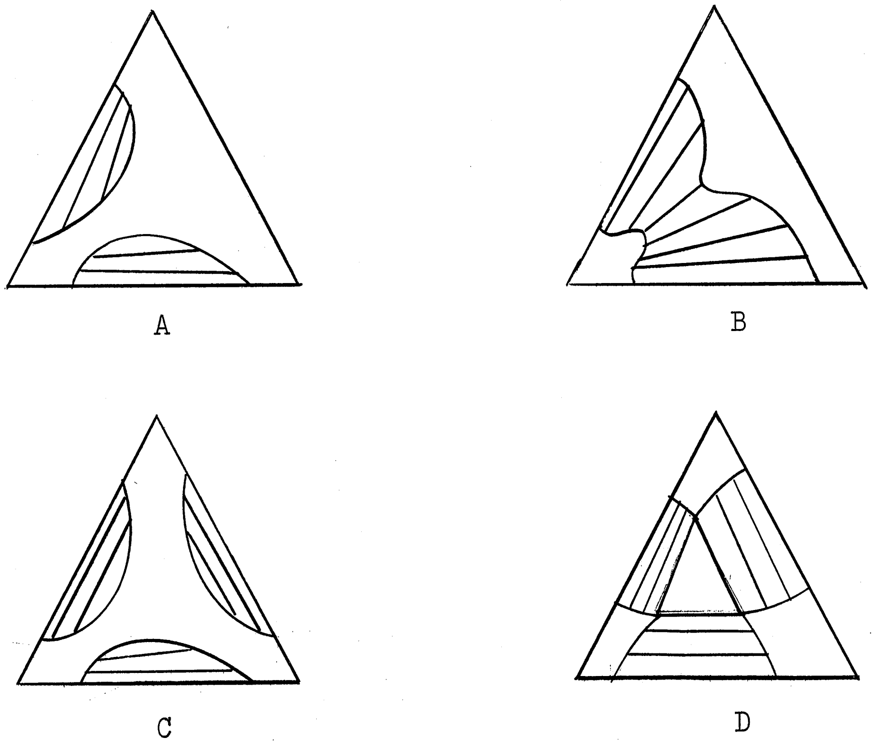


Figure 6. Examples of Ternary Isotherms - Two or More Partially Miscil Binaries.

In case A there are two regions of limited miscibility. In case B these two regions have fused together, case C shows three two phase regions. In D the two phase regions of C have fused together to give a three phase region. Given T_1, the compositions of the three phases in equilibrium are fixed by nature since the phase rule states that:

$$V_c = C + 1 - P = 3 + 1 - 3 = 1$$

Therefore specification of only one phase rule variable (i.e. T) specifies the system.

Note that in Figure 1, 2, and 3 the temperature range has been limited to that range where only liquid phases exist. At lower temperatures for most systems solid phases appear and the resulting phase diagrams become more complex. Figure 7 is an example of a ternary system of the type shown in Figure 4. The binary T-x diagrams are shown at the edges of the ternary diagram. The solid phases consist only of the pure components A, B, and C. The systems AC and BC are of the simple eutectic type. The system AB has two eutectics and a region of immiscibility in the liquid state similar to Figure 1. The triangular diagram shows the projection of lines of three phase equilibrium.

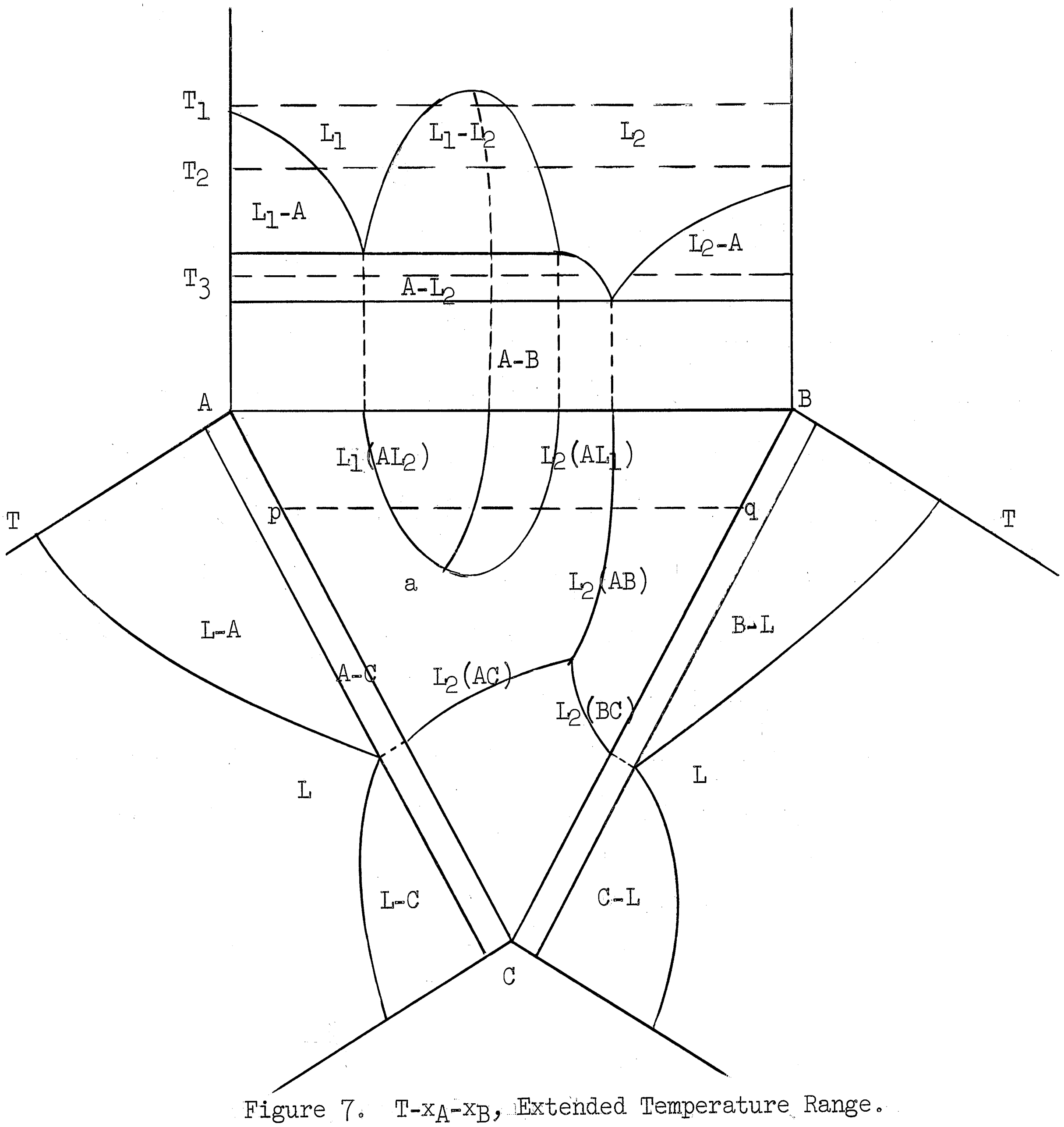


Figure 7. T-x_A-x_B, Extended Temperature Range.

At T_1 the isothermal section would look similar to Figure 4. Figure 8 shows the isothermal section at T_2. In addition to the two phase region L_1-L_2 there now appears a second two phase region L_1-A. The dotted curve is the locus of points giving liquid composition in the three phase equilibrium L_1-A-L_2 shown in Figure 7.

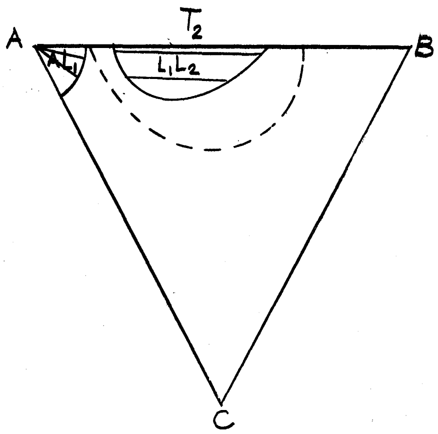
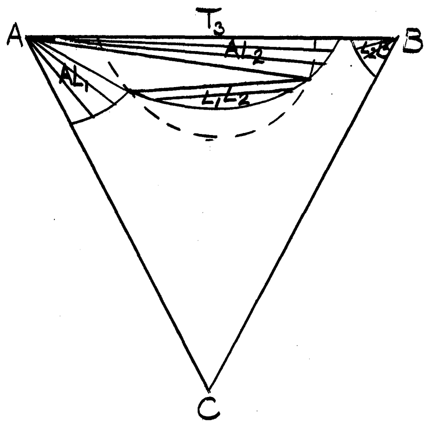


Figure 8. Isothermal Cuts of Figure 7.



ure 9. Isothermal Cuts of Figure 7.

The cut at T_3 is given in Figure 9. Since this temperature is below the AL_1 eutectic the dotted line is now intersected by the saturation curves and a three phase region occurs in which A-L_1 and L_2 are in equilibrium. Note also the appearance of the two phase region L_2B at this temperature. The L_1-L_2 region is now entirely within the ternary region. At the temperature corresponding to point a in Figure 7 the liquid-liquid region will disappear.

If one makes a vertical slice in the ternary temperature-composition figure perpendicular to the plane ABC at the line pq, Figure 10 is obtained.

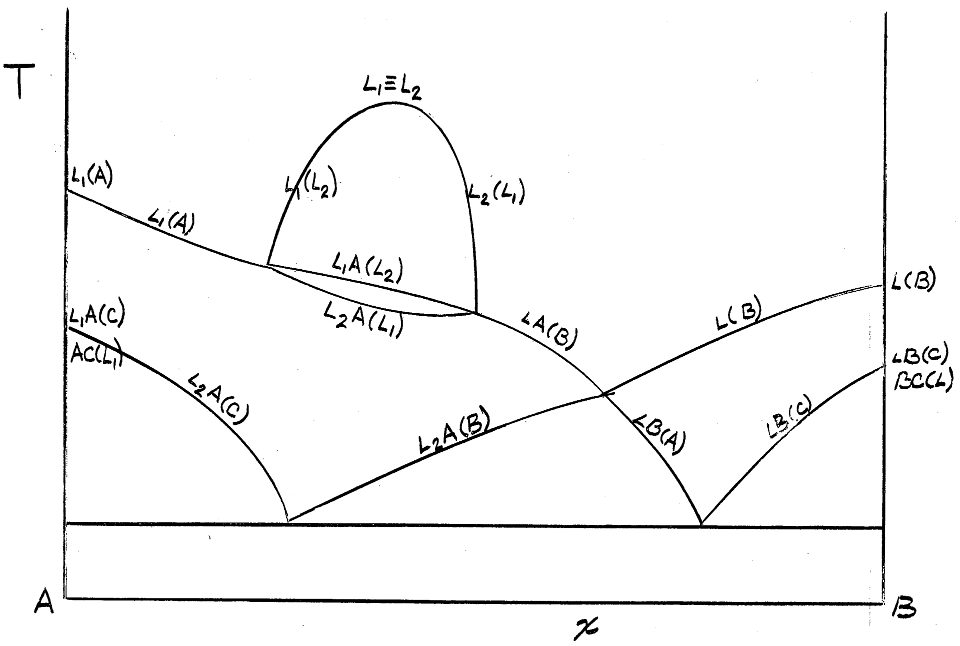


Figure 10. Vertical Section Taken Along the Line pq in Figure 7.

The notation of $L_2A(C)$ means a mixture of L_2 and A in equilibrium with C.

Numerous graphical tie line correlations have been used in the past.(14,41) A good summary of these may be found in Reference (46). These have utility in cases where systems have been partially determined experimentally in predicting those portions of the equilibrium curve where there are no data. They have little value in predicting systems for which there are no data at all.

The work this paper discusses deals with the prediction of the cases of two phase liquid equilibria shown in Figures 4 and 6B as these cases are the important ones industrially. However the methods of representation to be discussed in the next section are generally applicable to solutions of non-electrolytes.

B. The Representation of Equilibrium Data With Equations

There are two general classes of equations which have been used to correlate phase equilibria. One class consists of empirical equations relating phase rule variables directly such as the relation

$$y = ax + bx^2 + cx^3 \tag{2.1}$$

which has been used to correlate binary vapor-liquid equilibrium data, y being vapor phase composition, x being liquid phase composition.(13) The second and more important class are those equations which express the dependence of the thermodynamic function, the activity coefficient, on liquid phase composition. Because of the marked success of this latter type of representation of equilibrium data it has been chosen as the basis for the correlation of ternary liquid-liquid equilibria being developed.

1. Thermodynamic Foundations.(13)

In the case of a multicomponent system consisting of n_1, n_2 ---n_k moles of components 1, 2, ---k respectively the following is true of the free energy of the system:

$$G = G(T, P, n_1, n_2 \text{---} n_k)$$

or

$$dG = \left(\frac{\partial G}{\partial T}\right)dT + \left(\frac{\partial G}{\partial P}\right)dP + \sum_{i=1}^{k}\left(\frac{\partial G}{\partial n_i}\right)dn_i \tag{2.2}$$

where it is understood that in the partial differentiation all variables are constant except that appearing in the denominator of the partial derivative.

If we consider an infinitesimal reversible process in which neither the amount nor the composition of the system changes, i.e.:

$$dn_1 = dn_2 = \cdot\cdot\cdot\cdot = dn_k = 0 \ .$$

Then Equation (2.2) becomes:

$$dG = \left(\frac{\partial G}{\partial T}\right) dT + \left(\frac{\partial G}{\partial P}\right) dP \ . \qquad (2.3)$$

For this case from the first and second laws of thermodynamics:

$$dG = -SdT + VdP \ . \qquad (2.4)$$

Comparison of (2.3) and (2.4) gives

$$\left(\frac{\partial G}{\partial T}\right) = -S \quad , \quad \left(\frac{\partial G}{\partial P}\right) = V \ . \qquad (2.5)$$

The partial derivative $\frac{\partial G}{\partial n_i}$ is called the chemical potential of the ith component and is denoted by μ_i. It is also frequently denoted as $\overline{G}_i$, the partial molal ~~from~~ free energy of the ith constituent. This notation is used interchangeably.

On combination of (2.2) and (2.5) there results:

$$dG = -SdT + VdP + \sum_{i=1}^{k} \overline{G}_i \, dn_i \ . \qquad (2.6)$$

For the case of a system at constant temperature and pressure:

$$dG = \sum_{i=1}^{k} \overline{G}_i \, dn_i \qquad [T, P] \ . \qquad (2.7)$$

Integrating (2.7) at constant composition:

$$G = \sum_{i=1}^{k} \overline{G}_i \, n_i \ . \qquad (2.8)$$

If we make infinitesimal changes in P, T and the number of moles, we obtain:

$$G + dG = \sum_{i=1}^{k} (n_i + dn_i)(\bar{G}_i + d\bar{G}_i) \tag{2.9}$$

Subtracting (2.8) from (2.9) and neglecting higher order differentials:

$$dG = \sum_{i=1}^{k} (\bar{G}_i dn_i + n_i d\bar{G}_i) \tag{2.10}$$

On comparison of (2.10) with (2.6) there follows:

$$SdT - VdP + \sum_{i=1}^{k} n_i d\bar{G}_i = 0 \tag{2.11}$$

which is the Gibbs-Duhem equation.

At constant temperature and pressure, and dividing (2.11) by the total number of moles one obtains:

$$\sum_{i=1}^{k} x_i d\bar{G}_i = 0 \qquad [T,P] \tag{2.12}$$

The fugacity f_i, is defined by:

$$d\bar{G}_i = RT\, d\ln f_i \tag{2.13}$$

Combining (2.12) and (2.13)

$$\sum_{i=1}^{k} x_i\, d\ln f_i = 0 \qquad [T,P] \tag{2.14}$$

The activity, a_i is defined:

$$a_i = f_i / f_i^o \tag{2.15}$$

where f_i^o is the fugacity of component i at the same temperature as f_i, but in some standard state. In the case being considered the standard state would normally be the pure liquid i, at some specified temperature.

Taking the logarithm of both sides of (2.15) and differentiating we obtain since f_i^o is constant:

$$d \ln a_i = d \ln f_i \tag{2.16}$$

Thus Equation (2.14) may be written

$$\sum_{i=1}^{k} x_i \, d \ln a_i = 0 \qquad [T, P] \tag{2.17}$$

Defining the activity coefficient as:

(2.18)

we obtain upon Substitution into (2.17)

$$\sum_{i=1}^{k} (x_i \, d \ln x_i + x_i \, d \ln \gamma_i) = 0 \tag{2.19}$$

Since $$\sum_{i=1}^{k} x_i = 1 \quad , \quad \sum_{i=1}^{k} dx_i = 0 \tag{2.20}$$

Then since $x_i d \ln x_i = dx_i$:

$$\sum_{i=1}^{k} x_i \, d \ln x_i = 0 \tag{2.21}$$

It follows from (2.21) and (2.19) that:

$$\sum_{i=1}^{k} x_i \, d \ln \gamma_i = 0 \qquad [T,P] \qquad (2.22)$$

$$\text{or} \quad \sum_{i=1}^{k} n_i \, d \ln \gamma_i = 0 \qquad [T,P].$$

This may also be arranged to the form:

$$\sum_{i=1}^{k} n_i \frac{\partial \ln \gamma_i}{\partial n_i} = 0 \qquad [T,P]. \qquad (2.22a)$$

<u>Mixing and the Excess Free Energy:</u>(13) Consider the change in free energy, ΔG_M, in mixing the pure liquid components B, C, --- to form a solution consisting of b moles of B, c moles of C ----.

$$\begin{aligned} \Delta G_M &= b\bar{G}_B + c\bar{G}_C + \cdots\cdots - b\bar{G}_B^o - c\bar{G}_C^o \cdots\cdot \\ &= b(\bar{G}_B - \bar{G}_B^o) + c(\bar{G}_C - \bar{G}_C^o) + \cdots\cdots \end{aligned} \qquad (2.23)$$

where $\bar{G}_B^o$, $\bar{G}_C^o$ denote the partial molal free energies of the pure liquids B, C ---, taken to be the standard states of B, C --- respectively.

Note that combination of (2.16) with (2.13) and subsequent integration gives:

$$\bar{G}_i - \bar{G}_i^o = RT \ln a_i \quad . \qquad (2.24)$$

Substitution of (2.24) into (2.23) gives:

$$\Delta G_M = \sum_{i=1}^{k} n_i RT \ln a_i \quad . \qquad (2.25)$$

From (2.18) and (2.25):

$$\Delta G_M = \sum_{i=1}^{k} n_i RT \ln x_i + \sum_{i=1}^{k} n_i RT \ln \gamma_i \qquad (2.26)$$

For an ideal solution the activity coefficients are equal to unity and (2.26) becomes:

$$\Delta G_M^i = \sum_{i=1}^{k} n_i RT \ln x_i \qquad (2.27)$$

For real systems the activity coefficients are usually not equal to unity. The difference $\Delta G_M - \Delta G_M^i$ is called the excess free energy, ΔG^E:

$$\Delta G^E = \sum_{i=1}^{k} n_i RT \ln \gamma_i \qquad (2.28)$$

The partial molal excess free energy is obtained by differentiating partially with respect to n_i:

$$\Delta \bar{G}_i^E = \frac{\partial \Delta G^E}{\partial n_i} = RT \ln \gamma_i + RT \sum_{i=1}^{k} n_i \frac{\partial \ln \gamma_i}{\partial n_i} \qquad [T, P] \cdot (2.29)$$

Since by Equation (2.22a) $\sum_{i=1}^{k} n_i \frac{\partial \ln \gamma_i}{\partial n_i} = 0$

$$\Delta \bar{G}_i^E = RT \ln \gamma_i \qquad (2.30)$$

The Q function is defined as:

$$Q = \frac{\Delta G^E}{2.303\, RT \sum_i n_i} = \frac{\Delta \underline{G}^E}{2.303\, RT} \qquad (2.31)$$

where $\Delta \underline{G}^E$ represents the molar excess free energy.

The partial molar value of Q with respect to component i is:

$$\bar{Q}_i = \frac{\partial \sum_{i=1}^{k} n_i Q}{\partial n_i} = \frac{1}{2.303RT} \Delta \bar{G}_i^E \tag{2.32}$$

From (2.32) and (2.30) it follows:

$$\bar{Q}_i = \log_{10} \gamma_i \tag{2.33}$$

If either ΔG^E or Q are known as a function of composition, by partial differentiation with respect to n_i it is possible to obtain a relation giving the dependence of the activity coefficient of this constituent on the composition of the solution. Since the mole fractions of the various components are not all independent $\Delta \bar{G}_i^E$ is not equal to $\frac{\partial \Delta G^E}{\partial x_i}$ and $\bar{Q}_i$ is not equal to $\frac{\partial Q}{\partial x_i}$.

A formula may be derived which gives any partial molal quantity as a function of partial derivatives with respect to composition.(5) For any extensive property, R, as was shown in the case of Equation (2.2):

$$dR = \sum_{i=1}^{k=1} \bar{R}_i dn_i \tag{2.34}$$

Integrating (2.34) at constant composition:

$$R = \sum_{i=1}^{k} \bar{R}_i n_i \tag{2.35}$$

Differentiating (2.35):

$$dR = \sum_{i=1}^{k} \bar{R}_i dn_i + \sum_{i=1}^{k} n_i d\bar{R}_i \tag{2.36}$$

Comparing (2.34) and (2.36) it follows that:

$$\sum_{i=1}^{k} n_i d\bar{R}_i = 0 \tag{2.37}$$

Considering one mole of solution it follows from (2.34), (2.35) and (2.37) that:

$$d\underline{R} = \sum_{i=1}^{k} \overline{R}_i \, dx_i \tag{2.38}$$

$$\underline{R} = \sum_{i=1}^{k} x_i \overline{R}_i \quad . \tag{2.39}$$

$$\sum_{i=1}^{k} x_i \, d\overline{R}_i = 0 \quad . \tag{2.40}$$

$\underline{R}$ means R per mole of solution in (2.38), (2.39) and (2.40).

From the fact that $\sum_{i=1}^{k} x_i = 1$ we obtain:

$$dx_k = -\sum_{i=1}^{k-1} dx_i \quad . \tag{2.41}$$

Eliminating x_k from (2.38) by means of (2.41);

$$d\underline{R} = \sum_{i=1}^{k-1} (\overline{R}_i - \overline{R}_k) \, dx_i \tag{2.42}$$

Since x_1 --- x_{k-1} are independent variables:

$$\left(\frac{\partial \underline{R}}{\partial x_i} \right) = \overline{R}_i - \overline{R}_k \tag{2.43}$$

Noting that $\sum_{i=1}^{k} x_i = 1$, (2.39) becomes (2.44)

$$\underline{R} = \sum_{i=1}^{k-1} (\overline{R}_i - \overline{R}_k) x_i + \overline{R}_k \tag{2.45}$$

Substituting (2.43) into (2.45) and rearranging:

$$\overline{R}_k = \underline{R} - \sum_{i=1}^{k-1} x_i \frac{\partial \underline{R}}{\partial x_i} \tag{2.46}$$

This equation gives the partial molal value of R for the component k whose composition variable was eliminated. From (2.46) and (2.43) it follows that:

$$\bar{R}_i = \underline{R} + \frac{\partial \underline{R}}{\partial x_i} - \sum_{i=1}^{k-1} x_i \frac{\partial \underline{R}}{\partial x_i} \tag{2.47}$$

Equation (2.47) gives $\bar{R}_i$ for all components except the kth component.

Note that for the case of the Q function, Q is an intensive property. Therefore replacing $\underline{R}$ with Q

$$\log_{10} \gamma_i = Q + \frac{\partial Q}{\partial x_i} - \sum_{i=1}^{k-1} x_i \frac{\partial Q}{\partial x_i} \tag{2.48}$$

$$\log_{10} \gamma_k = Q - \sum_{i=1}^{k-1} x_i \frac{\partial Q}{\partial x_i} \quad . \tag{2.49}$$

Similar expressions may be obtained for $\underline{\Delta G^E}$. Expressions for the activity coefficients derived using Equations (2.48) and (2.49) are automatically consistent with the Gibbs-Duhem equation at constant [T,P].(13)

2. Representations of the Molar Excess Free Energy:

The Wohl Representation of $\underline{\Delta G^E}$: Wohl(54) expressed the dependence of $\underline{\Delta G^E}$, the molar excess free energy, on the composition of the liquid phase by the expansion:

$$\frac{\Delta G^E}{2.303\, RT \sum_i q_i x_i} = \sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} + \sum_{ijkl} z_i z_j z_k z_l a_{ijkl} + \cdots \tag{2.50}$$

where q_i, q_j, q_k, q_l --- are constants Wohl called the effective molar volumes of the constituents i, j, k, l, --- and z_i, z_j, z_k, z_l --- are the effective volumetric fractions of these constituents. z_i is defined by:

$$z_i = \frac{q_i x_i}{\sum_j q_i x_j} \tag{2.51}$$

Equation (2.50) is written as an equation of the fourth order. In practice equations of order higher than this are rarely used. Using Wohl's equation of the third order it can be shown that by making certain simplifying assumptions the third order equations of Van Laar(47) Margules(20) and Scatchard and Hamer(39) are obtained.

After introducing the new constants A and B:

$$A = q_1(2a_{12} + 3a_{122}) \quad , \quad B = q_2(2a_{12} + 3a_{112})$$

the third order equation for the binary case becomes:

$$\frac{\Delta G^E}{2.303\,RT} = \left(x_1 + \frac{q_2}{q_1} x_2\right) z_1 z_2 \left[z_1 B \frac{q_1}{q_2} + z_2 A\right] \tag{2.52}$$

It may then be shown that:

$$\log_{10} \gamma_1 = z_2^2 \left[A + 2 z_1 \left(B \frac{q_1}{q_2} - A\right)\right] \tag{2.53}$$

which is the Scatchard-Hamer representation of $\log \gamma_1$.

Table I gives the simplifications necessary to convert (2.53) to the forms derived by earlier authors.

TABLE I

COMPARISON OF THIRD ORDER EXPRESSIONS FOR LOG γ_1 FOR A BINARY

Type	Simplification	log γ_1	Ref.
Scatchard	$q_2/q_1 = V_2/V_1$	$(1 - z_1)^2[A+2z_1(BV_1/V_2-A)]$	39
Van Laar	$q_2/q_1 = B/A$	$\dfrac{A}{\left[1 + \dfrac{x_1}{x_2}\dfrac{A}{B}\right]^2}$	47
Margules	$q_2/q_1 = 1$	$(1 - x_1)^2[A+2x_1(B-A)]$	20

Much more complete tables similar to Table I may be found in Reference (13) for the binary and ternary cases.

The Redlich-Kister Equations: In 1948 Redlich and Kister introduced a simple, highly successful empirical representation of the Q function.$^{(33,34)}$ This representation can also be derived by suitable rearrangement of the Wohl equations.$^{(13)}$ For the binary case:

$$Q = x_1 x_2\left[B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \cdots\right. . \qquad (2.54)$$

Retaining only the B_{ij} and C_{ij} terms, application of Equations (2.48) and (2.49) gives:

$$\log_{10}\gamma_1 = x_2^2\left[B_{12} + C_{12}(-x_2 + 3x_1)\right] \qquad (2.55)$$

$$\log_{10}\gamma_2 = x_1^2\left[B_{12} + C_{12}(x_1 - 3x_2)\right] \qquad (2.56)$$

For the case of a ternary Q is represented:

$$\begin{aligned} Q = {} & x_1 x_2\left[B_{12} + C_{12}(x_1 - x_2) + D_{12}(x_1 - x_2)^2 + \cdots\right] + \\ & + x_2 x_3\left[B_{23} + C_{23}(x_2 - x_3) + D_{23}(x_2 - x_3)^2 + \cdots\right] + \\ & + x_3 x_1\left[B_{31} + C_{31}(x_3 - x_1) + D_{31}(x_3 - x_1)^2 + \cdots\right] + \\ & + x_1 x_2 x_3\left[C + D_1 x_1 + D_2 x_2 + \cdots\right] \end{aligned} \qquad (2.57)$$

where C_1 , D_1 , D_2 are ternary coefficients and B_{ij} , C_{ij} are binary coefficients. Again where only the binary B and C coefficients are retained applying (2.49) gives for a ternary:

$$\begin{aligned}\log_{10}\gamma_1 = {} & B_{12}x_2(1-x_1)-B_{23}x_2x_3+B_{31}x_3(1-x_1)\\ & +C_{12}(x_2(2x_1(-x_1+x_2-1)-x_2))+C_{23}(2x_2x_3(-x_2+x_3))\\ & +C_{31}(x_3(2x_1(x_1-x_3-1)+x_3))\end{aligned} \tag{2.58}$$

A cyclic permutation of the subscripts gives the expressions for log γ_2 , and log γ_3 . Hence forth in this dissertation the right hand sides of (2.58) and the expressions for log γ_2 and log γ_3 will be denoted as F_1 , F_2 and F_3 respectively.

The success of the Redlich-Kister equations in correlating vapor-liquid equilibria led to their selection as a basis for the correlation of ternary liquid-liquid equilibria. In practice it has been found that retaining only the binary B_{ij} and C_{ij} coefficients is sufficient to correlate most cases of ternary vapor liquid equilibria,(53) and only these coefficients have been retained in the equations to be used as the basis for the liquid-liquid correlation.

C. Composition-Free Energy Diagrams(5,7)

It can be seen from Equation (2.26) that at constant temperature, $\Delta\underline{G}_M$, the molar free energy of mixing is a function only of composition:

$$\Delta\underline{G}_M = \frac{\Delta G_M}{\sum_i n_i} = \sum_{i=1}^{k} x_i RT \ln x_i + \sum_{i=1}^{k} x_i RT \ln \gamma_i \tag{2.59}$$

For the binary liquid case $\Delta \underline{G}_M$ may be plotted against x_1, the mole fraction of component 1 in the liquid. If the activity coefficients of 1 and 2 are unity then a curve of the function

$$\Delta \underline{G}_M^i = RT\left[x_1 \ln x_1 + (1-x_1)\ln(1-x_1)\right]$$

will be obtained as is shown in Figure 11.

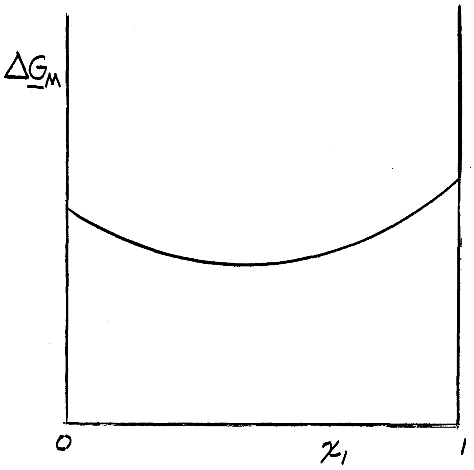


Figure 11. Ideal Binary at T_1.

In real systems the function for the molar excess free energy $\Delta \underline{G}^E$ is superimposed on the curve shown in Figure 11. Depending on the nature of the function $\Delta \underline{G}^E$, only one or more than one liquid phase will be encountered as x_1 increases from 0 to 1. Figure 12 shows a case where the system is homogeneous throughout the liquid range.

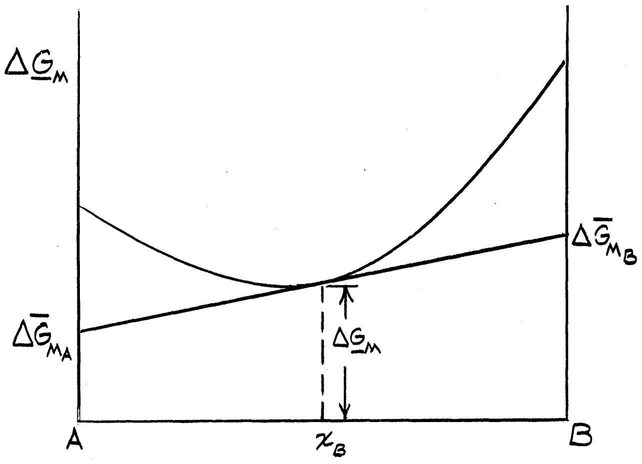


Figure 12. Real Homogeneous Binary.

It may now be seen graphically that for a solution of composition x_B, the partial molar free energy of mixing of component A is given by the intercept with the A axis of the tangent to the $\Delta\underline{G}_M$ curve at x_B. This follows from Equation (2.46). (See Appendix A).

$$\Delta\bar{G}_{M_A} = \frac{\partial \Delta G_M}{\partial n_A} = \Delta\underline{G}_M - x_B \frac{\partial \Delta\underline{G}_M}{\partial x_B}$$

$\Delta\underline{G}_M$ appearing in (2.61) is the value of the $\Delta\underline{G}_M$ versus composition curve at the point x_B shown.

Figure 13 shows the case of a binary system having limited miscibility in liquid phase.

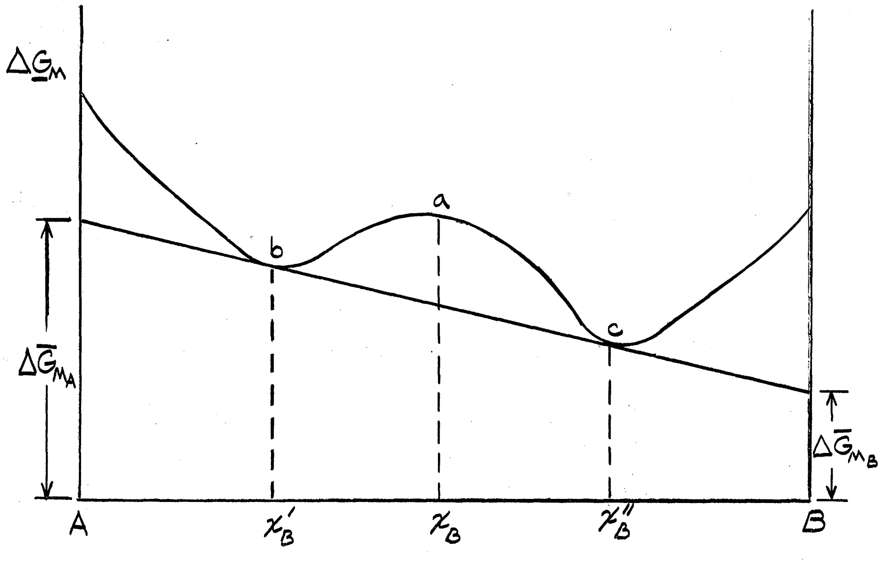


Figure 13. Binary Having Two Liquid Phases.

In this case there are two inflection points in the curve. Mixtures having a total composition between x_B' and x_B'' will break into phases of composition x_B' and x_B'' which are the abscissi of the points of common tangency to the curve. Note that there is only one set of these points at a given temperature, a consequence of the phase rule which states that when there are two phases, given pressure and temperature a binary system is completely specified.

In the general case equations similar to (2.6) may be written for any number of phases of which the total system may be composed:

$$\begin{aligned} dG' &= -S'dT + V'dP + \sum_{i=1}^{k} \bar{G}_i' dn_i' \\ dG'' &= -S''dT + V''dP + \sum_{i=1}^{k} \bar{G}_i'' dn_i'' \\ &\vdots \end{aligned} \qquad (2.62)$$

Since G represents the total free energy of the system:

$$G = G' + G'' + G''' + \cdots \qquad (2.63)$$

Note also

$$\Delta G_M' = G' - n_A' G_A^o - n_B' G_B^o \quad \cdots \qquad (2.64)$$

$$\Delta G_M'' = G'' - n_A'' G_A^o - n_B'' G_B^o \quad \cdots \qquad (2.65)$$

$$\vdots$$

At equilibrium Gibbs(9) proved that dG = 0; therefore

$$dG = dG' + dG'' + dG''' + \cdots = 0 \qquad (2.66)$$

From (2.66) and (2.62):

$$\sum_{i=1}^{k} \bar{G}_i' dn_i' + \sum_{i=1}^{k} \bar{G}_i'' dn_i'' + \cdots = 0 \qquad (2.67)$$

Since the total mass of each component remains constant:

$$\begin{aligned} dn_A' + dn_A'' + dn_A''' + \cdots &= 0 \\ dn_B' + dn_B'' + dn_B''' + \cdots &= 0 \\ \vdots \end{aligned} \qquad (2.68)$$

In order to satisfy (2.67) and (2.68) it is necessary that:

$$\begin{aligned} \bar{G}_A' = \bar{G}_A'' = \cdots &= \bar{G}_A^z \\ \bar{G}_B' = \bar{G}_B'' = \cdots &= \bar{G}_B^z \\ \vdots \end{aligned} \qquad (2.69)$$

From (2.65) it follows by partial differentiation with respect to n_i .

$$\Delta\bar{G}_{M_i}' = \bar{G}_i' - G_i^o \qquad (2.70)$$

It follows from (2.69) and (2.70) that:

$$\Delta\bar{G}_{M_i}' = \Delta\bar{G}_{M_i}'' = \Delta\bar{G}_{M_i}''' = \cdots \qquad (2.71)$$

The result given in (2.71) together with that of (2.61) is the mathematical statement of what is illustrated graphically in Figure 13. The common tangent at points b and c satisfies Equation (2.71).

Another way of looking at this is that at equilibrium a system is in a state of minimum free energy. Rather than remaining a single phase of composition x_B having a free energy corresponding to point a in Figure 13, the system can minimize its free energy by breaking into two phases each having a molar free energy given at b and c, the tangent points.

Addition of a third component to the hypothetical system of Figure 13 results in a three dimensional representation of the dependence of $\Delta \underline{G}_M$ on liquid composition shown in Figure 14.

The case shown is one in which component C is miscible with both A and B, A and B being partially miscible. The locus of points of common tangency of planes to the free energy surface projects in the plane ABC as the familiar binodal curve for a ternary liquid-liquid system. The lines connecting common points of tangency of a given tangent plane project in the ABC plane as the tie lines. As the plait point is approached the reverse cleavage in the free energy surface becomes less and less finally damping out; the surface becomes convex downward, and the solution is homogeneous.

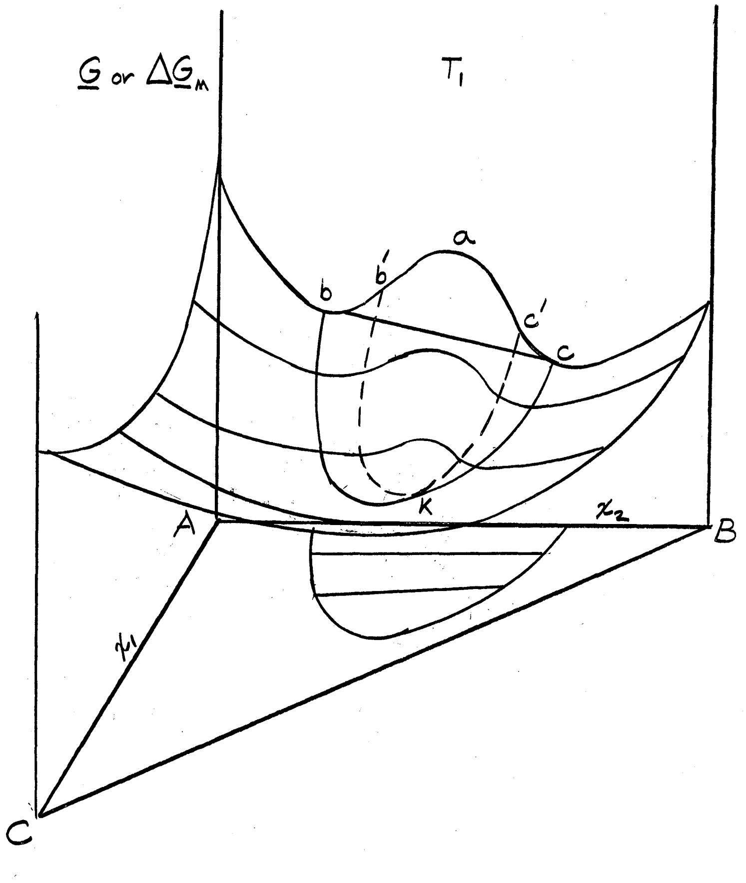


Figure 14. $\Delta \underline{G}_M - x_1 - x_2$, Partially Miscible Ternary Isotherm.

The Redlich-Kister representation for the ternary $\Delta \underline{G}_M$ surface,(34) employing only the first two binary coefficients is:

$$\frac{\Delta G_M}{2.303RT} = x_1 \log_{10} x_1 + x_2 \log_{10} x_2 + x_3 \log_{10} x_3 + x_1 x_2 \left(B_{12} + C_{12}(x_1 - x_2)\right) + x_2 x_3 \left(B_{23} + C_{23}(x_2 - x_3)\right) + x_3 x_1 \left(B_{31} + C_{31}(x_3 - x_1)\right) \qquad (2.72)$$

Figure 15 gives the contours of hypothetical surface calculated by assuming $B_{12} = 1.3$, $B_{31} = 0.5$, $B_{23} = C_{12} = C_{23} = C_{31} = 0$. The numbers on the graph are values of $\frac{\Delta G_M}{2.303RT}$.

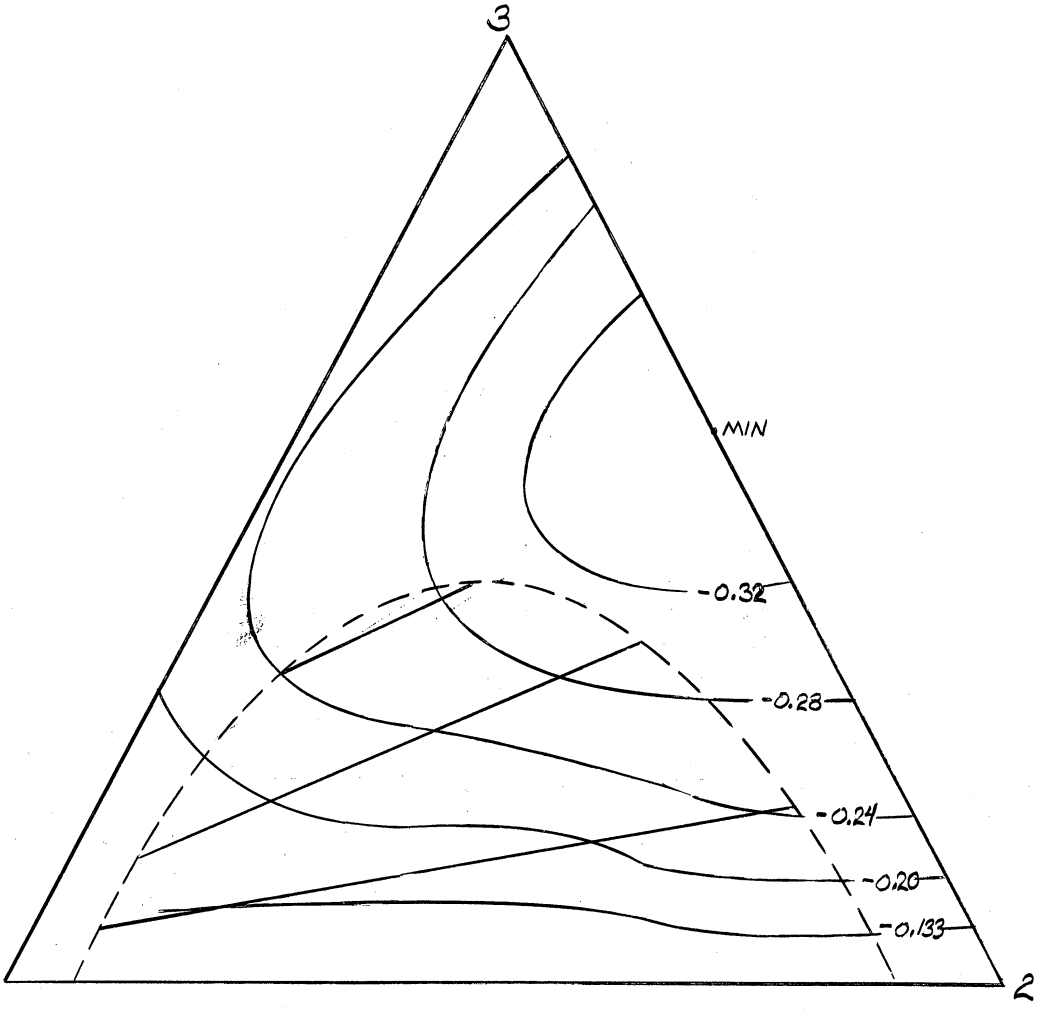


Figure 15. Hypothetical $\Delta \underline{G}_M$ Surface as Represented by Equation (2.72). $B_{12} = 1.3$, $B_{31} = 0.5$, $B_{23} = B_{31} = C_{12} = C_{23} = C_{31} = 0$.

D. Phase Stability and Critical Phases

Of considerable importance in this research are those relations which enable one to predict phase stability and critical mixing points. A knowledge of the location of a plait point in a partially miscible ternary is especially desirable in engineering considerations. The relations which follow were originally derived by Gibbs.(9) The development given by Haase(12) has been abstracted and presented here.

Consider a closed isolated system having a total entropy S. The second law of thermodynamics states that for any infinitesimal change:

$$dS \geqslant 0 \qquad \text{(isolated system)} . \qquad (2.73)$$

For an adiabatic change from state I to state II there are three situations:

$$\Delta S = S_{II} - S_{I} = 0 \qquad \text{(reversible change)} \qquad (2.74a)$$

$$\Delta S = S_{II} - S_{I} > 0 \qquad \text{(irreversible change)} \qquad (2.74b)$$

$$\Delta S = S_{II} - S_{I} < 0 \qquad \text{(impossible change)} \qquad (2.74c)$$

If we propose a reaction "old system → new system" then it follows from (2.74):

$$\Delta S > 0 \quad \text{(old system unstable)} \qquad (2.75a)$$

$$\Delta S = 0 \quad \text{(neutral equilibrium-a critical state)} \qquad (2.75b)$$

$$\Delta S < 0 \quad \text{(old system stable)} \qquad (2.75c)$$

Since the system under consideration is isolated (that is there is no energy transfer between system and surroundings, $Q = 0$, $W = 0$) the following additional relations hold:

$$\Delta U = 0, \ \Delta V = 0, \ \Delta n_i = 0 \quad (i = 1, 2, \ldots N) . \qquad (2.76)$$

where N is the number of components.

The simplest case of stability is thermal and mechanical stability. Consider an isolated system consisting of a single phase of unchanging composition ($\underline{U}, \underline{V}$). It is possible to form from n moles of the original phase n' moles of one phase ($\underline{U} + \Delta\underline{U}, \underline{V} + \Delta\underline{V}$) as well as n" moles of a second phase ($\underline{U} + \Delta\underline{U}^*, \underline{V} + \Delta\underline{V}^*$).

$$\mathrm{I}(\underline{U},\underline{V}) \rightarrow \mathrm{II}(\underline{U}+\Delta\underline{U}, \underline{V}+\Delta\underline{V}) + \mathrm{III}(\underline{U}+\Delta\underline{U}^*, \underline{V}+\Delta\underline{V}^*)$$

(isolated system)

In order that phase I be stable according to (2.75c):

$$\Delta S = n'\Delta\underline{S} + n''\Delta\underline{S}^* < 0 \qquad (2.77)$$

$$\Delta U = n'\Delta\underline{U} + n''\Delta\underline{U}^* = 0 \qquad (2.78)$$

$$\Delta V = n'\Delta\underline{V} + n''\Delta\underline{V}^* = 0 \qquad (2.79)$$

$$n = n' + n'' \quad . \qquad (2.80)$$

Expanding $\Delta\underline{S}$ as a function of $\underline{U}$ and $\underline{V}$ by Taylor series expansion:

$$\Delta\underline{S} = \frac{\partial\underline{S}}{\partial\underline{U}}\Delta\underline{U} + \frac{\partial\underline{S}}{\partial\underline{V}}\Delta\underline{V}$$

$$+ \frac{1}{2}\left[\frac{\partial^2\underline{S}}{\partial\underline{U}^2}(\Delta\underline{U})^2 + 2\frac{\partial^2\underline{S}}{\partial\underline{U}\,\partial\underline{V}}\Delta\underline{U}\Delta\underline{V} + \frac{\partial^2\underline{S}}{\partial\underline{V}^2}(\Delta\underline{V})^2\right] + \cdots$$

Similarly for $\Delta\underline{S}^*$ after utilizing (2.79), (2.80):

$$\Delta\underline{S}^* = -\frac{n'}{n''}\left[\frac{\partial\underline{S}}{\partial\underline{U}}\Delta\underline{U} + \frac{\partial\underline{S}}{\partial\underline{V}}\Delta\underline{V}\right]$$

$$+ \frac{1}{2}\left(\frac{n'}{n''}\right)^2\left[\frac{\partial^2\underline{S}}{\partial\underline{U}^2}(\Delta\underline{U})^2 + 2\frac{\partial^2\underline{S}}{\partial\underline{U}\,\partial\underline{V}}\Delta\underline{U}\Delta\underline{V} + \frac{\partial^2\underline{S}}{\partial\underline{V}^2}(\Delta\underline{V})^2\right] + \cdots$$

Combining these last two equations with (2.77) and (2.80):

$$\Delta S = \frac{n'n}{2n''}\left[\frac{\partial^2 \underline{S}}{\partial \underline{U}^2}(\Delta \underline{U})^2 + 2\frac{\partial^2 \underline{S}}{\partial \underline{U}\partial \underline{V}}\Delta \underline{U}\Delta \underline{V} + \frac{\partial^2 \underline{S}}{\partial \underline{V}^2}(\Delta \underline{V})^2\right] + \cdots < 0 \cdot$$

It follows from a property of the Taylor series that

$\delta^2 \underline{S}(\underline{U},\underline{V}) < 0$ or $\delta^2 \underline{S}(\underline{U},\underline{V})$ is negative definite (2.81) where $\delta^2 \underline{S}(\underline{U},\underline{V})$ represents the entity in the brackets of the preceeding equation. Similar consideration of additional terms in the series does not give additional independent relations.

It follows from a rule of algebra (see Appendix A) that the quadratic form $\delta^2 S(\underline{U},\underline{V})$ will be negative - definite if:

$$\frac{\partial^2 \underline{S}}{\partial \underline{U}^2} < 0 , \quad \frac{\partial^2 \underline{S}}{\partial \underline{U}^2}\frac{\partial^2 \underline{S}}{\partial \underline{V}^2} - \left(\frac{\partial^2 \underline{S}}{\partial \underline{U}\partial \underline{V}}\right)^2 > 0 \cdot \qquad (2.81a)$$

Phase I will have thermal and mechanical stability if the requirements of (2.81) are met.

By reasoning analogous to the above, other relations for phase stability may be derived. In the case of the Gibbs free energy function, G, it is easily shown that for the reaction "old system to new system" at constant T and P:

$\Delta G < 0$ (old phase unstable) (2.82)

$\Delta G = 0$ (neutral equilibrium-a critical state) (2.83)

$\Delta G > 0$ (old phase stable) (2.84)

For the case of a binary where C_V is positive, by introduction of suitable definitions it can be shown from (2.81) that for a stable phase

$$\delta^2 \underline{G}\ (T,P) > 0 \tag{2.85}$$

By an analogous procedure (see Appendix A) to that used in deriving (2.81) it may be shown that in the case of a binary for a stable phase

$$\left(\frac{\partial^2 \underline{G}}{\partial x^2}\right)_{T,P} > 0 \quad \text{or} \quad \left[\delta^2 \underline{G}(x)\right]_{T,P} > 0 \ . \tag{2.86}$$

(Note: the notation δ, δ^2,... refers to first order, second order terms, etc. in the Taylor series expansion).

Generalization of the development used to obtain (2.86) yields for the case of N components the following stability criterion:

$$\delta^2 \underline{G}\left(x_1, x_2, \cdots x_{N-1}\right)_{T,P} > 0 \quad [T, P \text{ const.}] \ . \tag{2.87}$$

In words this states that $\delta^2 \underline{G}(x_1, x_2, \text{---}\ x_{N-1})_{T,P}$ must be positive definite if the phase under consideration is stable. An algebraic rule states that a quadratic form is positive definite if the determinant of its coefficients with all principal minors is positive. From (2.87) it follows then that for stable phases:

$$D > 0 \quad , \tag{2.88}$$

where

$$D \equiv \begin{vmatrix} \frac{\partial^2 G}{\partial x_1^2} & \frac{\partial^2 G}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 G}{\partial x_1 \partial x_{N-1}} \\ \frac{\partial^2 G}{\partial x_2 \partial x_1} & \frac{\partial^2 G}{\partial x_2^2} & \cdots & \frac{\partial^2 G}{\partial x_2 \partial x_{N-1}} \\ \vdots & \vdots & & \vdots \\ \frac{\partial^2 G}{\partial x_{N-1} \partial x_1} & \frac{\partial^2 G}{\partial x_{N-1} \partial x_2} & \cdots & \frac{\partial^2 G}{\partial x_{N-1}^2} \end{vmatrix}$$

Note that if $\delta^2 \underline{G}(x_1 , x_2 , --- x_{N-1})_{T,P}$ or D is negative the phase under consideration is unstable. Therefore the space curve

$$D = 0$$ (2.8

separates the region in which $\delta^2 \underline{G}(x_1 , x_2 --- x_{N-1})_{T,P}$ is negative (unstable phases) from the region in which $\delta^2 \underline{G}(x_1 , x_2 --- x_{N-1})$ is positive (stable or metastable phases). Equation (2.89) is then the equation of the stability boundary. Graphically (2.89) is the curve b'Kc' in Figure 14 for a ternary system and is sometimes referred to as the spinodal curve. It is the loci of inflection points in the $\Delta \underline{G}_M$ curve found in planes perpendicular to the x_1 , x_2, plane and situated so that the tie lines lie in these planes. That region on the $\underline{G}(x_1 , x_2)$ surface between bKc and b'Kc' is known as the metastable region.

At a critical point, an infinitesimal variation in state properties causes appearance of disappearance of a phase. It must lie therefore on the stability boundary and Equation (2.89) is known as the first critical relation.

The second critical relation may be derived as follows. Consider a two phase system such as the ternary system in Figure 14. Let us formulate a path in the $\underline{G}(x_1, x_2)$ surface (at constant T and P) which passes through the unstable and metastable region, connecting two coexisting phases and which has zero length in the case of a critical phase. The equilibrium between two phases with N components at constant T and P is described by the N relations which follow from (2.69) together with $\sum_1^N x_k = 1$

$$\frac{\partial \underline{G}'}{\partial x_1} = \frac{\partial \underline{G}''}{\partial x_1}, \quad \frac{\partial \underline{G}'}{\partial x_2} = \frac{\partial \underline{G}''}{\partial x_2}, \quad \ldots \quad \frac{\partial \underline{G}'}{\partial x_{N-1}} = \frac{\partial \underline{G}''}{\partial x_{N-1}}$$

$$\underline{G}' - \sum_1^{N-1} x_i' \frac{\partial \underline{G}'}{\partial x_i} = \underline{G}'' - \sum_1^{N-1} x_i'' \frac{\partial \underline{G}''}{\partial x_i} \tag{2.90}$$

If of the N quantities:

$$\frac{\partial \underline{G}}{\partial x_1}, \quad \frac{\partial \underline{G}}{\partial x_2}, \quad \ldots \frac{\partial \underline{G}}{\partial x_{N-1}}, \quad \underline{G} - \sum_{i=1}^{N-1} x_i \frac{\partial \underline{G}}{\partial x_i} \tag{2.91}$$

N-2 are held constant, then a path is determined which behaves as that described above. Since a two phase equilibrium with N components has a variance of N, the constancy of N intensive variables (T, P, and N-2 of the quantities in (2.91) which have the same value for the two coexisting phases) corresponds to a traversing of $\underline{G}$ surface between the two phases.

Consider now a point on the stability boundary (D = 0). For an arbitrarily small variation of the state of a phase, considering only variations on the prescribed path where $\frac{\partial G}{\partial x_1}, \frac{\partial G}{\partial x_2}, \dots \frac{\partial G}{\partial x_{N-2}}$ are constant:

$$\delta D = \frac{\partial D}{\partial x_1}\delta x_1 + \frac{\partial D}{\partial x_2}\delta x_2 + \frac{\partial D}{\partial x_3}\delta x_3 + \dots \frac{\partial D}{\partial x_{N-1}}\delta x_{N-1} \tag{2.92}$$

$$\left.\begin{aligned}
\delta\left(\frac{\partial G}{\partial x_1}\right) &= \frac{\partial^2 G}{\partial x_1^2}\delta x_1 + \frac{\partial^2 G}{\partial x_1 \partial x_2}\delta x_2 + \dots \frac{\partial^2 G}{\partial x_1 \partial x_{N-1}}\delta x_{N-1} = 0 \\
\delta\left(\frac{\partial G}{\partial x_2}\right) &= \frac{\partial^2 G}{\partial x_2 \partial x_1}\delta x_1 + \frac{\partial^2 G}{\partial x_2^2}\delta x_2 + \dots \frac{\partial^2 G}{\partial x_2 \partial x_{N-1}}\delta x_{N-1} = 0 \\
&\text{— — — — — — — — — — — —} \\
\delta\left(\frac{\partial G}{\partial x_{N-2}}\right) &= \frac{\partial^2 G}{\partial x_{N-2} \partial x_1}\delta x_1 + \frac{\partial^2 G}{\partial x_{N-2} \partial x_2}\delta x_2 + \dots \frac{\partial^2 G}{\partial x_{N-2} \partial x_{N-1}}\delta x_{N-1} = 0.
\end{aligned}\right\} \tag{2.93}$$

Proceeding in the direction prescribed by (2.93) one passes from metastable phases on one side of the boundary curve (D = 0) to unstable phases on the other side. Only in the limiting case of a critical phase (which must lie on the stability curve) does one succeed in the direction prescribed by (2.93) in going continuously from stable to stable phases. At the arbitrary location on the boundary curve the expression δD can be positive as well as negative. If the point on the boundary curve coincides with a critical point δD must vanish. If δD were negative one would succeed in arriving at unstable phases ($D < 0$) on the path described by (2.93) which is impossible at the critical point. If δD were positive then it could be made negative by a sign change of the variations δx_1, δx_2, .. δx_{N-1}. Therefore for a critical phase under the constraints (2.93):

$$\delta D = 0 \tag{2.94}$$

Equations (2.92), (2.93), and (2.94) form a system of N-1 homogeneous linear equations consisting of N-1 variables. In order that these equations can be satisfied, the determinant of the coefficients must vanish. Therefore

$$D' = 0 \tag{2.95}$$

where

$$D' \equiv \begin{vmatrix} \frac{\partial^2 G}{\partial x_1^2} & \frac{\partial^2 G}{\partial x_2^2} & \cdots\cdots & \frac{\partial^2 G}{\partial x_1 \partial x_{N-1}} \\ \vdots & \vdots & & \vdots \\ \frac{\partial^2 G}{\partial x_{N-2} \partial x_1} & \frac{\partial^2 G}{\partial x_{N-2} \partial x_1} & \cdots\cdots & \frac{\partial^2 G}{\partial x_{N-2} \partial x_{N-1}} \\ \frac{\partial D}{\partial x_1} & \frac{\partial D}{\partial x_2} & \cdots\cdots & \frac{\partial D}{\partial x_{N-1}} \end{vmatrix} \tag{2.95a}$$

For a two component system at a critical solution point, therefore, it follows from (2.89) and (2.95):

$$D = \frac{\partial^2 G}{\partial x_1^2} = 0 \quad , \quad D' = \frac{\partial^3 G}{\partial x_1^3} = 0 \qquad [T, P] \ . \tag{2.96a,b}$$

Similarily for a three component system at a critical or plait point:

$$D = \frac{\partial^2 G}{\partial x_1^2}\,\frac{\partial^2 G}{\partial x_2^2} - \left(\frac{\partial^2 G}{\partial x_1\,\partial x_2}\right)^2 = 0 \qquad [T, P]\ (2.97a)$$

$$D' = \frac{\partial^2 G}{\partial x_1^2}\,\frac{\partial D}{\partial x_2} - \frac{\partial^2 G}{\partial x_1\,\partial x_2}\,\frac{\partial D}{\partial x_1} = 0 \qquad [T, P]\cdot(2.97b)$$

For a quartenary, the locus of plait points will be given by the relations:

$$D = \frac{\partial^2 G}{\partial x_1^2}\left(\frac{\partial^2 G}{\partial x_2^2}\,\frac{\partial^2 G}{\partial x_3^2} - \left(\frac{\partial^2 G}{\partial x_2\,\partial x_3}\right)^2\right) + \frac{\partial^2 G}{\partial x_2\,\partial x_1}\left(\frac{\partial^2 G}{\partial x_3\,\partial x_2}\,\frac{\partial^2 G}{\partial x_1\,\partial x_3} - \frac{\partial^2 G}{\partial x_3^2}\,\frac{\partial^2 G}{\partial x_1\,\partial x_2}\right)$$

$$+ \frac{\partial^2 G}{\partial x_3\,\partial x_1}\left(\frac{\partial^2 G}{\partial x_1\,\partial x_2}\,\frac{\partial^2 G}{\partial x_2\,\partial x_3} - \frac{\partial^2 G}{\partial x_2^2}\,\frac{\partial^2 G}{\partial x_1\,\partial x_3}\right) = 0 \qquad [T, P]\ (2.98a)$$

$$D' = \frac{\partial^2 G}{\partial x_1^2}\left(\frac{\partial^2 G}{\partial x_2^2}\,\frac{\partial D}{\partial x_3} - \frac{\partial^2 G}{\partial x_2\,\partial x_3}\,\frac{\partial D}{\partial x_2}\right) + \frac{\partial^2 G}{\partial x_1\,\partial x_2}\left(\frac{\partial^2 G}{\partial x_1\,\partial x_3}\,\frac{\partial D}{\partial x_2} - \frac{\partial^2 G}{\partial x_1\,\partial x_2}\,\frac{\partial D}{\partial x_3}\right)$$

$$+ \frac{\partial D}{\partial x_1}\left(\frac{\partial^2 G}{\partial x_1\,\partial x_2}\,\frac{\partial^2 G}{\partial x_2\,\partial x_3} - \frac{\partial^2 G}{\partial x_2^2}\,\frac{\partial^2 G}{\partial x_1\,\partial x_3}\right) = 0 \qquad [T, P]\cdot(2.98b)$$

The critical relations are of considerable utility in using algebraic representations of $\Delta \underline{G}_M$. A further discussion of the critical relations as applied to Redlich-Kister equations will be found in Part III.

E. Temperature Corrections to Activity$^{(13,34)}$

Expressions for Q or $\Delta \underline{G}^E$ involve a set of coefficients which are functions of temperature but not of composition. A given set of values for the coefficients pertain only to a single temperature. In order to predict equilibria at higher and lower temperatures a knowledge of B_{ij} and C_{ij} as functions of temperature is required.

It follows from (2.74) and the definition of activity that:

$$\ln a_i = \frac{1}{RT}\left(\bar{G}_i - \bar{G}_i^o\right) \tag{2.99}$$

Differentiating partially with respect to temperature we obtain:

$$\frac{\partial \ln a_i}{\partial T} = \frac{1}{R}\,\frac{\partial}{\partial T}\left(\frac{\bar{G}_i}{T} - \frac{\bar{G}_i^o}{T}\right) = -\,\frac{\bar{H}_i - \bar{H}_i^o}{RT^2} \tag{2.100}$$

where $\bar{H}_i$ is the partial molal free enthalpy of i in solution, $\bar{H}_i^o$ is that of pure i.

Since $a_i = x_i \gamma_i$ it follows that

$$\frac{\partial \ln \gamma_i}{\partial T} = -\,\frac{\bar{H}_i - \bar{H}_i^o}{RT^2} \tag{2.101}$$

If $(\bar{H}_i - \bar{H}_i^o)$ is known as a function of T, $\ln \gamma_i$ as a function of T may be found by integration of (2.93).

From the definitions of ΔG_M, its enthalpy analog ΔH_M, and ΔG^E given in (2.23), (2.26) and (2.38) it follows:

$$\frac{\partial\left(\frac{\Delta G_M}{T}\right)}{\partial\left(\frac{1}{T}\right)} = \Delta H_M \tag{2.102}$$

and

$$\frac{\partial\left(\frac{\Delta G_M}{T}\right)}{\partial\left(\frac{1}{T}\right)} = \frac{\partial\left[\sum_i n_i R \ln x_i + \frac{\Delta G^E}{T}\right]}{\partial\left(\frac{1}{T}\right)} = \frac{\partial\left(\frac{\Delta G^E}{T}\right)}{\partial\left(\frac{1}{T}\right)} \tag{2.103}$$

On a basis of one mole of solution from (2.102), (2.103), and (2.31) we obtain:

$$\frac{\partial\left(\frac{\Delta \underline{G}^E}{2.303RT}\right)}{\partial\left(\frac{1}{T}\right)} = \frac{\partial Q}{\partial\left(\frac{1}{T}\right)} = \frac{\Delta \underline{H}_M}{2.303R} \tag{2.104}$$

A representation of $\Delta \underline{H}_M$ has been proposed by Redlich and Kister similar to that for Q, For the binary case:$^{(34)}$

$$\Delta \underline{H}_M = x_1 x_2 \left[b_{12} + (x_1 - x_2)c_{12} + (x_1 - x_2)^2 d_{12} + \cdots\right] \tag{2.105}$$

Partial differentiation of (2.54) gives:

$$\frac{\partial Q}{\partial\left(\frac{1}{T}\right)} = x_1 x_2 \left[\frac{\partial B_{12}}{\partial\left(\frac{1}{T}\right)} + (x_1 - x_2)\frac{\partial C_{12}}{\partial\left(\frac{1}{T}\right)} + (x_1 - x_2)^2 \frac{\partial D_{12}}{\partial\left(\frac{1}{T}\right)} + \cdots\right] \tag{2.106}$$

From (2.104), (2.105) and (2.106) it follows that

$$\frac{\partial B_{12}}{\partial\left(\frac{1}{T}\right)} = \frac{b_{12}}{2.303R} \quad \text{and} \quad \frac{\partial C_{12}}{\partial\left(\frac{1}{T}\right)} = \frac{c_{12}}{2.303R} \tag{2.107}$$

If b_{12} and c_{12} are known as functions of temperature, B_{12} and C_{12} can be found as functions of T by integration of (2.107). In the absence of additional data, if B_{12} and C_{12} are known at two temperatures, b_{12} and c_{12} can be assumed to be constant, and B_{12} versus 1/T, and C_{12} versus 1/T plotted as straight lines. Hala(13) found that B_{12} , C_{12} ... versus ln $P°$ plot as straight lines, where $P°$ is the vapor pressure of some reference substance at the same temperature as B_{12} and C_{12} . Additional work in this area is needed.

III. APPLICATION OF THE REDLICH-KISTER EQUATIONS

A. Derivation of Equations for the Liquid-Liquid Case

For the case of two phases in equilibrium it was seen in Equation (2.69) that

$$\bar{G}_1' = \bar{G}_1'' \ , \ \bar{G}_2' = \bar{G}_2'' \ , \ \ldots \ \bar{G}_N' = \bar{G}_N'' \ [T,P] \cdot$$

Integration of (2.13) gives for either phase:

$$\bar{G}_i - \bar{G}_i^{\circ} = RT \ln f_i/f_i^{\circ} \tag{3.1}$$

If the standard states are chosen to be the same for component i in each of the phases then $\bar{G}_i^{\circ\prime} = \bar{G}_i^{\circ\prime\prime}$.

Since a_i is a definition f_i/f_i° it follows from (2.69) and (3.1) that:

$$a_1' = a_1'' \ , \ a_2' = a_2'' \ , \ \cdots \ a_N' = a_N'' \ . \tag{3.2}$$

From the definition of the activity coefficient (2.18) it follows:

$$\gamma_1' x_1' = \gamma_1'' x_1'' , \ \gamma_2' x_2' = \gamma_2'' x_2'' , \ \cdots \ \gamma_N' x_N' = \gamma_N'' x_N'' . \tag{3.3}$$

The Redlich-Kister equations for $\log_{10} \gamma_i$ retaining only the binary B_{ij} , C_{ij} coefficients may be written:

$$\log \gamma_i' = F_i'(B_{ij}, C_{ij} \cdot\cdot, x_1', x_2' \cdots x_{N-1}') \tag{3.4}$$

$$\log \gamma_i'' = F_i''(B_{ij}, C_{ij} \cdot\cdot, x_1'', x_2'' \cdots x_{N-1}'') \tag{3.5}$$

From (3.3), (3.4), (3.5) it follows:

$$\log\left(\frac{x_i'}{x_i''}\right) = F_i'' - F_i' \qquad (i = 1, 2, \cdots N). \qquad (3.6)$$

It is understood that these relations hold rigorously only at constant T and P (although small variations in P have negligible influence because we are dealing with condensed phases).

Equations (3.6) and N equations in 2(N-1) unknowns if values for the parameters B_{ij} , C_{ij} ..... are given. This means it is necessary to specify N-2 variables in addition to T and P to solve the system of of Equations (3.6). This result is obtained from the phase rule for in a system of N components and 2 phases at [T,P]:

$$V_{T,P} = C - P = N - 2 \qquad (3.7)$$

1. Binary Case:

For a two component system the Redlich-Kister representation of two phase equilibria retaining only the binary B_{ij} and C_{ij} coefficients follows from (2.55), (3.5), and (3.6):

$$\log x_1'/x_1'' = B_{12}\left(x_2''^2 - x_2'^2\right) + C_{12}\left(x_2''^2[3x_1'' - x_2''] - x_2'^2[3x_1' - x_2']\right) \qquad (3.8)$$

$$\log x_2'/x_2'' = B_{12}\left(x_1''^2 - x_1'^2\right) + C_{12}\left(x_1''^2[x_1'' - 3x_2''] - x_1'^2[x_1' - 3x_2']\right) \qquad (3.9)$$

where $x_2' = 1 - x_1'$ and $x_2'' = 1 - x_1''$

Given values for B_{12} and C_{12} Equations (3.8) and (3.9) may be solved for x_1' , x_1'' . Nothing in addition to the coefficients must be specified (specification of the coefficients corresponds to specification of T and P) since N = 2 and from Equation (3.7), $V_{P,T}$ = 0. Likewise specification of x_1' , x_1'' (binary solubility data) determines B_{12} , C_{12} in (3.8) and (3.9).

2. Ternary Case:

By a procedure analogous to that used in the binary case, Equations (3.10), (3.11), and (3.12) may be written which represent ternary liquid-liquid equilbria and retain only binary coefficients, B_{ij} , C_{ij} . Because of the length of these equations, they will be written henceforth as (3.10a), (3.11a), and (3.12a).

$$\begin{aligned}\mathcal{F} \equiv \log x_1'/x_1'' - \Big\{ & B_{12}[x_2''(1-x_1'')-x_2'(1-x_1')] + B_{23}[x_2'x_3'-x_2''x_3''] + B_{31}[x_3''(1-x_1'')-x_3'(1-x_1')] \\ & + C_{12}[x_2''(2x_1''(-x_1''+x_2''+1)-x_2'') - x_2'(2x_1'(-x_1'+x_2'+1)-x_2')] \\ & + C_{23}[2(x_2''x_3''(-x_2''+x_3'') - x_2'x_3'(-x_2'+x_3'))] \\ & + C_{31}[x_3''(2x_1''(x_1''-x_3''-1)+x_3'') - x_3'(2x_1'(x_1'-x_3'-1)+x_3')]\Big\} = 0\end{aligned} \tag{3.10}$$

$$\begin{aligned}\mathcal{G} \equiv \log \frac{x_2'}{x_2''} - \Big\{ & B_{12}[x_1''(1-x_2'')-x_1'(1-x_2')] + B_{23}[x_3''(1-x_2'')-x_3'(1-x_2')] + B_{31}[x_1'x_3'-x_1''x_3''] \\ & + C_{12}[x_1''(2x_2''(-x_1''+x_2''-1)+x_1'') - x_1'(2x_2'(-x_1'+x_2'-1)+x_1')] \\ & + C_{23}[x_3''(2x_2''(-x_2''+x_3''+1)-x_3'') - x_3'(2x_2'(-x_2'+x_3'+1)-x_3')] \\ & + C_{31}[2(x_1''x_3''(x_1''-x_3'') - x_1'x_3'(x_1'-x_3'))]\Big\} = 0\end{aligned} \tag{3.11}$$

$$\mathcal{H} \equiv \log\frac{x_3'}{x_3''} - \Big\{B_{12}\left[x_1'x_2' - x_1''x_2''\right] + B_{23}\left[x_2''(1-x_3'') - x_2'(1-x_3')\right] + B_{31}\left[x_1''(1-x_3'') - x_1'(1-x_3')\right]$$

$$+ C_{12}\left[2\left(x_1''x_2''(x_2''-x_1'') - x_1'x_2'(x_2'-x_1')\right)\right]$$

$$+ C_{23}\left[x_2''\left(2x_3''(-x_2''+x_3''-1)+x_2''\right) - x_2'\left(2x_3'(-x_2'+x_3'-1)+x_2'\right)\right]$$

$$+ C_{31}\left[x_1''\left(2x_3''(x_1''-x_3''+1)-x_1''\right) - x_1'\left(2x_3'(x_1'-x_3'+1)-x_1'\right)\right]\Big\} = 0; \tag{3.12}$$

where $x_3' = 1 - x_1' - x_2'$, $x_3'' = 1 - x_1'' - x_2''$.

$$\log x_1'/x_1'' - \phi_1 = 0 \tag{3.10a}$$

$$\log x_2'/x_2'' - \phi_2 = 0 \tag{3.11a}$$

$$\log x_3'/x_3'' - \phi_3 = 0 . \tag{3.12a}$$

Equations (3.10 - 12) are three equations in four independent variables (having specified the coefficients). Therefore by specifying one mole fraction we can solve the equations for the other three mole fractions. This coincides with the result from (3.7) for a ternary.

B. Utilization and Flexibility of the Equations

1. Solution of the Equations

Certainly if Equations (3.10), (3.11), and (3.12) can be used as a basis for a correlation, it must be possible to solve them, given numerical values for the coefficients. Because of the non-linearity of the equations it is apparent that successive approximation or iterative solution methods must be used. It was at once recognized that finding an iterative technique that would converge to solutions having physical meaning would be a major problem in this research.

Newton's iterations(37) was the first method tried. It was found to be unsuccessful because it converges to the trivial solution where $\log \frac{x_i'}{x_i''} = 0$, $\phi_i = 0$ $(i = 1, 2, 3)$. Another method based on half interval convergence(8) also failed.

The method that was found to be successful was far simpler, computationally than the Newton's or Half Interval methods. Having specified the coefficients in Equations (3.10), (3.11), (3.12) and one composition, say x_3 , the steps in the procedure are as follows:

1. Guess x_1', x_1'', x_2''.
2. Compute ϕ_1, ϕ_2, ϕ_3.
3. Print x_1', x_2', x_3', x_1'', x_2'', x_3''

if $\left[\sum_{i=1}^{3} \left| \log \frac{x_i'}{x_i''} - \phi_i \right| \right] < \epsilon$ where ϵ is specified depending on the accuracy of the desired solution.

4. Compute $a \equiv 10^{\phi_1}$, $b \equiv 10^{\phi_2}$.

5. Compute $x_3''^{[n+1]} = \left(x_3' / 10^{\phi_3} + x_3''^{[n]} \right) / 2$

where n denotes the number of the trial being performed.

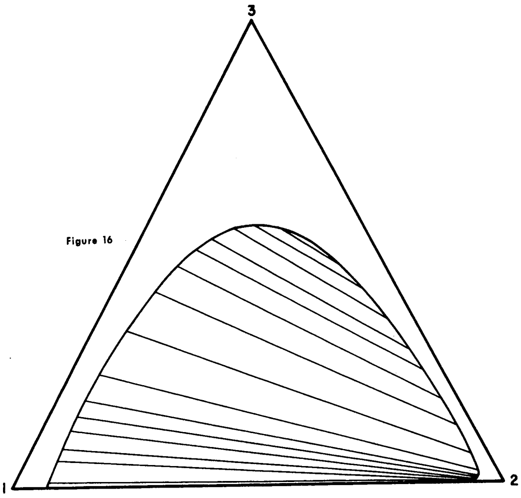
6. Compute $c = 1 - x_3'$, $d = 1 - x_3''^{[n+1]}$.

7. Compute $x_2''^{[n+1]} = \frac{ad-c}{a-c}$. (Note that $x_1' - x_2' = c$, $x_1'' - x_2'' = d$. Since $x_1' = ax_1''$ and $x_2' = bx_2''$ then $x_2'' = \frac{ad-c}{a-b}$.)

8. Compute $x_1''^{[n+1]} = d - x_2''^{[n+1]}$, $x_1'^{[n+1]} = a x_1''^{[n+1]}$, $x_2'^{[n+1]} = b x_2''^{[n+1]}$.

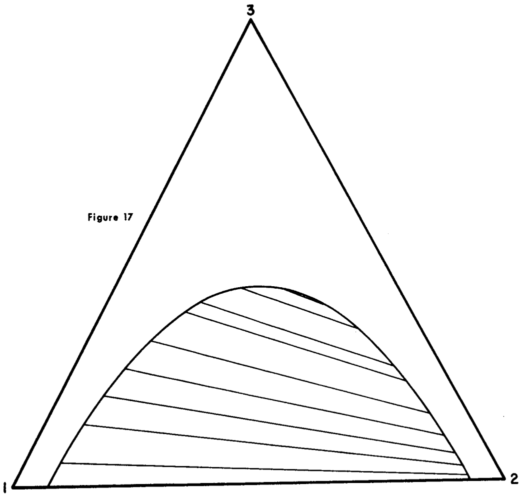
9. Using the N + 1 values of the mole fractions, go to step 2 and repeat the procedure until the condition of step 3 is satisfied.

Figure 16



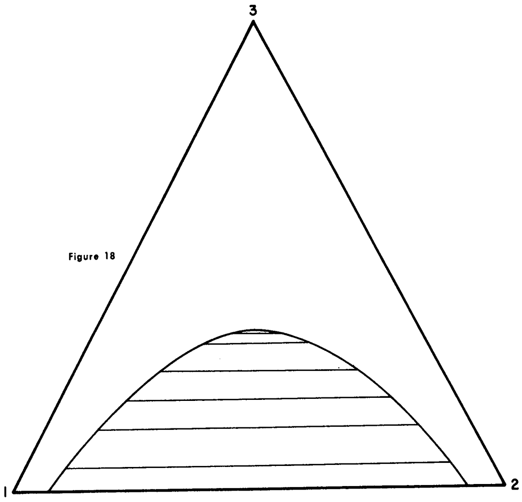
$B_{31} = -2.0$

Figure 17



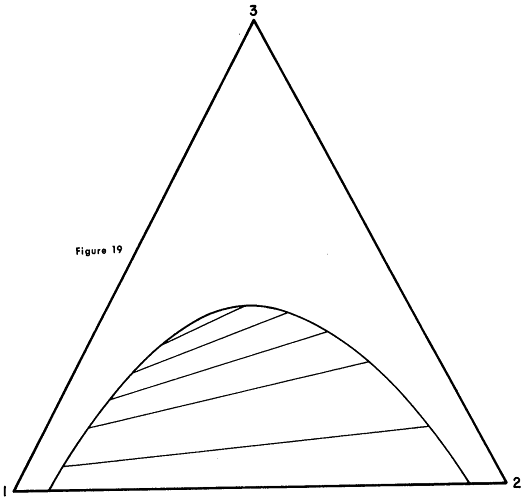
$B_{31} = -1.0$

Figure 18



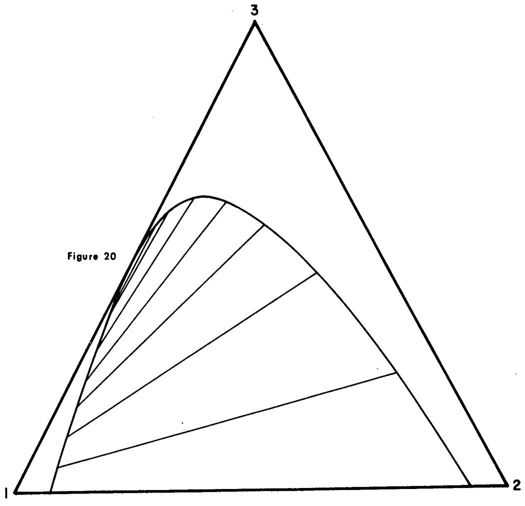
$B_{31} = 0$

Figure 19



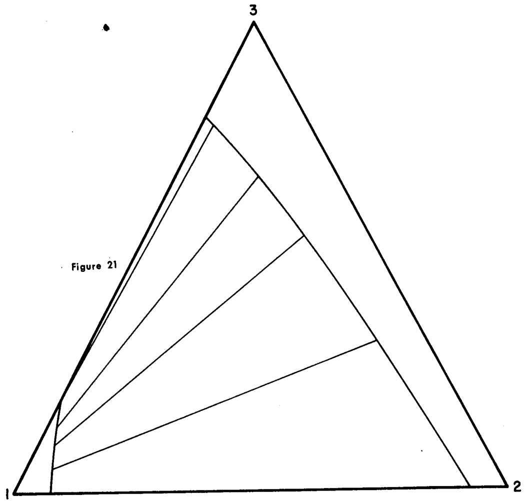
$B_{31} = 0.5$

Figure 20



$B_{31} = 0.87$

Figure 21



$B_{31} = 1.0$

Plots of Equations (3.10), (3.11) and (3.12)
$B_{12} = 1.3$, $B_{23} = C_{12} = C_{23} = C_{31} = 0$.

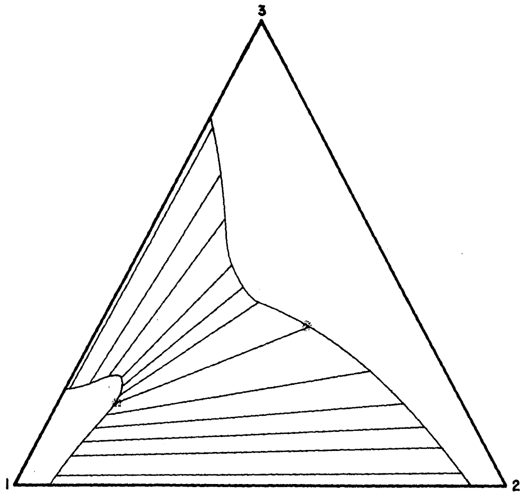
For a detailed description of the computer program based on this procedure, the reader is referred to Appendix B., Program 6. The procedure converges rapidly near a partially miscible binary, more slowly near a plait point. The initial guess must be quite accurate near a plait point, to insure convergence.

2. Demonstration of the Flexibility of the Equations

One of the first questions that can be raised is: do Equations (3.10), (3.11), and (3.12) represent ternary liquid-liquid systems and if so can they represent a wide variety of cases? In order to answer this a number of fictitious curves were calculated.

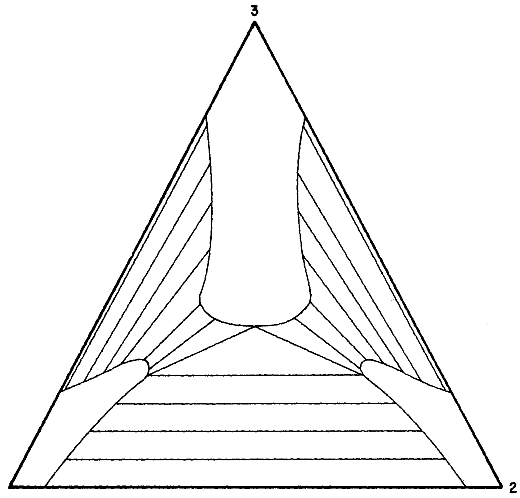
It was soon learned what the range of values of coefficients was that gave curves which looked like ternary liquid-liquid phase diagrams. Figures 16 - 21 were computed for one of the simplest of cases, that where $B_{23} = C_{12} = C_{23} = C_{31} = 0$ in (3.10), (3.11), and (3.12). B_{12} was set equal to 1.3 which is a value great enough to cause partial miscibility in the 1-2 binary. B_{31} was varied from -2.0 to 1.0. It is noted that the slope of the tie lines is negative for negative values of B_{31}, zero where $B_{31} = 0$ and positive for positive values of B_{31}. For $B_{31} = 0.87$ the solubility curve becomes tangent to the 3-1 edge at the plait point, and $x_1 = 0.5$. For $B_{31} > 0.87$ the 3-1 binary is partially miscible.

Equations (3.10), (3.11), and (3.12) are capable of more complicated representations by setting more than two coefficients not equal to zero. In Figure 22 $B_{23} = 0.87$, so that partial miscibility is just on



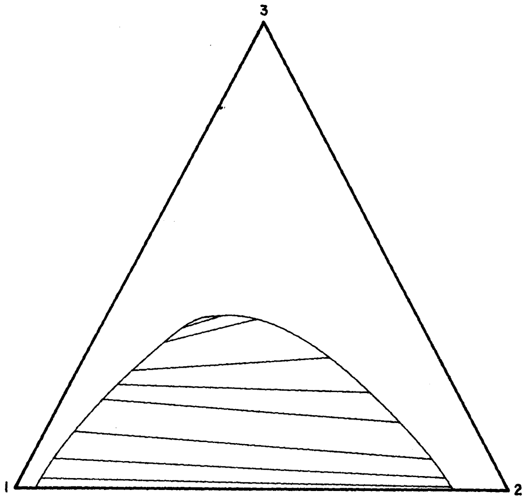
$B_{12} = 1.3$ $B_{23} = 0.87$ $B_{31} = 1.0$

$C_{12} = C_{23} = C_{31} = 0$



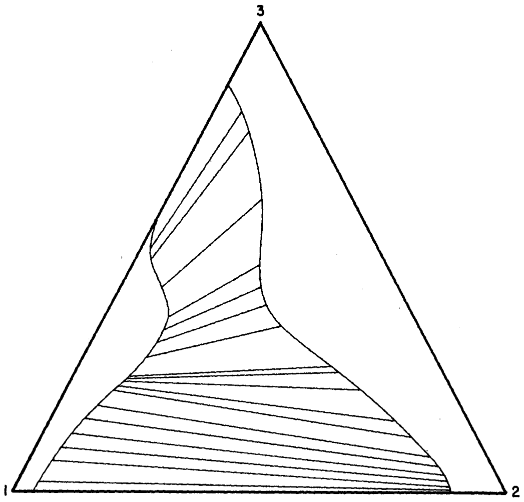
$B_{12} = 1.3$ $B_{23} = B_{31} = 1.0$

$C_{12} = C_{23} = C_{31} = 0$



$B_{12} = 1.3$ $B_{23} = B_{31} = 0.5$

$C_{12} = 0.2$ $C_{23} = C_{31} = 0.3$



$B_{12} = 1.3$ $B_{23} = B_{31} = 0.5$

$C_{12} = 0.2$ $C_{23} = C_{31} = 0.5$

the verge of appearing at the 2-3 edge. In Figure 23, B_{12}, B_{23}, and B_{31} are all greater than 0.87 therefore partial miscibility occurs for all three binary pairs. It must be realized that in the three phase region of Figure 23 Equations (3.10), (3.11), and (3.12) are not valid in the physical sense although they may be solved mathematically. One might imagine the system of Figure 23 to be the result of two superimposed systems of the type shown in Figure 22, one with partially miscible binaries 1-2 and 3-1, the other having partially miscible binaries 1-2 and 2-3. The calculation of Figure 23 was achieved by starting near the three binary regions and working in toward the center of the ternary region. Starting from the 1-2 binary and successively increasing x_3 a system identical to that in Figure 18 was computed. In general it has been found that systems of the Figure 18 type are obtained when $B_{jk} = B_{ki}$, and computation of the equilibrium curve starts at the ij binary, B_{ij} being great enough to give partial miscibility. In computing those portions of the equilibrium curve of Figure 23 which terminate in the 3-1 and 2-3 edges of the diagram, convergence is very slow near the points where contact is made with the portion of the curve terminating in the 1-2 edge.

Figures 24 and 25 show that setting the C_{ij} coefficients not equal to zero produces more complicated systems than those illustrated in Figures 16-23. Setting $C_{12} \neq 0$ produces asymmetry in the 1-2 partially miscible binary. Setting $C_{23} = C_{31}$ produces solutropic systems, that is systems in which the slope of the tie lines changes sign. Note that in Figures 24 and 25 the systems are solutropic and have asymmetric partially miscible binaries.

It was concluded from the above study that Equations (3.10), (3.11), and (3.12) are satisfactory representations of ternary liquid-liquid equilibria and that they can represent a wide variety of systems.

C. Critical Relations

Equations which enable prediction of critical points given numerical values for Redlich-Kister coefficients are of considerable importance. From these relations one can determine whether a set of Redlich-Kister coefficients will yield a ternary system having one, two, three or no partially miscible binaries, whether or not there will be a plait point, and if there is a plait point, what its location will be.

It was shown in Section II-D that at a critical mixing point the determinants D and D' vanish (Equations (2.89), (2.95)). These determinants involve the total free energy per mole of the system, $\underline{G}$. Since the Redlich-Kister equations are representations of the molar free energy of mixing $\Delta\underline{G}_M$ it is necessary to rewrite D and D' in terms of $\Delta\underline{G}_M$. The free energy of mixing is related to G, the total free energy of the system by

$$\Delta G_M = G - n_1\underline{G}_1^o - n_2\underline{G}_2^o \cdots\cdots n_N\underline{G}_N^o \; . \tag{3.13}$$

Dividing by $\sum_{i=1}^{N} n_i$ one obtains

$$\Delta\underline{G}_M = \underline{G} - x_1\underline{G}_1^o - x_2\underline{G}_2^o \cdots\cdots x_N\underline{G}_N^o \tag{3.14}$$

where the x's are mole fractions of the total system. Taking the second partial derivative of $\Delta\underline{G}_M$ with respect to x_i:

$$\frac{\partial^2\Delta\underline{G}_M}{\partial x_i^2} = \frac{\partial^2\underline{G}}{\partial x_i^2} \tag{3.15}$$

Noting that the determinants D and D' contain only derivatives of order two or higher, Equations (2.89) and (2.95) become:

$$D = \begin{vmatrix} \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_1^2} & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_1 \partial x_2} & \cdots\cdots\cdots & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_1 \partial x_{N-1}} \\ \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_2 \partial x_1} & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_2^2} & \cdots\cdots\cdots & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_2 \partial x_{N-1}} \\ \vdots & \vdots & & \vdots \\ \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_{N-1} \partial x_1} & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_{N-1} \partial x_2} & \cdots\cdots\cdots & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_{N-1}^2} \end{vmatrix} = 0 \qquad (3.16)$$

$$D' = \begin{vmatrix} \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_1^2} & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_1 \partial x_2} & \cdots\cdots\cdots & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_1 \partial x_{N-1}} \\ \vdots & \vdots & & \vdots \\ \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_{N-2} \partial x_1} & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_{N-2} \partial x_2} & \cdots\cdots\cdots & \dfrac{\partial^2 \Delta \underline{G}_M}{\partial x_{N-2} \partial x_{N-1}} \\ \dfrac{\partial D}{\partial x_1} & \dfrac{\partial D}{\partial x_2} & \cdots\cdots\cdots & \dfrac{\partial D}{\partial x_{N-1}} \end{vmatrix} = 0 \qquad (3.17)$$

1. Binary Critical Point:

From Equations (3.16) and (3.17), Equations (3.18a,b) may be written for the binary case:

$$\frac{\partial^2 \Delta \underline{G}_M}{\partial x_1^2} = 0 \quad , \quad \frac{\partial^3 \Delta \underline{G}_M}{\partial x_1^3} = 0 \qquad (3.18a,b)$$

Note that it follows from (2.26), (2.28) and (2.31):

$$\frac{\Delta G_M}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + 2.303\, Q \quad (3.19)$$

Substituting Q as given by Equation (2.54) and retaining terms multiplied by B_{12} and C_{12} it follows from (3.18a,b) that

$$2.303 B_{12}^c = \frac{1}{4}\left[\frac{3-4x_1^c}{(1-x_1^c)^2} + \frac{4x_1^c-1}{(x_1^c)^2}\right] \quad (3.20)$$

$$2.303 C_{12}^c = \frac{1}{12}\left[\frac{1}{(1-x_1^c)^2} - \frac{1}{(x_1^c)^2}\right] \quad (3.21)$$

where x_1^c is the composition of the system at a critical solution point (the point (T_c, x_B^c)in Figure 1).

Equations (3.20) and (3.21) may be obtained by a different route without consideration of ΔG_M. For simplicity let us write (3.8) and (3.9) as

$$L_1 = B_{12} X_1 + C_{12} X_2 \quad (3.8a)$$

$$L_2 = B_{12} X_3 + C_{12} X_4 \quad (3.9a)$$

Solving (3.8a) and (3.9a) for B_{12} and C_{12} one obtains:

$$B_{12} = \frac{L_1 X_4 - L_2 X_2}{X_1 X_4 - X_2 X_3}\,, \qquad C_{12} = \frac{L_2 X_1 - L_1 X_3}{X_1 X_4 - X_2 X_3} \quad (3.22)$$

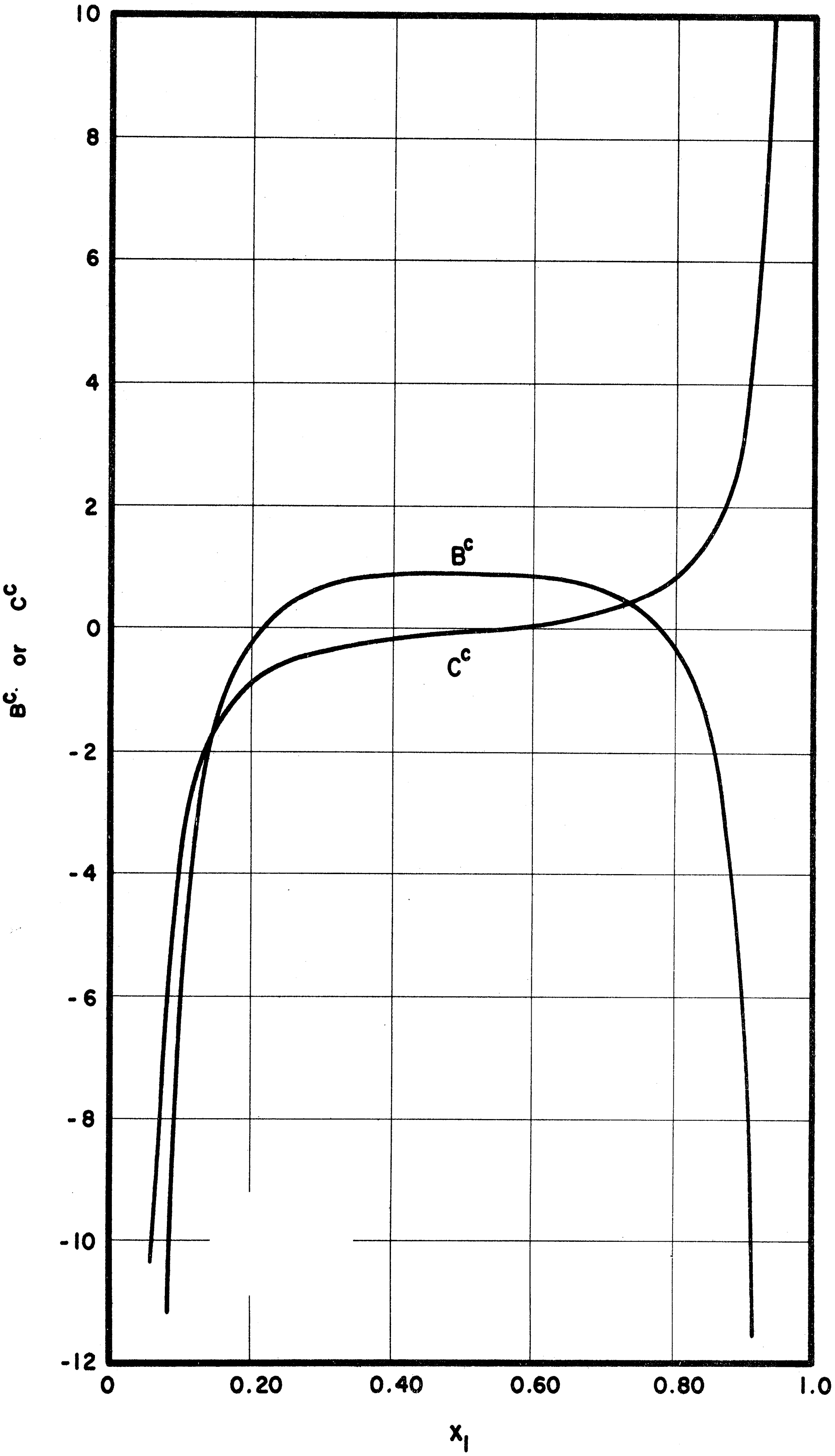


Figure 26. Critical Values of B, C vs x_1.

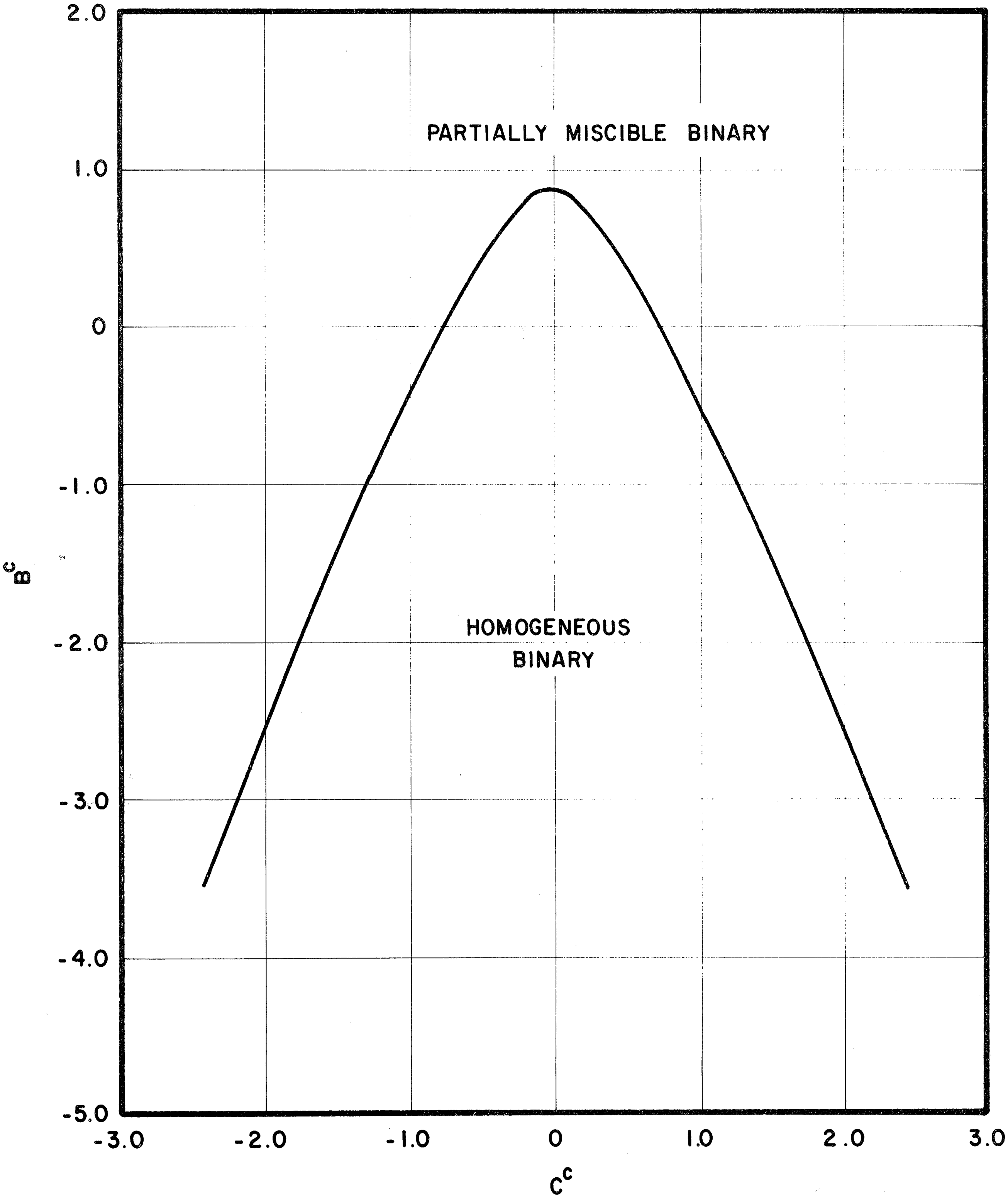


Figure 27. B^c vs. C^c .

The critical values of the coefficients, B_{12}^{c} , C_{12}^{c} corresponding to the critical point (T_c, x_B^c) in Figure 1 may be expressed as

$$B_{12}^{c} = \lim_{\substack{x_1' \to x_1^c \\ x_1'' \to x_1^c}} B_{12} \quad , \quad C_{12}^{c} = \lim_{\substack{x_1' \to x_1^c \\ x_1'' \to x_1^c}} C_{12} \tag{3.23}$$

where B_{12} and C_{12} are given by (3.20). The limits in (3.23) may be evaluated by postulating that

$$\lim_{\substack{x_1' \to x_1^c \\ x_1'' \to x_1^c}} B_{12} = \lim_{x_1' \to x_1^c} \lim_{x_1'' \to x_1^c} B_{12}$$

and then showing for the case in question

$$\lim_{x_1' \to x_1^c} \lim_{x_1'' \to x_1^c} B_{12} = \lim_{x_1'' \to x_1^c} \lim_{x_1' \to x_1^c} B_{12} .$$

Taking the limits in (3.23) and applying l'Hospital's rule$^{(56)}$ one obtains Equations (3.20) and (3.21). The details of the two derivations of Equations (3.20) and (3.21) are given in Appendix A.

Equations (3.20) and (3.21) are presented graphically in Figure 26, as a plot of B_{12}^{c} and C_{12}^{c} versus x_1^c, and in Figure 27, as a plot of B_{12}^{c} versus C_{12}^{c} . Note that when $C_{12}^{c} = 0$, B_{12}^{c} goes through a maximum of 0.87 (2.0 if the Redlich-Kister equations are written with the logarithm to the base e rather than the base 10). Thus for the case of $C_{12} = 0$, values of $B_{12} > 0.87$ give a partially miscible binary, 1-2, and values of $B_{12} < 0.87$ give a homogeneous binary 1-2. This result explains what was observed in Figures 16-21, that partial miscibility is on the verge of occurring in the i-j edge of a ternary when $B_{ij} = 0.87$, $C_{ij} = 0$. In general, points in Figure 27, that lie above the curve, B^c versus C^c have as their coordinates values of B_{ij} and C_{ij} that give partially miscible binaries, those below the curve, homogeneous binaries.

3. Ternary Critical Point or Plait Point :

As in the case of a binary mixture, the two constraints $D = 0$ and $D' = 0$ also hold for a ternary at a critical mixing point; thus it follows from (3.16) and (3.17):

$$D = \frac{\partial^2 \Delta G_M}{\partial x_1^2}\,\frac{\partial^2 \Delta G_M}{\partial x_2^2} - \left(\frac{\partial^2 \Delta G_M}{\partial x_1 \partial x_2}\right)^2 = 0 \qquad (3.23)$$

$$D' = \frac{\partial^2 \Delta G_M}{\partial x_1^2}\,\frac{\partial D}{\partial x_2} - \frac{\partial^2 \Delta G_M}{\partial x_1 \partial x_2}\,\frac{\partial D}{\partial x_1} = 0\,. \qquad (3.24)$$

For the special case where $C_{12} = C_{23} = C_{31} = 0$ substituting Equation (2.72) into Equations (3.23) and (3.24), carrying out the indicated differentiation and simplifying:

$$\left(\frac{2.3}{x_1} + \frac{2.3}{x_3} - 2B_{31}\right)\left(\frac{2.3}{x_2} + \frac{2.3}{x_3} - 2B_{23}\right) - \left(\frac{2.3}{x_3} + B_{12} - B_{23} - B_{31}\right)^2 = 0 \qquad (3.23a)$$

$$\left[\frac{1}{x_3^2}\left(\frac{2.3}{x_1} + \frac{2.3}{x_2} - 2B_{12}\right) - \frac{1}{x_2^2}\left(\frac{2.3}{x_1} + \frac{2.3}{x_3} - 2B_{31}\right)\right]\left(\frac{2.3}{x_1} + \frac{2.3}{x_3} - 2B_{31}\right)$$

$$- \left[\frac{1}{x_3^2}\left(\frac{2.3}{x_1} + \frac{2.3}{x_2} - 2B_{12}\right) - \frac{1}{x_1^2}\left(\frac{2.3}{x_2} + \frac{2.3}{x_3} - 2B_{23}\right)\right]\left(\frac{2.3}{x_3} + B_{12} - B_{23} - B_{31}\right) = 0 \qquad (3.24a)$$

Inclusion of terms multiplied by C_{12}, C_{23}, and C_{31} lead to considerably more complicated equations than (3.23a) and (3.24a). Given numerical values for the coefficients, Equations (3.23) and (3.24) can be solved for x_1 and x_2, the composition at a plait point. A plait point cannot be determined by direct experimental methods but must be estimated graphically from neighboring experimental tie lines. This graphical estimation is open to error, however. If one determines values for the Redlich-Kister coefficients which enable Equations (3.10), (3.11) and (3.12) to represent accurately a given set of experimental equilibrium data for a ternary liquid-liquid system, one may use these values of the coefficients in Equations (3.12) and (3.13) to solve for the plait point composition directly.

Equations (3.16) and (3.17) are especially valuable in determining the locus of critical mixing points in systems of more than three components where it is not possible to locate the critical graphically as in the case of a ternary system. A knowledge of the experimentally determined coefficients in the coefficients in the Redlich-Kister equations, or in any other representation of $\Delta \underline{G}^{\epsilon}$, is all that is needed with Equations (3.16) and (3.17) to solve for a critical locus, regardless of the number of components.

IV. DETERMINATION OF COEFFICIENTS FROM EXPERIMENTAL DATA

The determination of coefficients in the Redlich-Kister equations from experimental data is of prime importance. In the case of ternary liquid-liquid equilibria determination of the coefficients which enables the equations to best fit a given set of experimental data was by far the most difficult problem encountered during this research.

In fitting a set of data to a mathematical function, or system of functions such as the Redlich-Kister equations one attempts to determine those values of a set of parameters that enable the function(s) to minimize the deviations of the experimental data from the mathematical curve. One selects a dependent variable or variables and minimizes the error in this variable, that is the difference of the experimental value from the mathematically predicted value for all of the data points. This presents the first major problem: what variable(s) should be chosen as the dependent variable(s)? The choice is arbitrary.

There will be two kinds of deviations: first, those which are due to random scatter of the data, i.e. experimental error, and second, those which are due to the fact that the mathematical functions are not capable of perfect representation of the data. In this research, the number of parameters in the equations has been limited to twice the number of pairs of components. The number of data points for a given system is far more than twice the number of pairs of components. Where this is so, deviations of the second type must be expected.

The second major problem occurs because of the nature of the Redlich-Kister equations, or for that matter any algebraic representation of the logarithm of the activity coefficient. These equations are long, complicated expressions which are implicit in the experimentally measured variables such as composition. If one designates a directly measured quantity to be the dependent variable(s) the computational problem becomes quite considerable.

Let us consider first the simple case of an algebraic expression which relates the dependent variable, y, to independent variables $z_1, z_2, \ldots z_m$.

$$y = f(z_1, z_2 \cdots z_m, \beta_1, \beta_2, \cdots \beta_k) \qquad (4.1)$$

where $\beta_1, \beta_2 \cdots \beta_k$ are parameters.

The experimental data points are denoted

$$Y_i, Z_{1i}, Z_{2i} \cdots Z_{mi} \quad . \quad (i = 1, 2 \cdots n) \qquad (4.2)$$

Statistical techniques are based upon the concept of a particular set of data called the <u>sample</u>, which is drawn from an infinitely large <u>population</u> of values. From the sample one obtains estimates $(c_1, c_2, \ldots c_k)$ of the population parameters $(\beta_1, \beta_2 \cdots \beta_k)$. Under quite general conditions, the appropriate statistical criterion for adjusting the values of the parameters in order to best fit the data is the least squares criterion.(21) The assumption in choosing this criterion is that the deviations of the experimental data from the predicted values for the data should follow a Gaussian distribution.(38) Let $\overset{*}{Y}_i$ denote the predicted value for y when, for the ith data point, the values of the independent variables are substituted into Equation (4.1):

$$\overset{*}{Y}_i = f(Z_{1i}, Z_{2i}, \cdots Z_{mi}, c_1, c_2 \cdots c_k) \ . \qquad (4.3)$$

The least squares criterion states that the sample estimates of the population parameters shall have values such that

$$\Delta = \sum_{i=1}^{n} [Y_i - \overset{*}{Y}_i]^2 \qquad (4.4)$$

be a minimum. Δ is a minimum when the partial derivatives of Δ with respect to each of the parameters vanish:

$$\frac{\partial \Delta}{\partial c_1} = \frac{\partial \Delta}{\partial c_2} = \cdots = \frac{\partial \Delta}{\partial c_k} = 0 \ . \qquad (4.5)$$

Equations (4.5) are k simultaneous equations in k unknown parameters. If Equations (4.5) are linear in the parameters, they may be solved directly for c_1, c_2 ... c_k. If the equations are non-linear, problems in methodology present themselves as it is practically impossible to solve a system of non-linear equations of the type (4.5). Methods of obtaining estimates of c_1, c_2 ...c_k for non-linear cases are discussed in detail in Section III, B, 1.

A. Binary Case

There is considerable interest in the possibility of using binary Redlich-Kister coefficients determined from binary vapor-liquid, or liquid-liquid (solubility) data to predict equilibrium in multicomponent systems.

The determination of the binary B_{ij} and C_{ij} coefficients from binary solubility data is trivial. Substitution of x_1' and x_1'' into Equations (3.8) and (3.9) give two simultaneous linear equations, which may be easily solved for B_{12} and C_{12}. A computer program (Program 5) was written for this purpose.

The determination of B_{ij} and C_{ij} from binary vapor-liquid equilibrium data is less straight forward. A number of different variables may be chosen as the dependent variable, for example:

x_1, y_1, P, t, $\Delta \underline{G}_M$, $\log \gamma_1$, Q ...... etc.

Suppose it were decided to minimize the deviation of the experimental value of Q from that value predicted by the Redlich-Kister equations. Then:

$$\Delta = \sum_{i=1}^{n} \left(Q_i - \overset{*}{Q}_i \right)^2 \tag{4.6}$$

where Δ is to be minimized.

For the binary vapor liquid case:

$$Q_i = x_{1i} \log_{10} \left(\frac{P y_1}{P_1^\circ x_1} \right)_i + x_{2i} \log_{10} \left(\frac{P y_2}{P_2^\circ x_2} \right)_i \tag{4.7}$$

$$\overset{*}{Q}_i = x_1 x_2 \left(B_{12} + (x_1 - x_2) C_{12} \right) \tag{4.8}$$

(Equation (4.7) assumes that the total pressure, P, is low enough that fugacity corrections need not be included.) Equations (4.5) then become

$$\sum_{i=1}^{m} x_{1i} x_{2i} (Q_i - \overset{*}{Q}_i) = 0$$

$$\sum_{i=1}^{m} x_{1i} x_{2i} (x_{1i} - x_{2i})(Q_i - \overset{*}{Q}_i) = 0 \tag{4.9}$$

Note that the choice of Q as the dependent variable is advantageous because Equations (4.9) are linear in B_{12} and C_{12} and solution is straightforward. Another choice of dependent variable that leads to linear Equations (4.5) is $\log\gamma_1$, or $\log\gamma_2$. Since it is normally desirable to minimize the error in $\log\gamma_1$ and $\log\gamma_2$ simultaneously we may define Δ as:

$$\Delta = \sum_{i=1}^{n} \left[(\log\gamma_1 - \log\overset{*}{\gamma}_1)^2 + (\log\gamma_2 - \log\overset{*}{\gamma}_2)^2 \right] \tag{4.10}$$

where $\log\gamma_i = \log\left(\frac{P y_i}{P_i^{\circ} x_i}\right)$ $\qquad \log\overset{*}{\gamma}_i = x_j^2 \left[B_{ij} + C_{ij}(3x_i - x_j) \right]$

(It is important to note here that $B_{ij} = B_{ji}$ but $C_{ij} = -C_{ji}$. The reader is referred to Equations (2.55), and (2.56).) Two computer programs have been written to solve for the values of B_{12} and C_{12} which minimize the Δ defined in Equation (4.10), and these are described in Appendix B. Program 1 handles data at constant temperature. Program 3 handles data at constant pressure. In the constant pressure (variable temperature) case B_{12}, C_{12} rigorously cannot be assumed constant since B_{12} and C_{12} are functions of temperature. If the temperature variation is small, say 10°C, the error in assuming the coefficients to be constant is small. Figure 29 in Section V, A, gives x-y plots of four systems for which B_{12} and C_{12} were determined by minimization of Δ defined in (4.10). In each case the fit is excellent.

Although the selection of Q or $\log_{10}\gamma$ as the dependent variable leads to linear Equations (4.5), these variables may not be of direct engineering importance. In addition they are not quantities that are determined by direct physical measurement such as total pressure, but require introduction of the independent variable x_1 or x_2 in their determination which under certain conditions may be undesirable. In a situation in which the total pressure, P, is especially important, one might wish to minimize Δ defined as

$$\Delta = \sum_{i=1}^{m} \left(P_i - P_i^* \right)^2 \tag{4.11}$$

where $P_i^* = x_1 P_1^\circ(x_2^2(B_{12}+(3x_1-x_2)C_{12})+x_2 P_2^\circ(x_1^2(B_{12}-(3x_2-x_1)C_{12})\cdot$

(P_i is assumed low enough here that fugacity correctionsare not needed). For this case however Equations (4.5) are not linear in B_{12} and C_{12} and it is somewhat more difficult to obtain the values of B_{12} and C_{12} that minimize Δ (4.11). Marquardt(21) describes procedures for minimization of (4.11) for the case where P_i^* is represented by the Van Laar Equations. (See Table I).

B. Ternary Case

The ternary liquid-liquid case has curve fitting problems which differ somewhat from those of the case of binary vapor-liquid equilibria.

Use of the molar free energy of mixing or the Q function as the dependent variable is usually impossible because the partial pressures of the individual components are usually not measured in determining two phase liquid equilibria. Without a knowledge of the partial pressures of the individual components, the values of the activity coefficients, and thus of Q and ΔG_M are not known. If the Equations (4.5) are to be linear in the Redlech-Kister coefficients for the ternary liquid-liquid case, some linearizing approximations must be introduced. Linearizing approximations as it will be seen often do not give good fits of the experimental data. The failure of linearizing approximations led to the development of "hand methods" for guessing successively better estimates of the coefficients.

Scheibel(40) has described an approximate method of determining Redlich-Kister coefficients. The basis of the method is that, theoretically, equilibrium data for two tie lines should determine the six coefficients in Equations(3.10), (3.11) and (3.12). This amounts to determining values of equation parameters that force the mathematical functions to pass through two specific points. This method was tried in the present work without success. It was found that although the equations are forced to pass through two selected points there is no assurance that they will pass through or near the remaining points.

1. Hand Methods:

In many cases, good estimates of the coefficients in Equations (3.10), (3.11), and (3.12) can be obtained by visual curve fitting. Good initial estimates of the coefficients are desirable to insure convergence of the iterative non-linear methods described in a later section for determination of highly accurate least squares estimates of the coefficients. A hand fitting procedure which usually gives good curve fits in a few trials is outlined below.

For cases of ternary systems having one partially miscible binary, components 1 and 2:

1) Determine B_{12} and C_{12} from binary solubility data for the 1-2 binary by solving Equations (3.8) and (3.9) after substitution of x_1' and x_1''. Extrapolation of the ternary data to the 1-2 binary may be necessary if the binary data are not available.

2) Note whether the experimental tie lines tend to parallel the 2-3 binary or the 3-1 binary on a triangular diagram as the plait point is approached. Assume that the coefficients corresponding to the binary edge which the tie lines <u>do not</u> tend to parallel are zero. If the tie lines tend to parallel the 3-1 binary; then set $B_{23} = C_{23} = 0$.

3) Determine the values of B_{31}, C_{31} which cause the calculated plait point to coincide with the experimentally estimated plait point by solving Equations (3.23) and (3.24) after substitution of the values of B_{12} and C_{12} determined in part one and the composition of the plait point as established graphically from the experimental data. Alternatively, B_{31} and C_{31} may be adjusted by trial and error to give an approximate fit of the experimental equilibrium binodal and convolute curves. In order that the tie lines tend to parallel the 3-1 binary B_{31} must be greater than B_{23} if $C_{23} = C_{31} = 0$.

4) If after B_{31} and C_{31} have been determined in part 3, additional accuracy of the fit is desired, B_{23} and C_{23} may be adjusted by trial and error. In case it was found to be impossible to solve Equations (3.23) and (3.24) for real values of B_{31} and C_{31} with $B_{23} = C_{23} = 0$, B_{23} and C_{23} might be set not equal to zero and solution of (3.23) and (3.24) for B_{31} and C_{31} tried again. Often the fit of points in the ternary region may be improved by modifying the values of B_{12} and C_{12} i.e. tolerating some error at the 1-2 binary. Increasing the values of the coefficients especially B_{12}, increases the area under the binodal curve.

In guessing values of coefficients corresponding to binary systems that are homogeneous throughout it is advisable to use Figure 27, the plot of B^c versus C^c, to make sure the assumed coefficients lie in the homogeneous region.

If partial miscibility occurs in two binaries, say the 1-2 and the 3-1 binary:

1) Determine B_{12}, C_{12}, B_{31}, and C_{31} by solution of Equations (3.8) and (3.9) after substitution of the solubility data for the 1-2 and the 3-1 binaries respectively.

2) Calculate the ternary equilibrium curve by solution of Equations (3.10), (3.11) and (3.12) with B_{12}, B_{31}, C_{12}, and C_{31} equal to the values determined in step 1, and $B_{23} = C_{23} = 0$. If greater accuracy of fit is desired one may adjust the values of B_{23} and C_{23} by trial and error, using Figure 27 to insure that assumed values of B_{23} and C_{23} do not make the 2-3 binary heterogeneous.

It is often helpful to make use of any available binary vapor-liquid equilibrium data to get initial estimates of B_{ij}, C_{ij} for homogeneous binaries. Also it is advisable to study previously calculated ternary equilbrium curves before guessing coefficients. Note that the fictitious curves Figures 24 and 25 illustrate that setting $B_{23} = B_{31}$ and $C_{23} = C_{31}$ gives equilibrium curves that are solutropic (i.e. the slope of the tie lines changes sign.)

Usually after a little experience is attained, less than four trials are needed to give a satisfactory curve fit if the above procedures are followed. Visual curve fitting however suffers from the disadvantages that it is a trial and error process, and does not necessarily minimize some specific deviation defined in a least squares sense.

2. Least Squares Using Approximate Linearizations:

When one is concerned with a system of n equations in m+n variables and k parameters for estimation by least squares, n of the m+n variables may be designated as dependent variables and the remaining m, the dependent variables. Using the notation of Equation (4.2) where $\overset{*}{Y}$'s are dependent variables predicted by the equations and Z's are the independent variables, the system of equations $\mathcal{S}$ may be written:

$$\mathcal{S}(\overset{*}{Y}_{1i}, \overset{*}{Y}_{2i} \cdots \overset{*}{Y}_{ni}, Z_{1i}, Z_{2i} \cdots Z_{mi}, c_1, c_2 \cdots c_k) = 0 \qquad (4.12)$$

The least squares criterion states that the parameters will have such values that

$$\Delta = \sum_{i=1}^{M}\left[\sum_{j=1}^{n}\left(Y_{ji} - \overset{*}{Y}_{ji}\right)^2 \omega_{ji}\right] \qquad (4.13)$$

be a minimum where Y_{ji} is the experimental value for the jth dependent variable, ith data point, and w_{ji} is the corresponding weight factor. If all data points and dependent variables can be determined with equal precision and are of equal importance w_{ji} is set equal to unity.

It is not necessary that the equations $\mathscr{S}$ be explicit in the dependent variables. All that is necessary is that given values for the parameters and the independent variables the equations $\mathscr{S}$ may be solved for the dependent variables $\overset{*}{Y}_{ji}$. In the case under consideration in this research the Equations (3.10), (3.11), and (3.12) which comprise the system $\mathscr{S}$ are implicit functions of four of the mole fractions x_1', x_2', x_3', x_1'' , x_2'' , x_3'' , selected such that there are no more than two per phase (eg. x_1', x_2', x_2'' , x_3'' , not x_1', x_2', x_3', x_1'').

If one arbitrarily selects x_1', x_2', x_2'' , x_3'' as the variables in Equations (3.10), (3.11), and (3.12) and designates x_2' as the independent variable then Δ becomes:

$$\Delta = \sum_{i=1}^{M} \left[(x_1' - \overset{*}{x}_1')^2 w_1 + (x_2'' - \overset{*}{x}_2'')^2 w_2 + (x_3'' - \overset{*}{x}_3'')^2 w_3 \right]_i \qquad (4.14)$$

Unfortunately the Equations (4.5) for Δ(4.14) are not linear in the Redlich-Kister coefficients, and their solution is difficult. In order that the Equations (4.5) be made linear in the coefficients we modify Δ(4.14) by minimizing the deviations of the logarithms of the dependent variables. Assuming $w_1 = w_2 = w_3 = 1$, (4.14) then becomes:

$$\Delta = \sum_{i=1}^{M} \left[(\log x_1' - \log \overset{*}{x}_1')^2 + (\log x_2'' - \log \overset{*}{x}_2'')^2 + (\log x_3'' - \log \overset{*}{x}_3'')^2 \right]_i \qquad (4.15)$$

From Equations (3.10), (3.11), and (3.12) it follows

$$\log_{10}\overset{*}{x}_1' = \log_{10}\overset{*}{x}_1'' + \phi_1^* \approx \log_{10} x_1'' + \phi_1$$

$$\log_{10}\overset{*}{x}_2'' = -\log_{10}\overset{*}{x}_2' - \phi_2^* \approx -\log_{10} x_2' - \phi_2$$

$$\log_{10}\overset{*}{x}_3'' = -\log_{10}\overset{*}{x}_3' - \phi_3^* \approx -\log_{10} x_3' - \phi_3 \qquad (4.16)$$

Substitution of the approximations (4.16), Δ (4.15) becomes:

$$\Delta = \sum_{i=1}^{M}\left[\left(\log_{10}\frac{x_1'}{x_1''} - \phi_1\right)^2 + \left(\phi_2 - \log_{10}\frac{x_2'}{x_2''}\right)^2 + \left(\phi_3 - \log_{10}\frac{x_3'}{x_3''}\right)^2\right]_i$$

or

$$\Delta = \sum_{i=1}^{M}\sum_{j=1}^{3}\left(\log_{10} x_j'/x_j'' - \phi_j\right)_i^2 \quad . \qquad (4.17)$$

For the purposes of simplification let us write Equations (3.10), (3.11), and (3.12) as

$$\log x_1'/x_1'' + \sum_{j=1}^{6} c_j f_j = 0$$

$$\log x_2'/x_2'' - \sum_{j=1}^{6} c_j g_j = 0$$

$$\log x_3'/x_3'' - \sum_{j=1}^{6} c_j h_j = 0$$

where c_1 ... c_6 are the Redlich-Kister coefficients B_{12}, B_{23}, B_{31}, C_{12}, C_{23}, C_{31}. The Equations (4.5) for Δ(4.17) may then be written:

$$\sum_{i=1}^{M}\left[\sum_{j=1}^{6} c_j(f_j f_k + g_j g_k + h_j h_k)\right] = \sum_{i=1}^{M}\left[f_k \log x_1'/x_1'' + g_k \log x_2'/x_2'' + h_k \log x_3'/x_3''\right]_i$$

$$(k = 1, 2 \ldots 6) . \qquad (4.18)$$

The six linear Equations (4.18) are linear in the coefficients c_i and may be solved directly for c_1 ... c_6. A computer program (Program 7, Appendix B) has been written which computes the values of c_1 ... c_6 that minimize Δ(4.17) by solution of Equations (4.18).

The success of the linearized approximation of Δ(4.15) depends on the accuracy of the approximation in Equations (4.16). This approximation is good when the experimentally determined compositions, the x's, are nearly equal to the $\overset{*}{x}$'s, the mole fractions obtained by solution of Equations (3.10), (3.11), and (3.12) using the parameters c_1 ... c_6 which minimize Δ(4.15). If the precision of the experimental data is not very good, or if Equations (3.10), (3.11), and (3.12) are not capable of highly accurate representation of the experimental data, i.e. a fair amount of non-random error must be tolerated, then the approximations (4.16) will not be good and minimization of Δ(4.17) will not yield an estimate of the coefficients that will give an accurate fit of the experimental data. In particular it has been found that for systems where the tie lines are nearly parallel the data must be extremely precise if minimization of Δ(4.17) is to give satisfactory results.

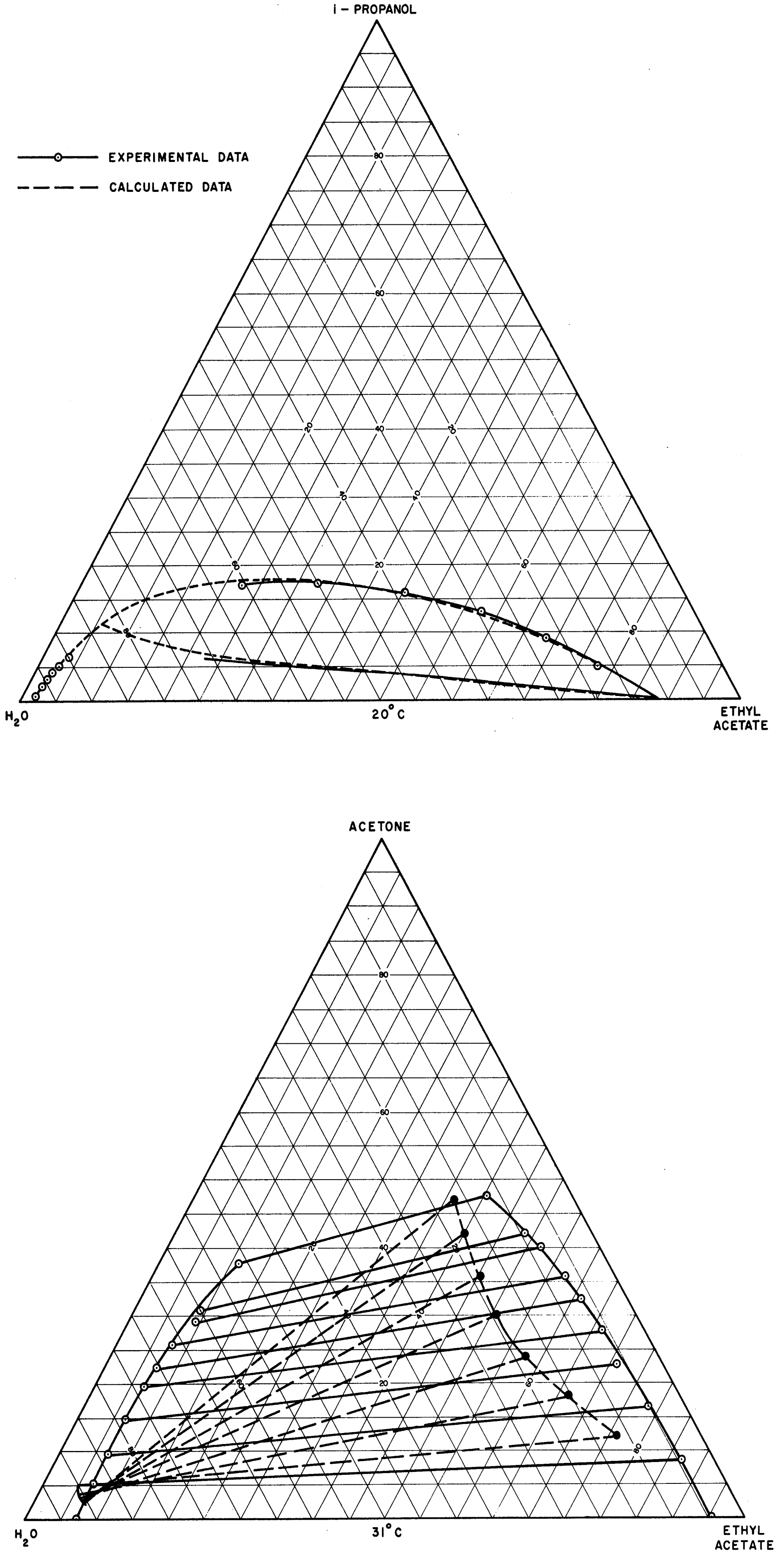


Figure 28. Examples of Fits Obtained Using Approximate Linearization.

Figure 28 shows that the estimate of the coefficients by minimization of Δ (4.17) was excellent in the case of i-propanol-water-ethyl acetate 20°C(2) where the equations were capable of highly accurate representation of the data, and the precision of the data is good. In the case of the system ethyl acetate-water-acetone 30°C(49) where the precision of the data is only fair and the tie lines are nearly parallel, the curve calculated using the coefficients obtained by solution of the Equations (4.18) is completely unsatisfactory. Although the solution of Equations (4.18) frequently does not give satisfactory values for the coefficients it is advisable to use the linearized approximation to see if it does give satisfactory values as it is much faster to solve Equations (4.16) than it is to use the hand methods described in section one or the non-linear methods described in the next section. If using the original experimental data in Equations (4.18) fails, and it is only desired to obtain an initial estimate of the coefficients for use in the non-linear least squares method described in the next section then data obtained from a smoothed curve through the original data should be used.

3. Least Squares Without Approximate Linearizations:

It was seen in the last section that the appropriate Δ that should be minimized to obtain best estimates of the coefficients is of the type:

$$\Delta = \sum^{M} \left[(x_j' - \overset{*}{x}_j')^2 \omega_1 + (x_k'' - \overset{*}{x}_k'')^2 \omega_2 + (x_\ell'' - \overset{*}{x}_\ell'')^2 \omega_3 \right] \tag{4.19}$$

$$(k \neq \ell)$$

where j, k, and l can have any values from one to three. Solution of the Equations (4.5) for Δ (4.19) is practically impossible. However, determination of the least squares estimates of the coefficients is possible by direct, iterative, minimization of Δ (4.19). Two methods are available and these have been described in Reference (21).

The Method of Steepest Descent: This method seeks at each trial to calculate corrections to the coefficients such that the value of Δ will decrease "most rapidly". The steepest descent direction is defined by the partial derivatives

$$\left(-\frac{\partial\Delta}{\partial c_1}, -\frac{\partial\Delta}{\partial c_2} \quad \cdots\cdots \quad -\frac{\partial\Delta}{\partial c_6}\right)$$

calculated at the nth trial values of the parameters c_1 ... c_6. Experience has shown that the minimum Δ is reached in fewer trials if the corrections to the parameters are not made exactly proportional to the partial derivatives of Δ but proportional rather to the normalized value of $-\frac{\partial\Delta}{\partial c_\ell}$ after multiplication by $(1 + c_\ell)$:

$$D_\ell = -(1+c_\ell^2)\frac{\partial\Delta}{\partial c_\ell} \Big/ \left[\sum_{j=1}^{6}\left((1+c_j^2)\frac{\partial\Delta}{\partial c_\ell}\right)^2\right]^{\frac{1}{2}}. \tag{4.20}$$

The n + 1 trial values of the coefficient c is calculated:

$$c_\ell^{[n+1]} = c_\ell^{[n]} + \alpha^{[n]} D_\ell^{[n]} \tag{4.21}$$

where $\alpha^{[n]}$ is the step size which determines the absolute magnitude of the corrections.

The calculation procedure that was found to be best suited to the Redlich-Kister equations may now be described. Assume that the calculation has proceeded to the nth iteration and it is desired to advance to the n + 1 iteration.

a. $\Delta^{[n]}$, $D_\ell^{[n]}$ ($\ell = 1, 2....6$) are calculated.

b. If $\Delta^{[n]} < \Delta^{[n-1]}$ proceed to step c., if not, divide $\alpha^{[n-1]}$ used in calculating $c_\ell^{[n]}$ by 4 and repeat step a.

c. Calculate the cosine of the angle θ, between the meterized steepest-descent directions at the (n - 1)th and nth trials

$$\cos\theta = \sum_{\ell=1}^{6} D_\ell^{[n]} D_\ell^{[n-1]} \quad . \tag{4.22}$$

d. Calculate a tentative value for $\alpha^{[n]}$ based upon $\cos\theta$. Note that if $\cos\theta$ is negative (i.e. $\theta > 90°$), it is desirable to reduce $\alpha^{[n]}$ to prevent undesirable oscillation between successive trial values of $c_1 \ldots c_6$. If $\cos\theta$ is near one the angle between successive trial directions is too small and it is desirable to increase the value of $\alpha^{[n]}$ to speed the convergence. To achieve this end the following formula has been devised:

$$\alpha^{[n]} = \alpha^{[n-1]} \left| e_2 + e_1 \cos^3\theta \right| \tag{4.23}$$

where e_1 and e_2 are always positive. The combination $e_1 = 0.5$ and $e_2 = 1.0$ has been found to be satisfactory.

e. Calculate the new trial values of the coefficients using (4.21) and return to step a.

This procedure converges from any reasonable initial guess of the parameters and it adjusts the step size automatically to the local topography of the Δ-c_1-c_2---c_6 surface. Convergence is slow in the neighborhood of the minimum Δ however and it is generally desirable to supplement the steepest descent method with a second method described below which converges only when the initial guesses are quite good but does converge rapidly.

The Truncated Taylor Series Method:$^{(21,37)}$ If values of the predicted mole fractions $\overset{*}{x}_j$, $\overset{*}{x}_k$, $\overset{*}{x}_\ell$ are expanded about current trial values of the coefficients c_1 ... c_6 and the series is truncated after terms that are linear in Δc_1 ... Δc_6:

$$\overset{*}{x}_j(c_1+\Delta c_1, \cdots c_6+\Delta c_6) \approx \overset{*}{x}_j(c_1, c_2, \cdots c_6)+\sum_{\ell=1}^{6}\Delta c_\ell\left(\frac{\partial \overset{*}{x}_j}{\partial c_\ell}\right) \qquad (4.24)$$

and similarly for $\overset{*}{x}_k$ and $\overset{*}{x}_L$. Substitution of (4.24) into Δ (4.19) gives:

$$\Delta=\sum_{i=1}^{M}\left[\left(x_j'-\left(\overset{*}{x}_j'+\sum_{\ell=1}^{6}\Delta c_\ell\frac{\partial \overset{*}{x}_j'}{\partial c_\ell}\right)\right)^2+\left(x_k''-\left(\overset{*}{x}_k''+\sum_{\ell=1}^{6}\Delta c_\ell\frac{\partial \overset{*}{x}_k''}{\partial c_\ell}\right)\right)^2+\left(x_L''-\left(\overset{*}{x}_L''+\sum_{\ell=1}^{6}\Delta c_\ell\frac{\partial \overset{*}{x}_L''}{\partial c_\ell}\right)\right)^2\right]_i. \qquad (4.25)$$

The minimum Δ is reached, when for the nth trial

$$\left(\frac{\partial\Delta}{\partial(\Delta c_1)}\right)^n=\left(\frac{\partial\Delta}{\partial(\Delta c_2)}\right)^n=\cdots\cdots=\left(\frac{\partial\Delta}{\partial(\Delta c_6)}\right)=0 \qquad (4.26)$$

which are six simultaneous equations linear in $\Delta c_1 \dots \Delta c_6$. The Equations (4.26) may be written after substitution of (4.25) and differentiation:

$$\sum_{i=1}^{M}\left[\sum_{\ell=1}^{6}\Delta c_\ell\left(\frac{\partial \overset{*}{x}{}'_j}{\partial c_\ell}\,\frac{\partial \overset{*}{x}{}'_j}{\partial c_r}+\frac{\partial \overset{*}{x}{}''_k}{\partial c_\ell}\,\frac{\partial \overset{*}{x}{}''_k}{\partial c_r}+\frac{\partial \overset{*}{x}{}''_L}{\partial c_\ell}\,\frac{\partial \overset{*}{x}{}''_L}{\partial c_r}\right)\right]=-\sum_{i=1}^{M}\left[\Delta x_j\frac{\partial \overset{*}{x}{}'_j}{\partial c_r}+\Delta x_k\frac{\partial \overset{*}{x}{}''_k}{\partial c_r}+\Delta x_L\frac{\partial \overset{*}{x}{}''_L}{\partial c_r}\right]$$

$$(r = 1, 2, \cdots 6) \qquad (4.27)$$

where $\Delta x_j = x_j - \overset{*}{x}_j\,(c_1, c_2 \dots c_6)$ and similarly for Δx_k and Δx_L. The six Equations (4.27) may be easily solved for $\Delta c_1 \dots \Delta c_6$ and the n + 1th trial of the coefficients calculated:

$$c_\ell^{[n+1]} = c_\ell^{[n]} + \Delta c_\ell^{[n]} \qquad (\ell = 1, 2 \cdots 6) \qquad (4.28)$$

If the approximation made by truncating the Taylor series after linear terms is good enough then the method converges and

$$\left|\Delta c_\ell^{[n+1]}\right| < \left|\Delta c_\ell^{[n]}\right|$$

A computer program (Program 8 - Appendix B) for the IBM 704 has been written which uses both methods described here to obtain the estimates of the parameters which minimize

$$\Delta = \sum_{i=1}^{M}\left[\left(x'_2 - \overset{*}{x}{}'_2\right)^2\omega_1 + \left(x''_2 - \overset{*}{x}{}''_2\right)^2\omega_2 + \left(x''_3 - \overset{*}{x}{}''_3\right)^2\omega_3\right]_i \qquad (4.29)$$

The steepest descent method is used initially, then, when in the proximity of the minimum Δ(4.29), the truncated Taylor series method is used. If the equations are not capable of fitting the experimental data with high precision the latter method diverges and the estimates of the coefficients obtained by the steepest descent must be used.

The most difficult part of the two procedures is the computation of the Δ and the partial derivatives of Δ with respect to the coefficients. Note that solution of Equations (3.10), (3.11), and (3.12) is required for every experimental tie line where $x_3' = \overset{*}{x}_3'$ (the chosen independent variable in the case of Program 8). Thus the solution procedure for Equations (3.10), (3.11) and (3.12) described in part III is required. Unfortunately this solution procedure will not converge unless the initial guesses of the compositions are quite good and frequently, especially in the neighborhood of a plait point, use of the experimental data (the x's) as an initial guess is not good enough that convergence to the values of the predicted molfractions (the $\overset{*}{x}$'s) is obtained. This problem was solved by a procedure of solving Equations (3.10), (3.11), and (3.12) in very small steps of increasing x_3' from experimental tie line to experimental tie line, using as the initial guesses of the x's for each step those values obtained by linear extrapolation from the last two steps. This method has been found to be highly satisfactory.

One must be especially careful that the initial guesses of the parameters give an equilibrium curve for which at every $\overset{*}{x}_3' = x_3'$ a non-trivial solution of Equations (3.10), (3.11), and (3.12) exists. An equilibrium curve should always be calculated with the initial guess of the coefficients at the outset to make sure this is so before proceeding.

The development of the partial derivatives $\frac{\partial \Delta}{\partial c_{\ell}}$ is given in Appendix A, and follows the procedures outlined in text books on advanced calculus pertaining to the differentiation of implicit functions.(55)

All of the calculated curves for specific systems given in part V were determined using coefficients which minimize Δ (4.29), $w_1 = w_2 = w_3 = 1$. Initial guesses of the coefficients were determined by the hand methods described in Section 1, except for the systems ethyl-acetate-water with ethanol, iso-propanol, n-propanol and t-butanol, where the initial estimates were obtained using the linearized approximation, Δ (4.17).

V. TESTING OF THE RESEARCH HYPOTHESES

The problem now remains to determine the feasibility of using the Redlich-Kister Equations (3.10), (3.11), and (3.12) to correlate and predict equilibria for liquid-liquid systems. Restating the questions raised earlier in the affirmative we may write the following research hypotheses for the specific case of the Redlich-Kister equations applied to ternary liquid-liquid equilibria:

(1) The vast majority of ternary liquid-liquid equilibria can be represented by Equations (3.10), (3.11), and (3.12) which retain only the binary B_{ij} and C_{ij} coefficients.

(2) B_{ij} and C_{ij} are independent of component k. That is B_{ij} and C_{ij} have the same values in the binary system i-j as in the ternary system i-j-k. If this is true then coefficients determined from binary data can be used to predict ternary data.

(3) B_{ij} and C_{ij} are simple functions of some property of k. If this is true then coefficients for a homologous series of ternary systems i-j-k_1, i-j-k_2, ... i-j-k_n, where k_1, k_2, ... k_n are homologs could be used to predict the coefficients for a system i-j-k_i for which no data are available.

Hypothesis (1) has already been supported by the computation of the several fictitious equilibrium curves (Figures 16-25). Over twenty actual systems have been fitted by Equations (3.10), (3.11) and (3.12) during the course of this investigation as a further test of Hypothesis (1). These systems are illustrated later in this section.

A. Binary Coefficients from Binary Versus Ternary Data

The possibility of prediction of multicomponent data from binary data has long interested workers in the field of phase equilibrium. Probably the most recent effort in this area was that of Kenny(18) who determined coefficients in the two suffix Van-Laar equations (see Table I) from total pressure measurement of binary systems to predict equilibria in the ternary system iso-octane-furfural-benzene, 20°C. The predicted binodal curve deviated considerably from the experimental curve near the plait point and agreed fairly well near the partially miscible binary iso-octane-furfural. The predicted tie lines did not agree well at all with the experimental tie lines. It was found that including some ternary data in the determination of equation coefficients, improved the fit somewhat.

Two ternary systems were found for which binary data are available at or near the same temperature as the ternary data. These systems are ethyl acetate-water-ethanol (70°C)(11) with binary data: ethyl acetate-ethanol (1 atm.)(11), ethyl acetate-water (70°C),(11) ethanol-water (74.79°C),(56) and benzene-water-1,4 dioxane (25°C)(3) with binary data: benzene-water (25°C),(43) benzene-dioxane (25°C),(45) and dioxane-water (25°C).(49)

The binary B and C coefficients were determined in the cases of the partially miscible binary systems using Program 5, Appendix B. Program 1 determined least squares values for B_{ij} and C_{ij} for binary vapor-liquid systems at constant temperature. Program 3 was used for systems at constant pressure.

TABLE II

COMPARISON OF COEFFICIENTS DETERMINED FROM BINARY VERSUS TERNARY DATA

$H_2O(1)$ - Ethyl Acetate(2) - Ethanol(3) 70°C

	B_{12}	B_{23}	B_{31}	C_{12}	C_{23}	C_{31}
From Binary Data	1.130	0.3630	0.5400	0.6910	-0.0092	-0.1730
From Ternary Data	1.172	-5.339	-7.733	0.6450	1.517	-3.338

$H_2O(1)$ - Benzene(2) - 1.4 Dioxane(3) 25°C

	B_{12}	B_{23}	B_{31}	C_{12}	C_{23}	C_{31}
From Binary Data	3.060	0.1080	0.7900	-0.2400	-0.0320	0.05730
From Ternary Data	2.704	0.1135	0.7659	-0.2407	-0.03483	-0.1283

All of the binary systems of ternary H_2O-benzene-dioxane and the ternary itself were determined at 25°C. In the case of the ethyl acetate-H_2O-ethanol ternary although only the binary solubility data are at exactly the same temperature as the ternary, the correction of the coefficients for the ethyl acetate-ethanol system (1 atm., 77.2-78.4°C) and the ethanol-water system (74.79°C) to 70°C is negligible.

Figure 29 gives the Redlich-Kister B_{ij} , C_{ij} least squares fits of the x-y data for the four vapor-liquid binary systems. In all cases the fits are good indicating that the coefficients have been accurately determined and that the data are thermodynamically consistent (otherwise the Redlich-Kister equations would have been unable to fit the data).

The binary B and C coefficients were redetermined using only ternary data by minimization of Δ (4.29), utilizing Program 8. Table II compares the values for the coefficients determined from the binary and ternary data. Note that for the system ethyl acetate-water-ethanol at 70°C, except in the case of the coefficients that correspond to the partially miscible binary, the coefficients from binary data do not agree with those from ternary data.

Figure 30 compares the fits of the experimental data using binary data to determine the coefficients (solid curve). The convolute lines have been drawn to enable location of the tie lines. Note that all equilibrium curves reach the partially miscible binary regions at about the same location and that the accuracy of the curve predicted from binary data is best near the partially miscible binary, poorest near the plait point which agrees with Kenny's observation.

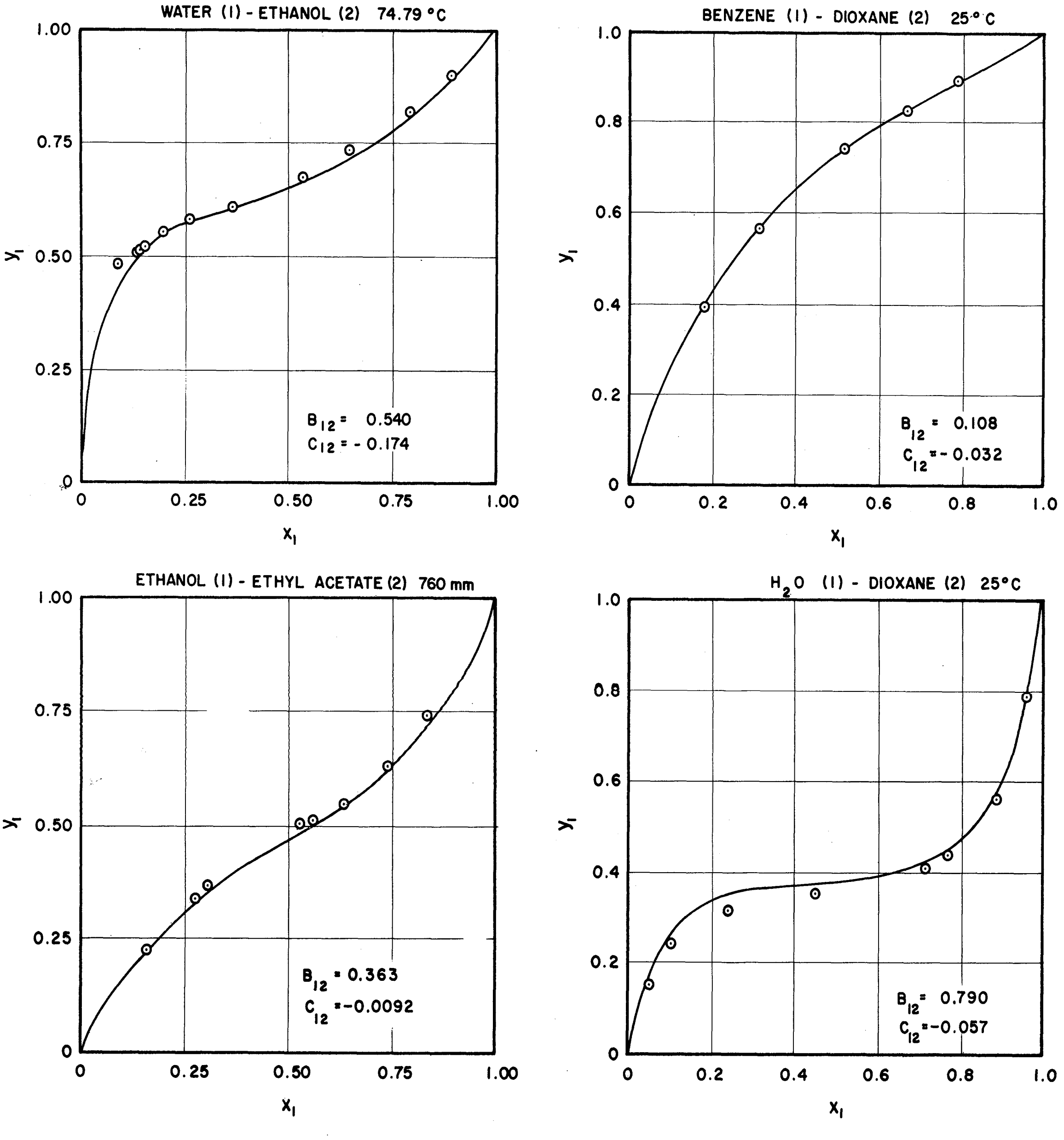


Figure 29. B_{ij} - C_{ij} Fit of Binary X-Y Data.

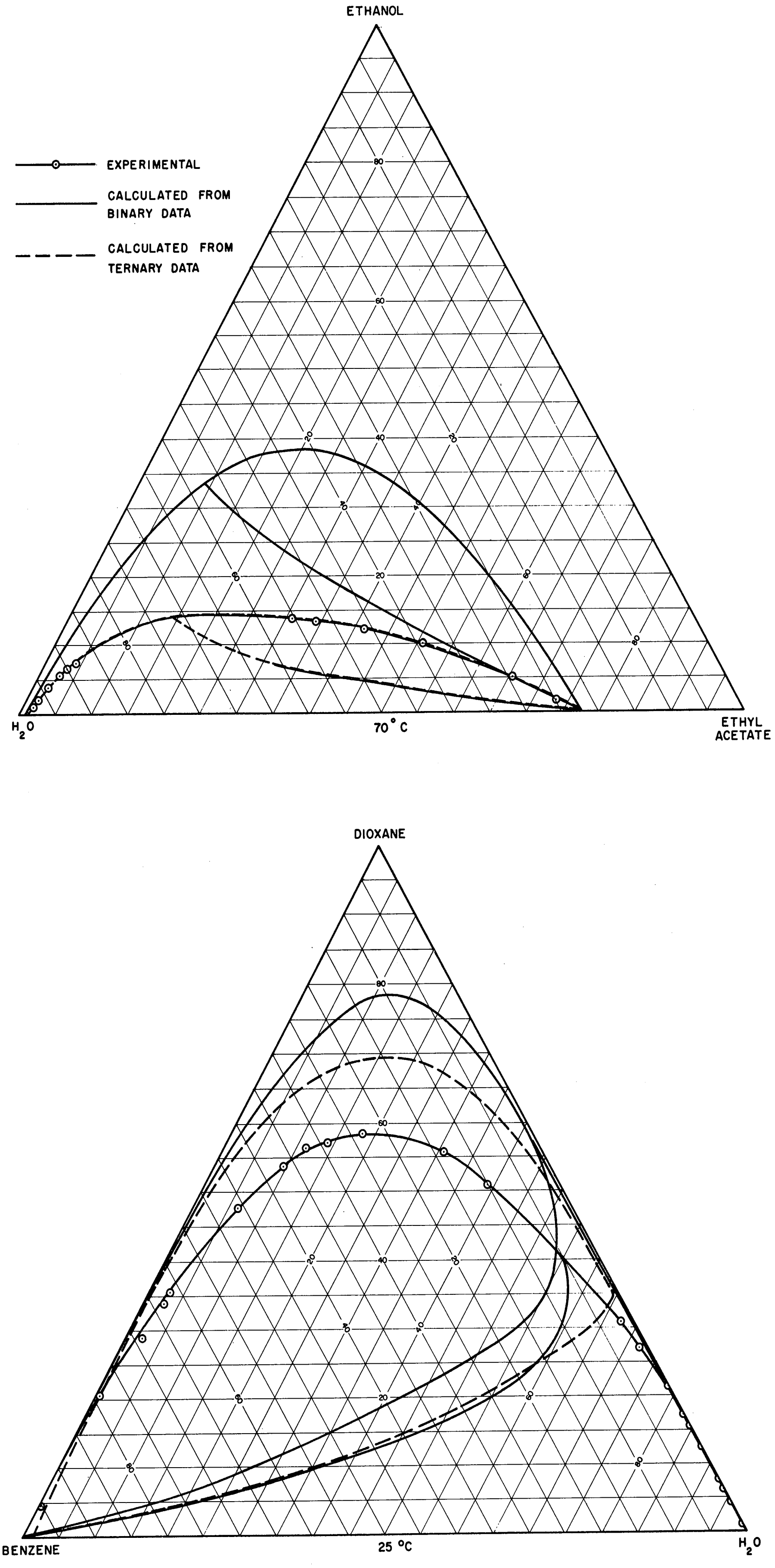


Figure 30. Comparison of Fits Obtained Using Coefficients Determined from Binary Versus Ternary Data.

It must be concluded that for partially miscible systems there is enough ternary interaction that ternary equilibria cannot be accurately predicted from binary equilibrium data, except near a partially miscible binary. Hypothesis(2) must be rejected.

Ternary interaction coefficients need not be introduced in Equations (3.10), (3.11), and (3.12) to enable correlation of the ternary liquid-liquid equilibria of the ethyl acetate-water-ethanol system at 70°C, where a nearly perfect fit was obtained using values of B_{ij} and C_{ij} determined from ternary data. (dashed curve). The binary coefficients take on new values for the ternary liquid-liquid case reflecting the ternary interaction which could not be predicted from data on the individual binaries.

The fit of the data using coefficients determined from ternary data for the system benzene-water-dioxane (25°C), though not perfect, is an improvement over the fit predicted from the binary data. Apparently more coefficients are required to correlate this system accurately.

B. Homologous Series of Systems

It remains to test Hypothesis (3) to determine whether the Redlich-Kister equations have utility as a basis for a correlation of ternary liquid-liquid equilibria. If Hypothesis (3) is valid then experimental data for systems $i\text{-}j\text{-}k_1$, $i\text{-}j\text{-}k_2$, ... $i\text{-}j\text{-}k_n$ where k_1, k_2, ... k_n are homologs can be used to predict the equilibrium in the system $i\text{-}j\text{-}k_i$ which has not been determined experimentally. A fairly large number of homologous series of systems have been determined experimentally. Table III gives some of these having at least three members per series.

TABLE III*

HOMOLOGOUS SERIES OF SYSTEMS

SYSTEMS INVOLVING HYDROCARBONS	i	j	k_1	k_2	k_3	k_4	Temp.	Ref.
1)	Benzene	Sulfur Dioxide	n-Butane	n-Hexane	n-Heptane	n-Decane	-20°F	(35)
2)	Benzene	n-Heptane	ββ'-imino-*	ββ'-oxy-*	ββ'-thio-*	αβ'-oxy-*	25°C	(36)
3)	Benzene Benzene	Water Water	Ethanol n-Propanol	i-Propanol i-Butanol	t-Butanol	n-Butanol	25°C 38°C, 25°C	(48),(26),(44),(51) (24),(1)
4)	n-Heptane	Water	Methanol	Ethanol	n-Propanol		25°,30°,38°C	(19),(42),(24)
5)	n-Heptane	ββ'-thio*	Benzene	Toluene	p-Xylene	Ethyl benzene	25°C	(36)
6)	Methanol	Water	n-Hexane	n-Heptane-	n-Octane	n-Nonane	10° & 15°C	(19)
OTHER SYSTEMS								
1)	Acetic acid	Water	Methyl**	Propyl**	Butyl**		30°C	(25)
2)	Acetone Acetone	Water Water	Methyl** Amyl**	Ethyl**	n-Propyl**	n-Butyl**	30°C 30°C	(49)
3)	Acetone	Water	Ethyl Acetate	Ethyl Propionate	Ethyl Butyrate		30°C	(49)
4)	n-Butanol	Water	Ethylene***	Diethylene***	Triethylene***		20° & 40°C	(23)
5)	Ethyl** Ethyl**	Water Water	Methanol t-Butanol	Ethanol s-Butanol	i-Propanol i-Butanol	n-Propanol n-Butanol	0° & 20°C 0° & 20°C	(2)
6)	Ethyl benzoate	Water	Formic acid	Acetic acid	Propionic acid	Butyric acid	30°C	(31)
7)	Ethylene Glycol	Acetone	Ethyl**	Butyl**	Amyl**		31°C	(30)
8)	Ethylene Glycol	Acetone	Ethyl**	Ethyl propionate	Ethyl butyrate		31°C	(30)
9)	Methanol	Water	Ethyl**	n-Butyl**	Pentyl**		30°C	(32)
10)	M.I.B.C.	Water	Formic acid	Acetic acid	Propionic acid	Butyric acid	30°C	(28)
11)	Di-Phenyl Ether	Water	Methanol	Ethanol	n-Propanol	n-Butanol	25°C	(27)
12)	Di-Phenyl Ethyl	Water	Acetic acid	Propionic acid	Butyric acid		25°C	(27)
13)	i. Propanol	Water	CCl_4	$CHCl_3$	CH_2Cl_2		25°C	(17)
14)	Propionic acid	Water	Ethyl**	Ethyl**	Ethyl**		30°C	(29)

*Dipropionitrile
**Acetate
***Glycol
M.I.B.C. ≡ methyl isobutyl carbinol

One question that might be raised is: for the purpose of the correlation must one consider a homologous series to be that defined in its strictest sense (e.g. methanol, ethanol, n-propanol, n-butanol) or may isomers be included (e.g. methanol, ethanol, i- and n-propanol, t-, s-, i-, and n-butanol)? In compilation of Table III isomers have been included.

In order to test Hypothesis(3), four homologous series of systems taken from Table III have been used, Three situations have been studied:

(a) k, the variable component in the series, is miscible with both components i and j. Two series of systems having this characteristic were studied: water-ethyl acetate-alcohols (20°C) and water-benzene-alcohols (25°C).

(b) k is partially miscible with j, completely miscible with i. The series studied having this characteristic is n-paraffins-sulfur dioxide-benzene (-20°F).

(c) k is partially miscible with both i and j. The series studied was n-paraffins-water-methanol (15°C).

1. Water-Ethyl Acetate-Alcohols:

Counting both normal alcohols and iso-alcohols the data of Beech and Glasstone(2) provide the longest homologous series of experimentally determined systems found in the literature. Figures 31-38 illustrate the least squares fits of the data obtained using Program 8 which minimizes Δ (4.29). Convolute lines have been used to permit location of the tie lines. Calculated points (+) appearing in figures are calculated at $x_3' = \overset{*}{x}_3'$ for each experimentally determined tie line, (') referring to the water phase, (") the ester phase.

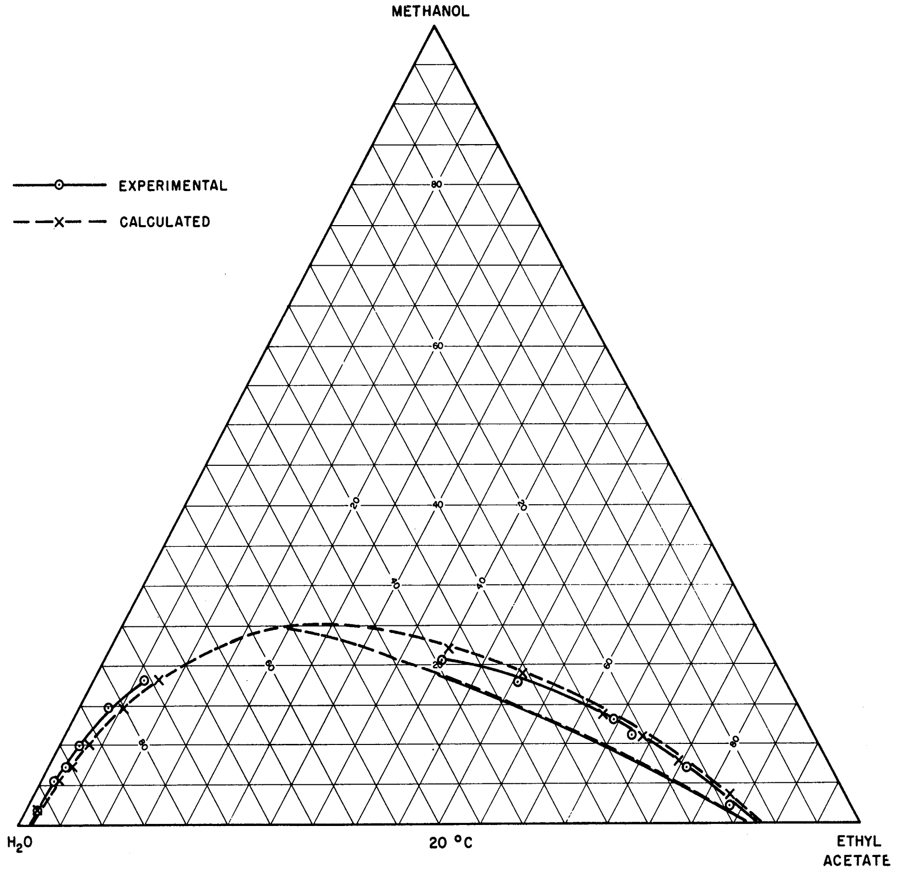


Figure 31. H_2O (1) - Ethyl Acetate (2) - Methanol (3).

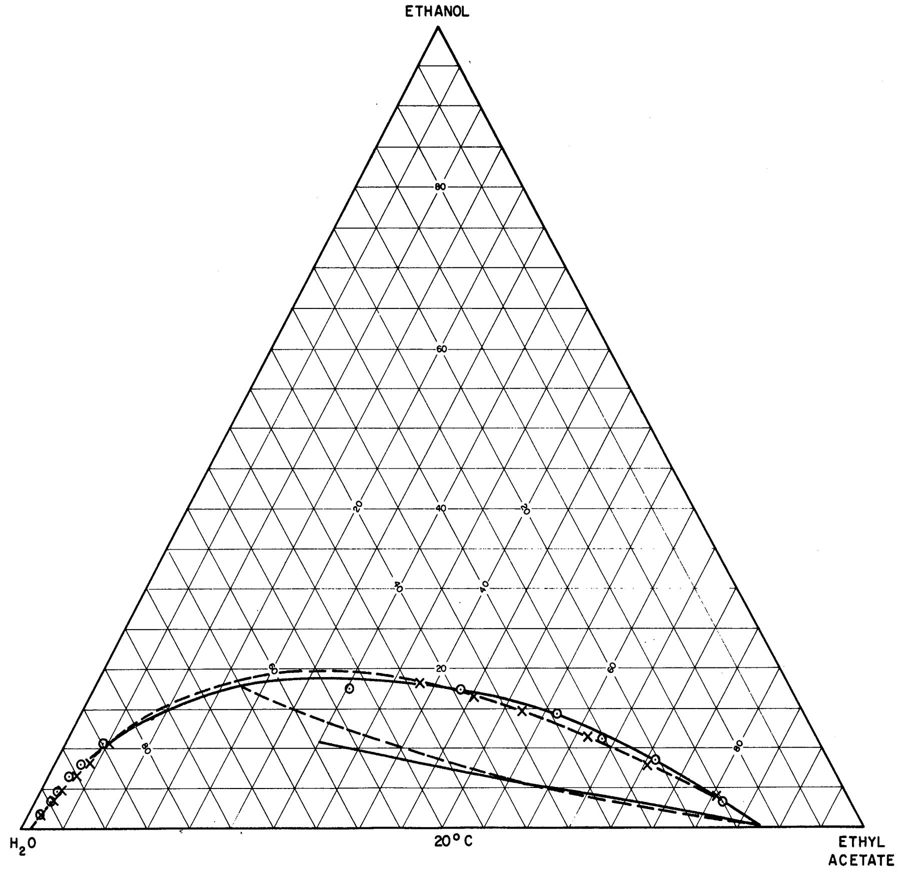


Figure 32. H_2O (1) - Ethyl Acetate (2) - Ethanol (3).

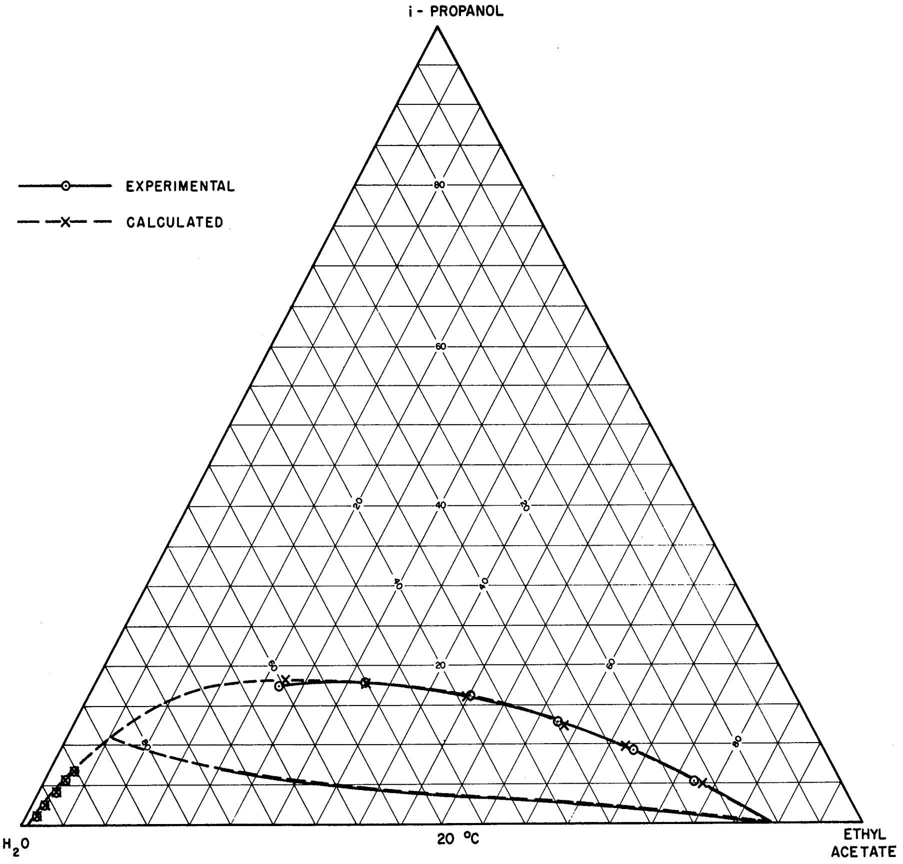


Figure 33. H_2O (1) - Ethyl Acetate (2) - i-Propanol (3).

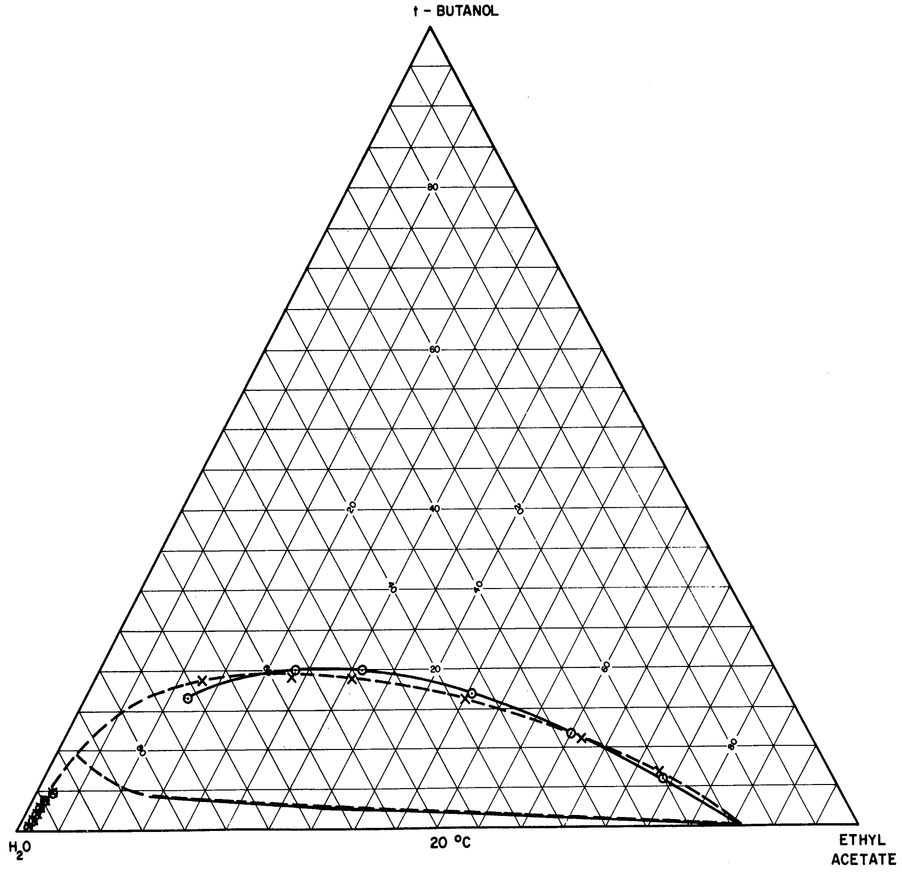


Figure 34. H_2O (1) - Ethyl Acetate (2) - t-Butanol (3).

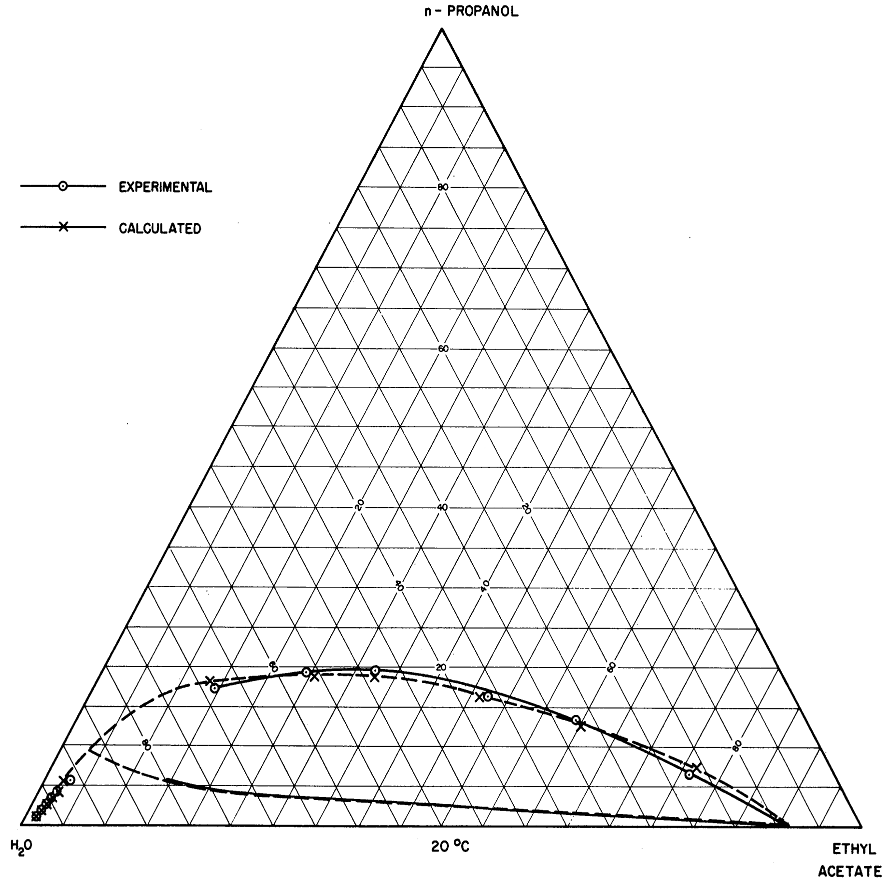


Figure 35. H_2O (1) - Ethyl Acetate (2) - n-Propanol (3).

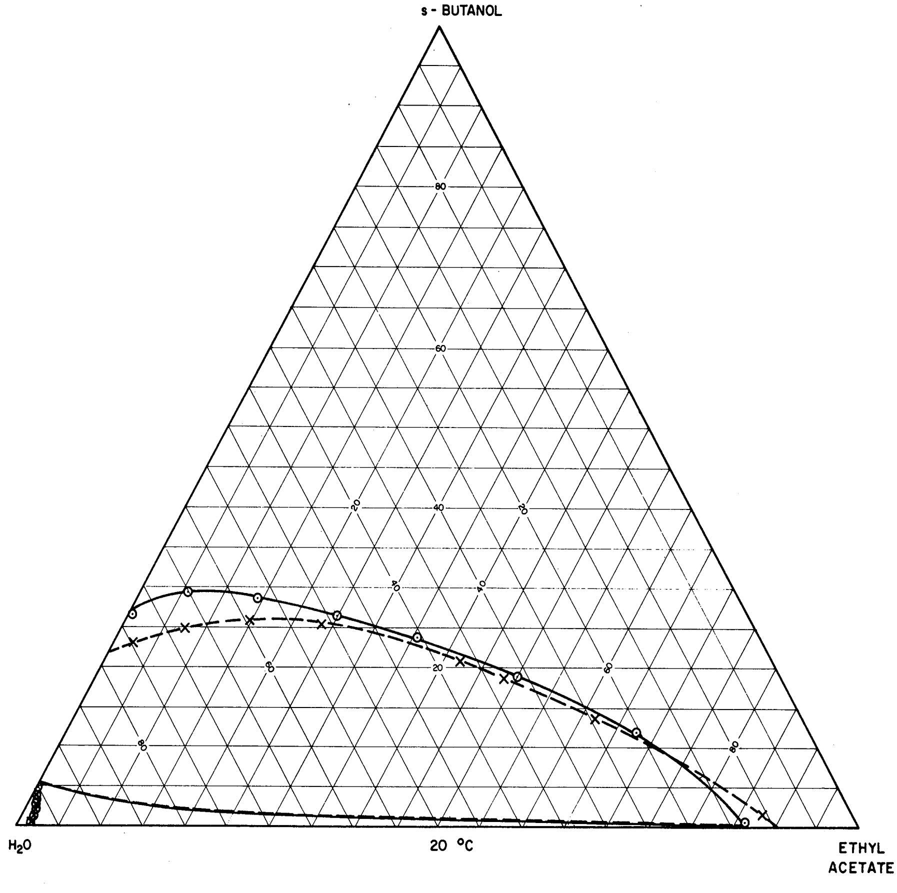


Figure 36. H_2O (1) - Ethyl Acetate (2) - s-Butanol (3).

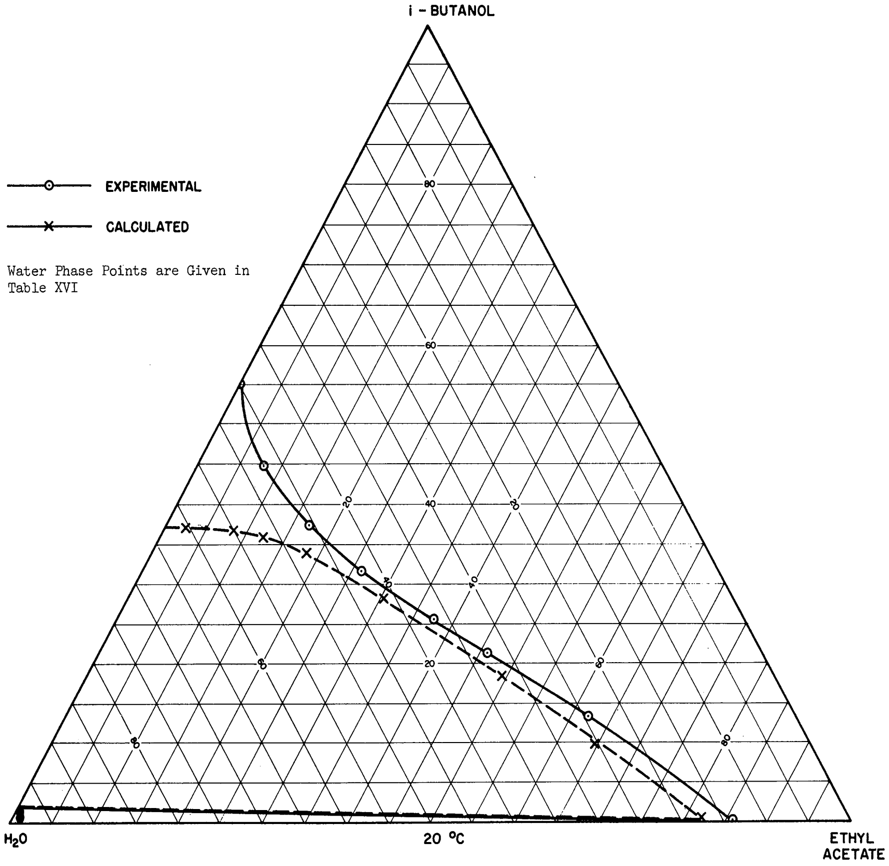


Figure 37. H_2O (1) - Ethyl Acetate (2) - i-Butanol (3).

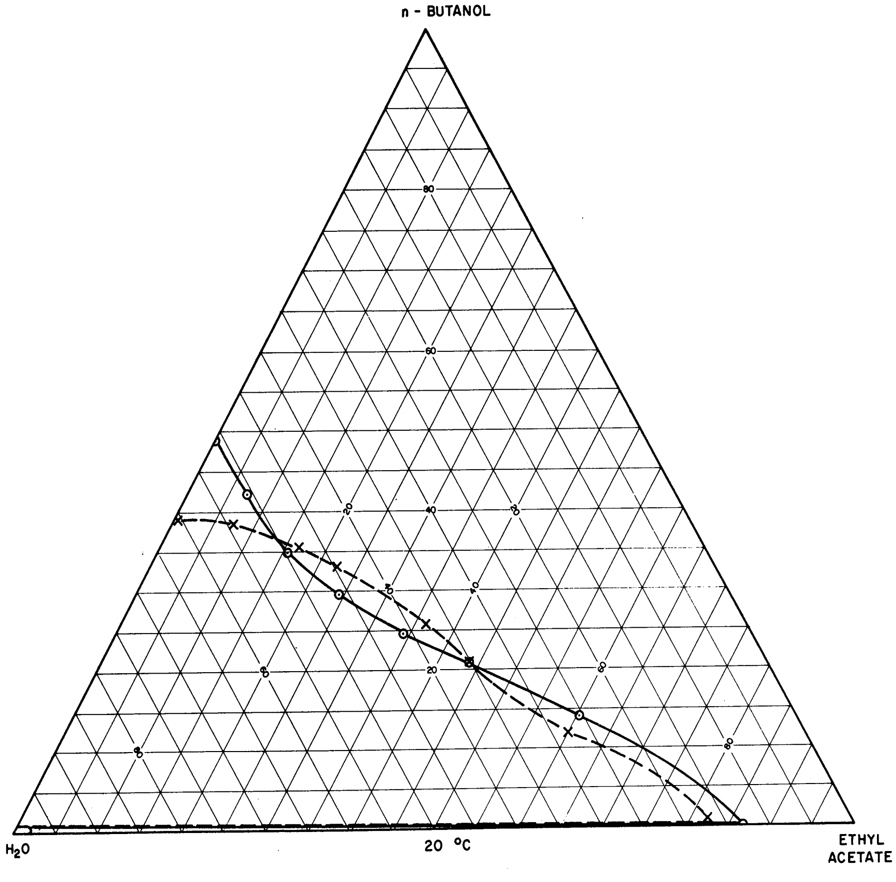


Figure 38. H_2O (1) - Ethyl Acetate (2)- n-Butanol (3).

TABLE IV*

REDLICH-KISTER COEFFICIENTS
$H_2O(1)$ - ETHYL ACETATE(2) - ROH(3), 20°C

ROH	Boiling Pt. °C	B_{12}	B_{23}	B_{31}	C_{12}	C_{23}	C_{31}	$\Delta^*/N \times 10^3$	Method
Methanol	64.7	1.426	-2.612	-2.838	0.4677	1.005	-1.074	0.395	S.D.
Ethanol	78.4	1.403	-4.329	-4.602	0.4345	1.642	-1.758	1.605	S.D.
i-Propanol	82.5	1.427	-3.677	-5.244	0.4017	0.8167	-2.794	0.0916	Trunc.
t-Butanol	82.9	1.460	-4.121	-5.925	0.4610	0.8599	-3.282	0.179	Trunc.
n-Propanol	97.8	1.488	-3.666	-4.910	0.2967	0.8540	-2.782	0.1005	Trunc.
s-Butanol	99.5	1.452	-2.912	-3.503	0.3601	0.9161	-2.527	1.685	S.D.
i-Butanol	107.5	1.248	-1.458	-1.724	0.4336	1.201	-2.175	7.161	S.D.
n-Butanol	117	1.265	-1.411	-1.734	0.4296	1.219	-2.050	1.621	S.D.

TABLE V*

REDLICH-KISTER COEFFICIENTS
$(H_2O)_8(1)$ - BENZENE(2) - ROH(3), 25°C

ROH	Boiling Pt. °C	B_{12}	B_{23}	B_{31}	C_{12}	C_{23}	C_{31}	$\Delta^*/N \times 10^3$	Method
Ethanol	78.4	2.782	0.8246	-0.9976	-0.5004	0.0150	0.0008	6.35	S.D.
i-Propanol	82.5	2.823	0.2890	-0.2538	-0.5035	0.3741	0.2460	0.724	S.D.
t-Butanol	82.9	2.773	0.0814	0.1848	-0.4747	0.5981	0.5246	8.60	S.D.
n-Propanol	97.8	2.802	0.0000	0.0954	-0.4870	0.4553	0.3562	0.585	S.D.
i-Butanol	107.5	2.778	0.4717	1.140	-0.5096	0.2163	0.3165	15.21	S.D.
n-Butanol	117	2.754	0.4317	1.148	-0.5113	0.1438	0.2297	15.48	S.D.

*Δ(4.29) divided by N, the number of experimental tie lines.

In those systems where there is only one partially miscible binary the fit of the data is excellent. The fits obtained for the systems having two partially miscible binary systems is good near the H_2O- ethyl acetate binary but rather poor near the alcohol-water binary. This suggest the possibility that more than the B and C binary coefficients are required to correlate an entire ternary having two partially miscible binaries.

Table VI gives the least-squares coefficients used to determine the calculated curves in Figures 31-38. It also gives the alcohol boiling point, Δ divided by N, N being the number of experimental tie lines, and the method by which Δ was minimized (steepest descent or truncated Taylor series). Note that in those cases where Δ was minimized by the truncated Taylor series method, one is fairly sure that Δ is a minimum. Where convergence using the truncated Taylor series was not obtained and results using the method of steepest descent must be relied upon, it is difficult to be sure that the minimum has been reached or if a region of exceptionally slow convergence is being traversed, such as a trough or saddle point. It is possible that this could explain the fact that the deviations from the experimental data are greater in the cases of the systems having two immiscible pairs as what appears to be Δ_{MIN} was reached by steepest descent for these cases.

2. Water-Benzene-Alcohols:

The water-benzene-alcohol series constitutes the second longest series of experimentally determined systems, six systems in all. With the exception of water-benzene-n-propanol (38°C) all were determined at 25°C.

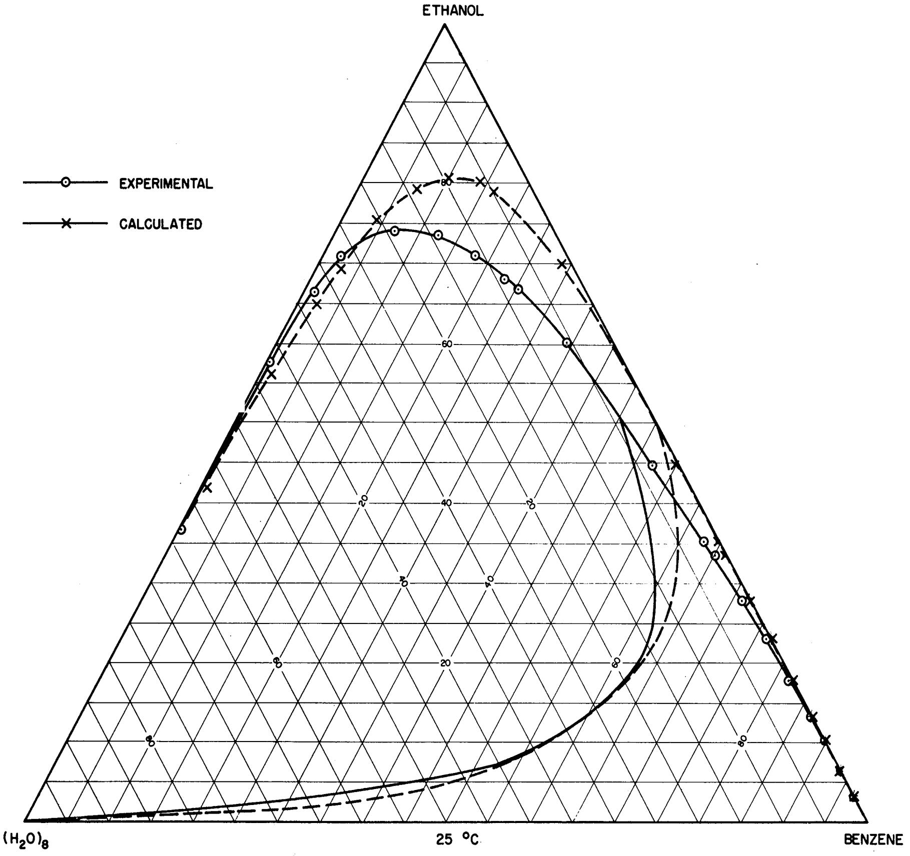


Figure 39. $(H_2O)_8$ (1) - Benzene (2) - Ethanol (3).

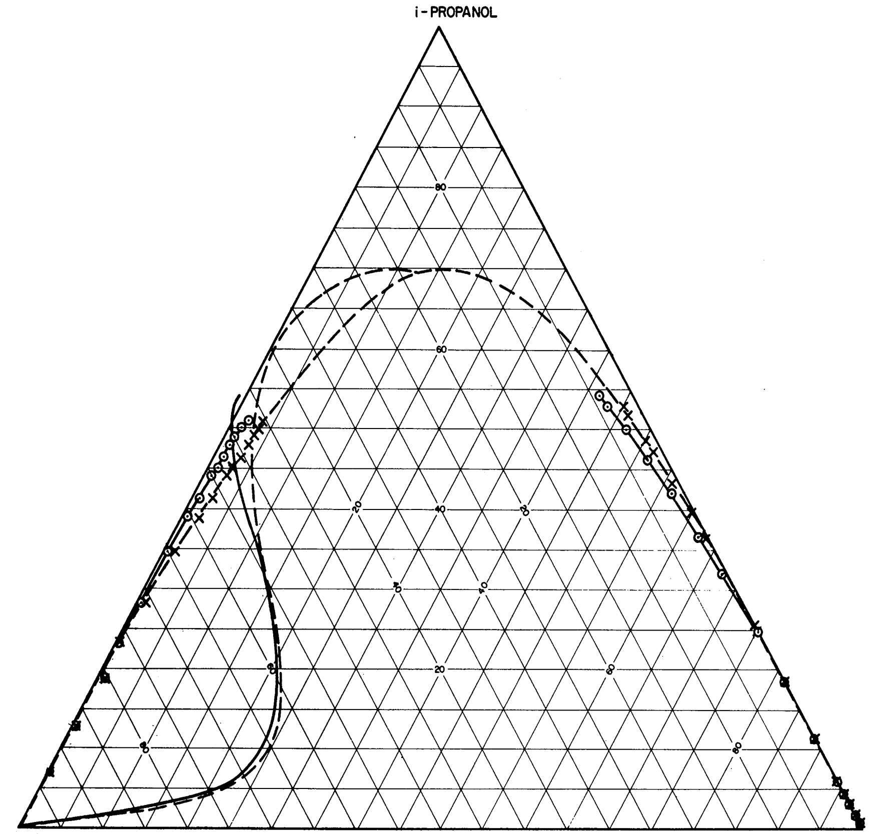


Figure 40. $(H_2O)_8$ (1) - Benzene (2) - i-Propanol (3).

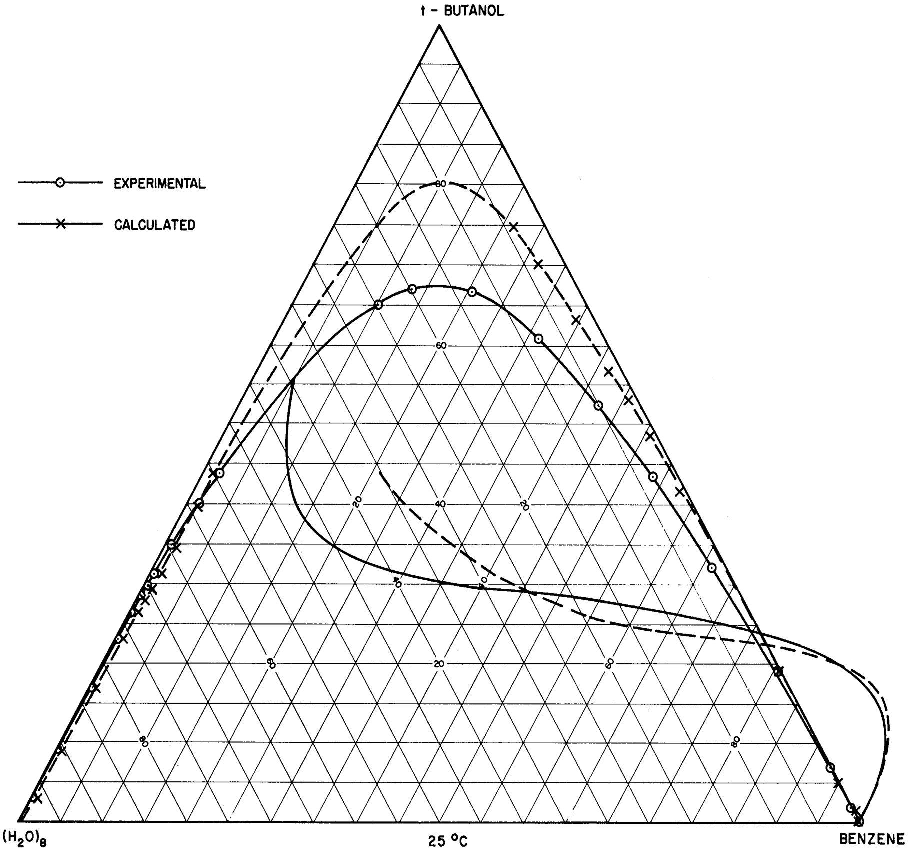


Figure 41. $(H_2O)_8$ (1) - Benzene (2) - t- Butanol (3).

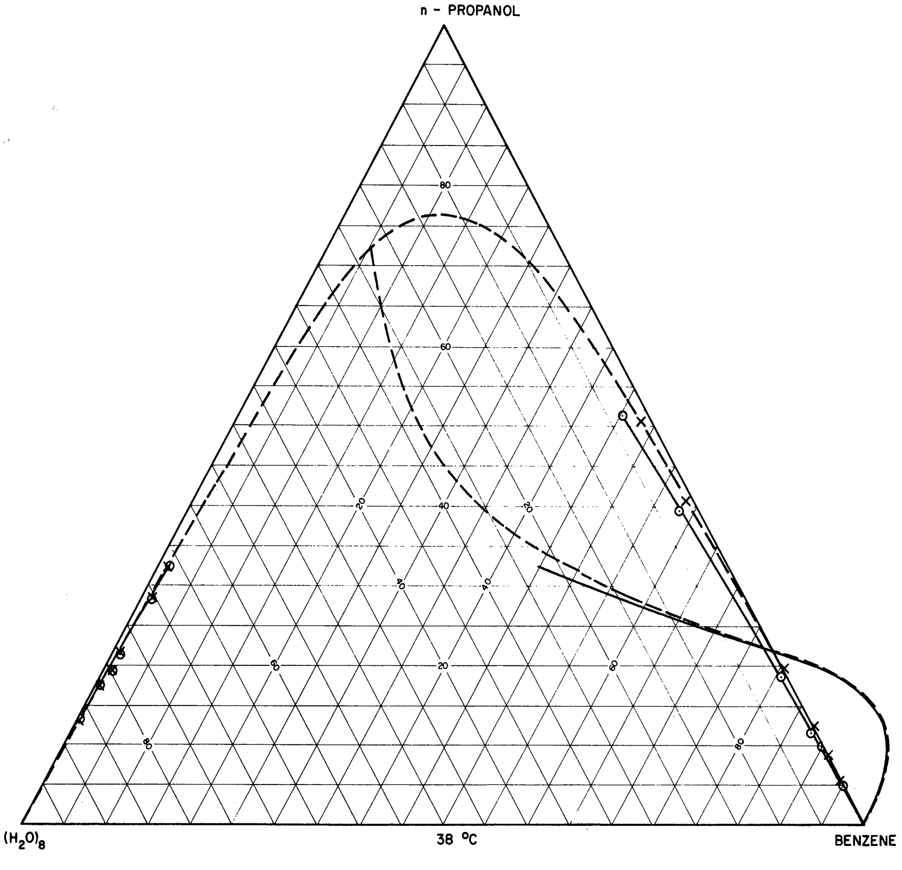


Figure 42. $(H_2O)_8$ - Benzene (2) - n- Propanol (3).

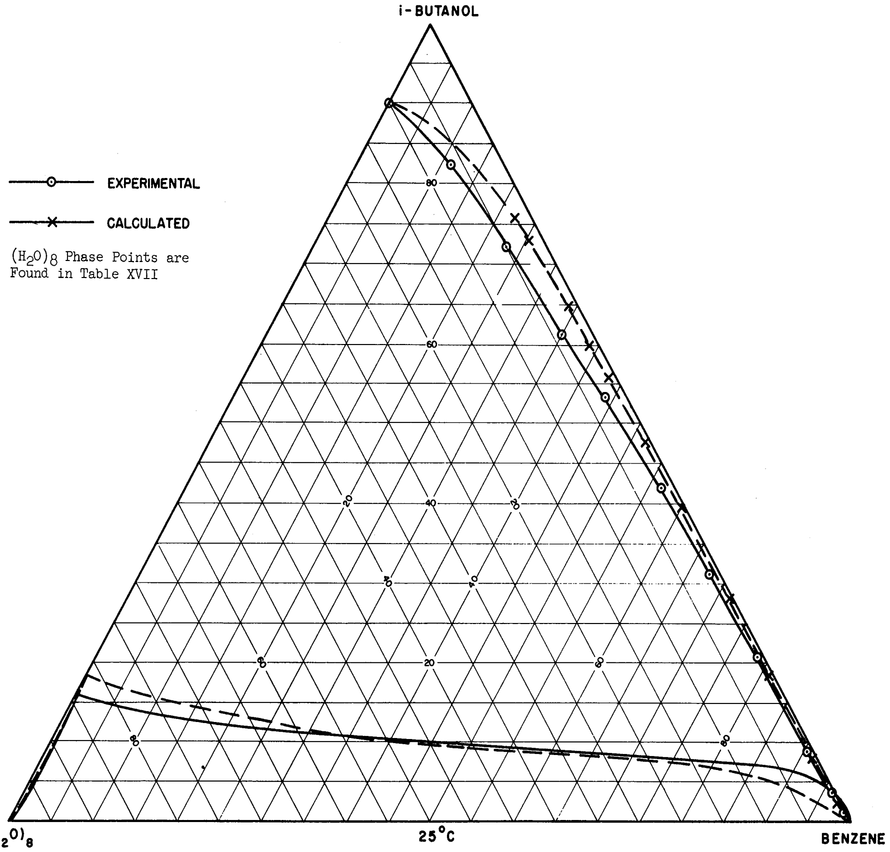


Figure 43. $(H_2O)_8(1)$ - Benzene (2) i-Butanol (3).

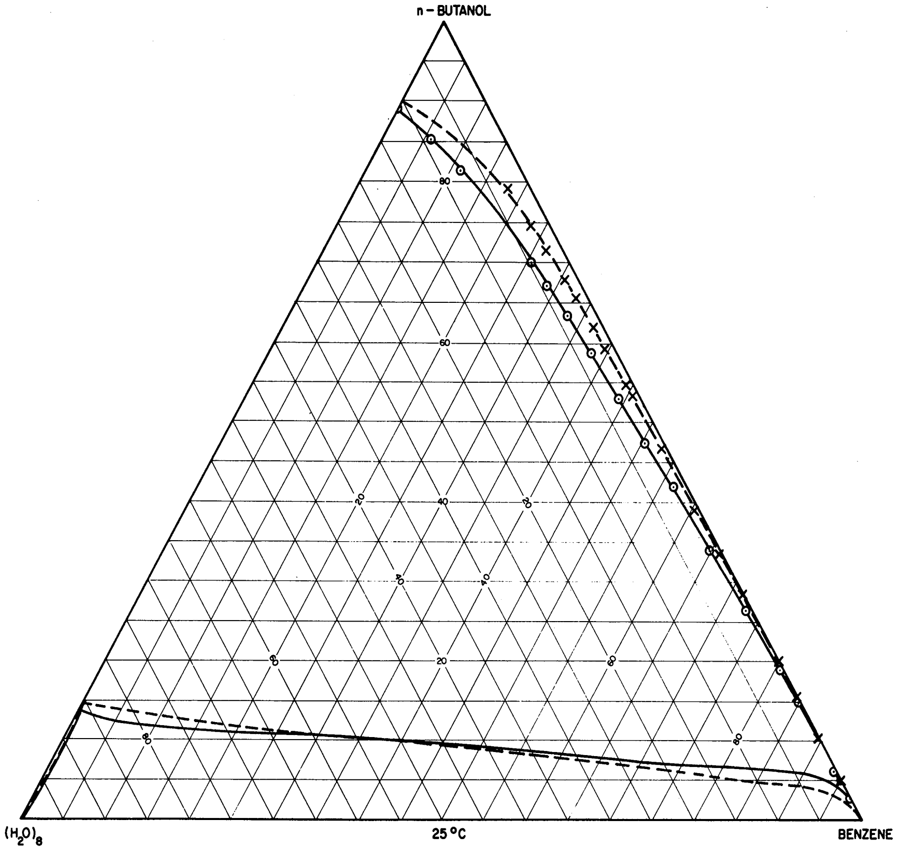


Figure 44. $(H_2O)_8(1)$ - Benzene (2) n-Butanol (3).

Because of the extent of the miscibility gap in the benzene-water binary these systems may be considered to be a severe test of the ability of Equations (3.10), (3.11), and (3.12) to fit ternary liquid-liquid equilibrium data.

It was found that using 18 as the molecular weight of water (i.e. assuming a monomolecular specie) gave equilibrium curves for the benzene-water systems that could not be fitted accurately by the equations. Assuming water to exist as an octa-molecular specie, equilibrium curves were obtained that were readily fitted (see Figures 39-44).

Excellent fits of the experimental data were obtained in the cases of i-propanol (Figure 40) and n-propanol (Figure 41). The fits were not as good for the other systems in the series, but certainly good enough for engineering purposes. In the cases of ethanol and t-butanol (Figures 39 and 41) the error of the calculated curve is greatest near the plait point.

Note that in the cases of i-butanol (Figure 43) and n-butanol (Figure 44), the error in predicted values of x_2'' and x_3'' (the points denoted +) is fairly large, Δ (4.29) having been minimized and (") denoting the benzene phase. If (") is taken to denote the water phase and Δ (4.29) minimized the error in x_3'' is less than four mole per cent. Thus, although the quotient $\frac{\Delta}{N}$ given in Tables IV-VII is a measure of the relative goodness of fit, it is often misleading due to the arbitrariness of the definition of Δ . Either way it must be concluded that the error of fit is greater for the systems having two partially binaries than for the systems having only one partially miscible binary.

Table V gives the values of the least squares coefficients determined by minimization of Δ (4.29), the method used, and the alcohol boiling point.

3. <u>N-Paraffins-Sulfur Dioxide-Benzene</u>:

The data of Satterfield <u>et. al.</u>(35) on hydrocarbon-sulfur dioxide (liquid) systems provide a series of systems in which the variable component, an n-paraffin, is partially miscible with liquid sulfur dioxide and completely miscible with benzene.

It was found that assuming sulfur dioxide to exist as a polymolecular specie, $(SO_2)_8$, gave equilibrium curves upon conversion to mole fraction that were readily fitted by Equations (3.10), (3.11), and (3.12). Equilibrium curves based on the molecular weight of monomolecular SO_2 could not be fitted by the equations. Multiplying the molecular weight of a specie by some factor has the effect of increasing the area under the binodal curve which appears to be helpful from a curve fitting standpoint as very flat binodal curves which subtend a small area have not been found to be well fitted by Equations (3.10), (3.11), and (3.12). Often as in the cases of $(H_2O)_8$ and $(SO_2)_8$ there is some theoretical justification of the use of polymolecular weights. Because of the polarity of these molecules, the existance of associated species is more plausible than the existence of monomolecular H_2O and SO_2 in the liquid state.

The fit of the data for the system: n-Butane-$(SO_2)_8$ -Benzene (Figure 44) is particularly good. As the molecular weight of the paraffin and the immiscibility in the paraffin-$(SO_2)_8$ binary increase, the error of the calculated curve in the neighborhood of the plait point increases, although not seriously.

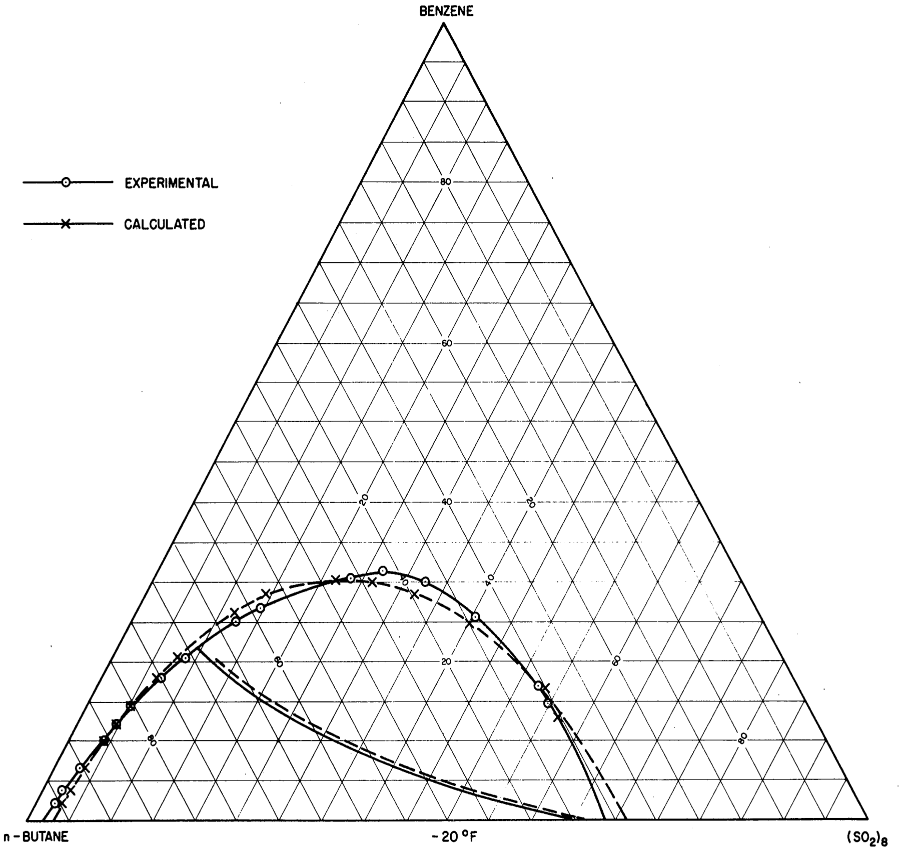


Figure 45. n-Butane (1) - $(SO_2)_8$ (2) - Benzene (3).

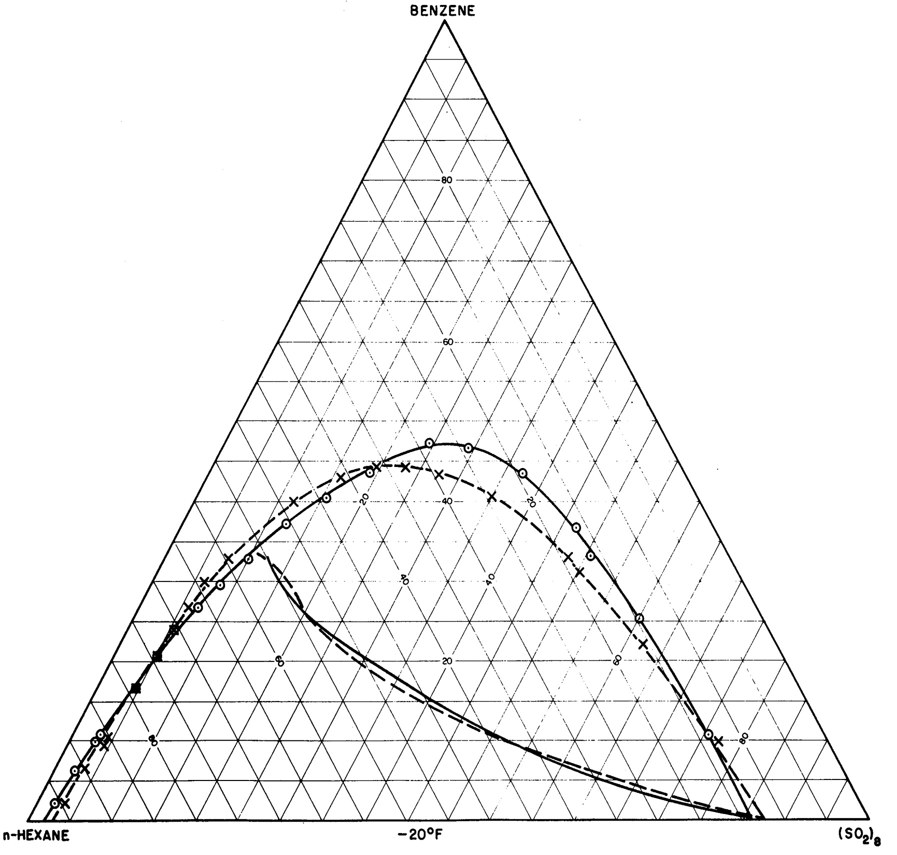


Figure 46. n-Hexane (1) - $(SO_2)_8$ (2) - Benzene (3).

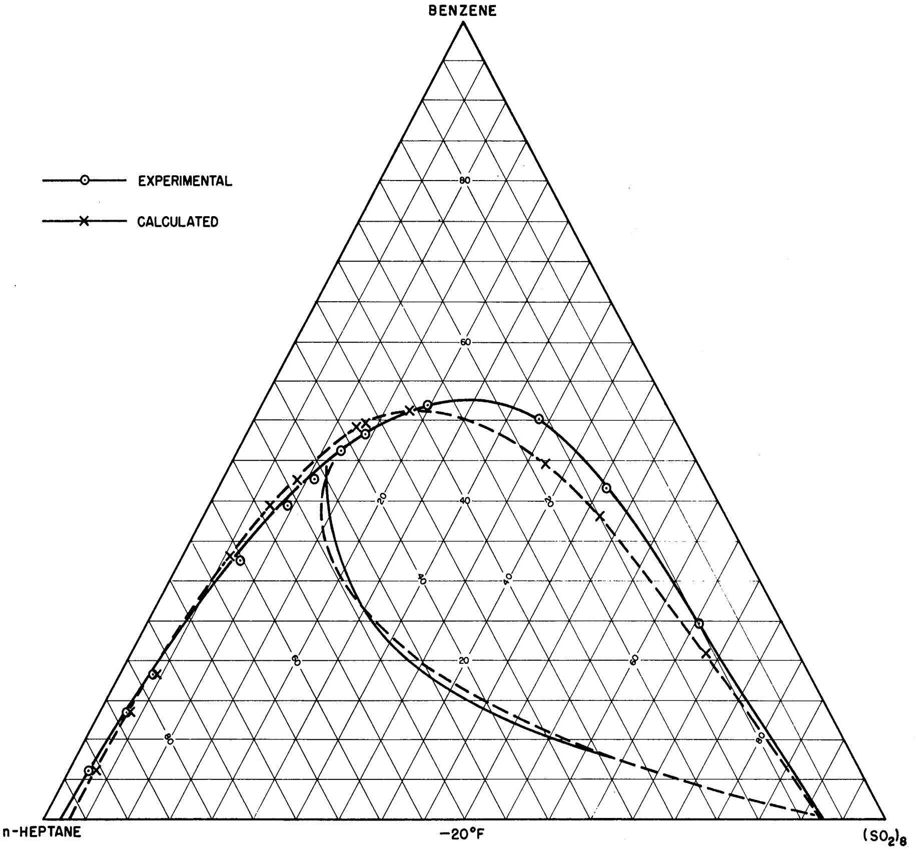


Figure 47. n-Heptane (1) - $(SO_2)_8$ (2) - Benzene (3).

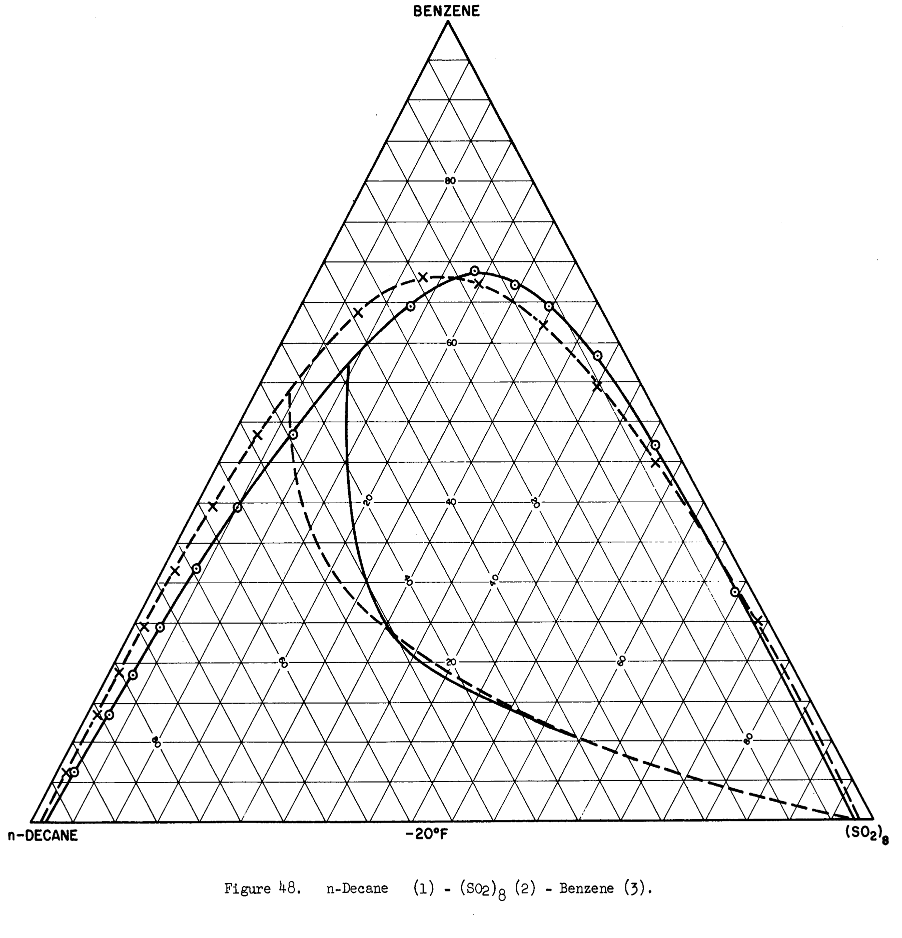


Figure 48. n-Decane (1) - $(SO_2)_8$ (2) - Benzene (3).

TABLE VI*

REDLICH-KISTER COEFFICIENTS
N-PARAFFINS(1) - $(SO_2)^{\gamma}_{8}$(2) - BENZENE(3), -20°F

N-Paraffin	Boiling Pt. °C	B_{12}	B_{23}	B_{31}	C_{12}	C_{23}	C_{31}	$\Delta^*/N \times 10^3$	Method
n-Butane	-0.6	0.9402	-0.4397	0.1217	0.4986	-0.2316	-0.4750	0.509	Trunc.
n-Hexane	69.0	1.289	-0.0013	0.6041	0.2572	0.0002	-0.1044	1.089	S.D.
n-Heptane	98.4	1.389	-0.0001	0.6503	0.2190	0.0000	-0.0002	1.540	S.D.
n-Decane	174.	2.095	-0.0203	0.7046	-0.1409	0.0048	0.0343	2.810	S.D.

TABLE VII*

REDLICH-KISTER COEFFICIENTS
N-PARAFFINS(1) - H_2O(2) - METHANOL(3), 15°C

N-Paraffin	Boiling Pt. °C	B_{12}	B_{23}	B_{31}	C_{12}	C_{23}	C_{31}	$\Delta^*/N \times 10^3$	Method
n-Hexane	69.0	4.532	0.1756	1.027	0.0000	0.0501	-0.0037	242.	S.D.
n-Heptane	98.4	5.046	0.1674	1.160	0.0000	0.0508	0.1806	300.	S.D.
n-Octane	125.7	5.588	0.1745	1.182	0.0000	0.0495	0.1976	555.	S.D.
n-Nonane	150.5	6.100	0.1701	1.337	0.0000	0.0511	0.1514	236.	S.D.

* Δ(4.29) divided by N, the number of experimental tie lines.

Table VI gives the least squares values of the coefficients used in computing the calculated curves found in Figures 45-48.

4. N-Paraffins-H_2O-Methanol:

In this series the variable component, an n-paraffin, is partially miscible with both of the other two components. These systems, provide probably the most severe test of the ability of Equations (3.10), (3.11), and (3.12) retaining only the binary B and C coefficients to represent equilibrium data, first because of the very high degree of immiscibility of n-paraffins with water, and second because there are two binaries with miscibility gaps. Table VII gives the values of the coefficients calculated by Program 8 and used to compute the calculated curves in Figures 49-52.

The fit of the data is considerably better than one would conclude on the basis of Δ/N given in Table VII . The calculated binodal curves for these systems are in close agreement with those determined experimentally. There is some error in the predicted tie lines. The situation is that encountered in the cases of i-butanol-$(H_2O)_8$ -benzene and n-butanol-$(H_2O)_8$ -benzene where if one minimized Δ (4.29), calling (') the hydrocarbon phase, as was actually done, the predicted values of x_2'' , and x_3'' indicated as + in Figures 49-52 are in considerable error for every $x_3' = \overset{*}{x}{}_3'$ except near the binary regions. However, if (') designates the water phase the error in x_2'' and x_3'' (now mole fractions of H_2O, methanol in the hydrocarbon phase) is very much less. The cause of this error is the fact that the tie lines are pinched low in the hydrocarbon corner, a situation that apparently Equations (3.10), (3.11) and (3.12) cannot handle. It is recommended that the use of additional coefficients in the representation of systems having two partially miscible binary systems be studied.

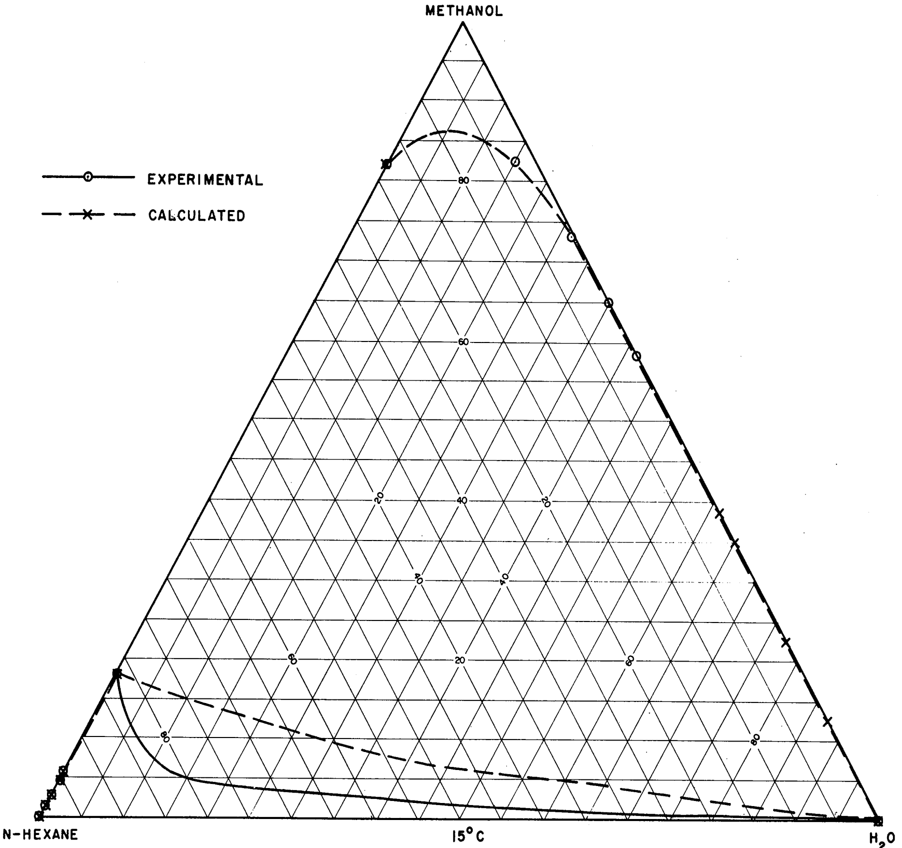


Figure 49. N-Hexane (1) - H_2O (2) - Methanol (3).

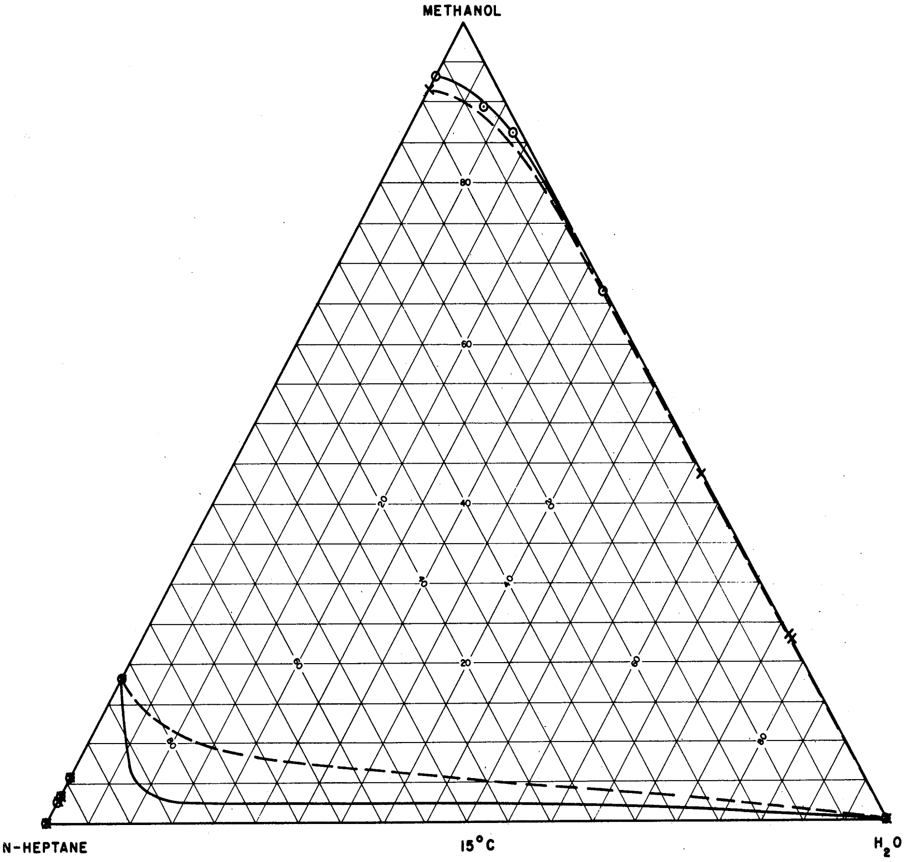


Figure 50. N-Heptane (1) - H_2O (2) - Methanol (3).

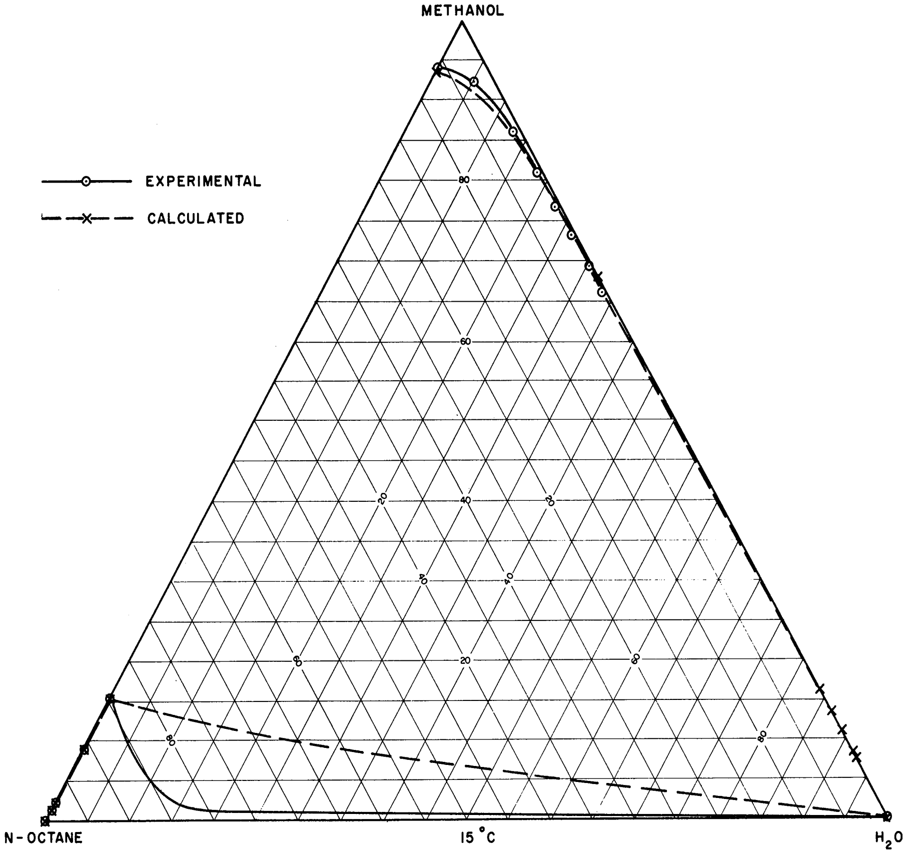


Figure 51. N-Octane (1) - H_2O (2) - Methanol (3).

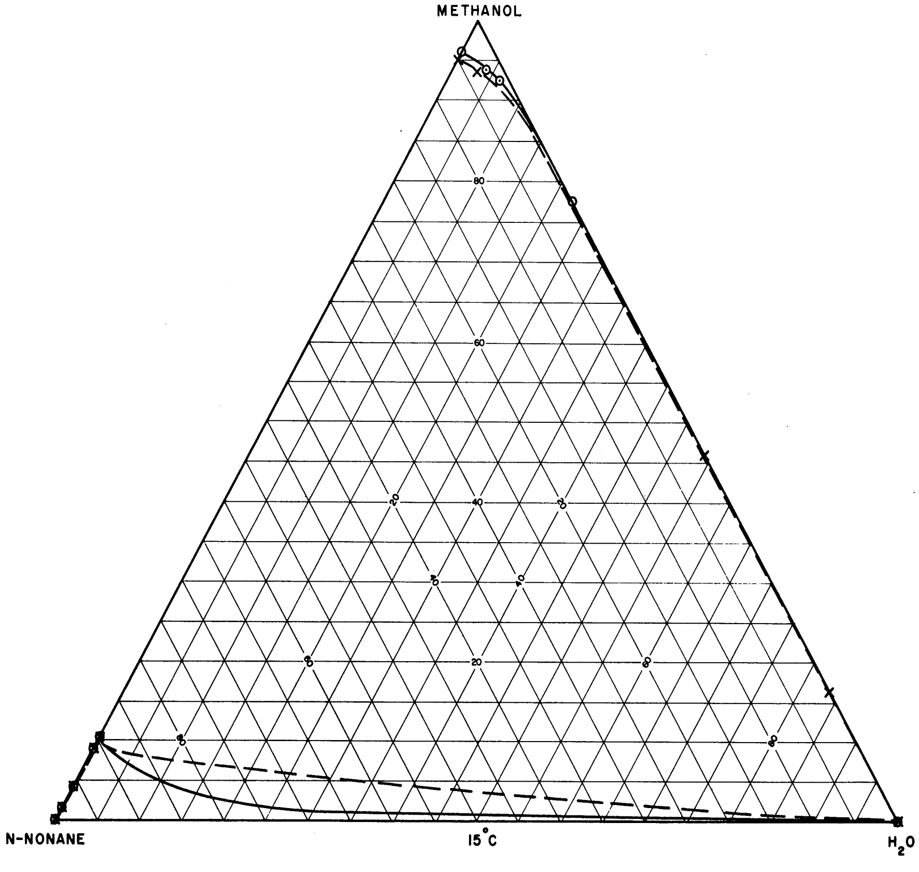


Figure 52. N-Nonane (1) - H_2O (2) - Methanol (3).

C. Correlation of Coefficients

It now remains to be shown whether or not for a homologous series of systems the coefficients in Equations (3.10), (3.11), and (3.12) can be correlated with some property of the variable component, k. If molecular weight or number of carbon atoms is chosen as the correlating property, then isomers must be excluded from our definition of a homologous series. In order that isomers be included, the boiling point (at 1 atm.) has been chosen as the correlating property.

Figures 53-56 are plots of B_{ij} and C_{ij} versus variable component boiling point for the four homologous series of systems discussed in the preceeding section. The least squares values of the coefficients given in Tables IV-VII have been plotted. For the series of systems H_2O (1)-Ethyl Acetate(2)-Alcohols(3) at 20°C (Figure 53) B_{12} and C_{12} are nearly constant, as might be expected. The coefficients for the ethyl acetate-alcohol binary (B_{23} , C_{23}) and the alcohol-water binary (B_{31} , C_{31}) show some scatter. In the case of B_{23} , B_{31} and C_{31} lines were drawn only through the points for normal alcohols. It appears that some property other than boiling point as the correlating property is required if iso-alcohols are included in the homologous series. It is recommended that additional work be carried out on this subject.

The scatter of the points may be attributed in part to inaccuracies of the data for it is true that equilibrium data are difficult to obtain. Since the vapor phase is usually not analyzed in liquid-liquid equilibrium determinations, it is generally not possible to check the data

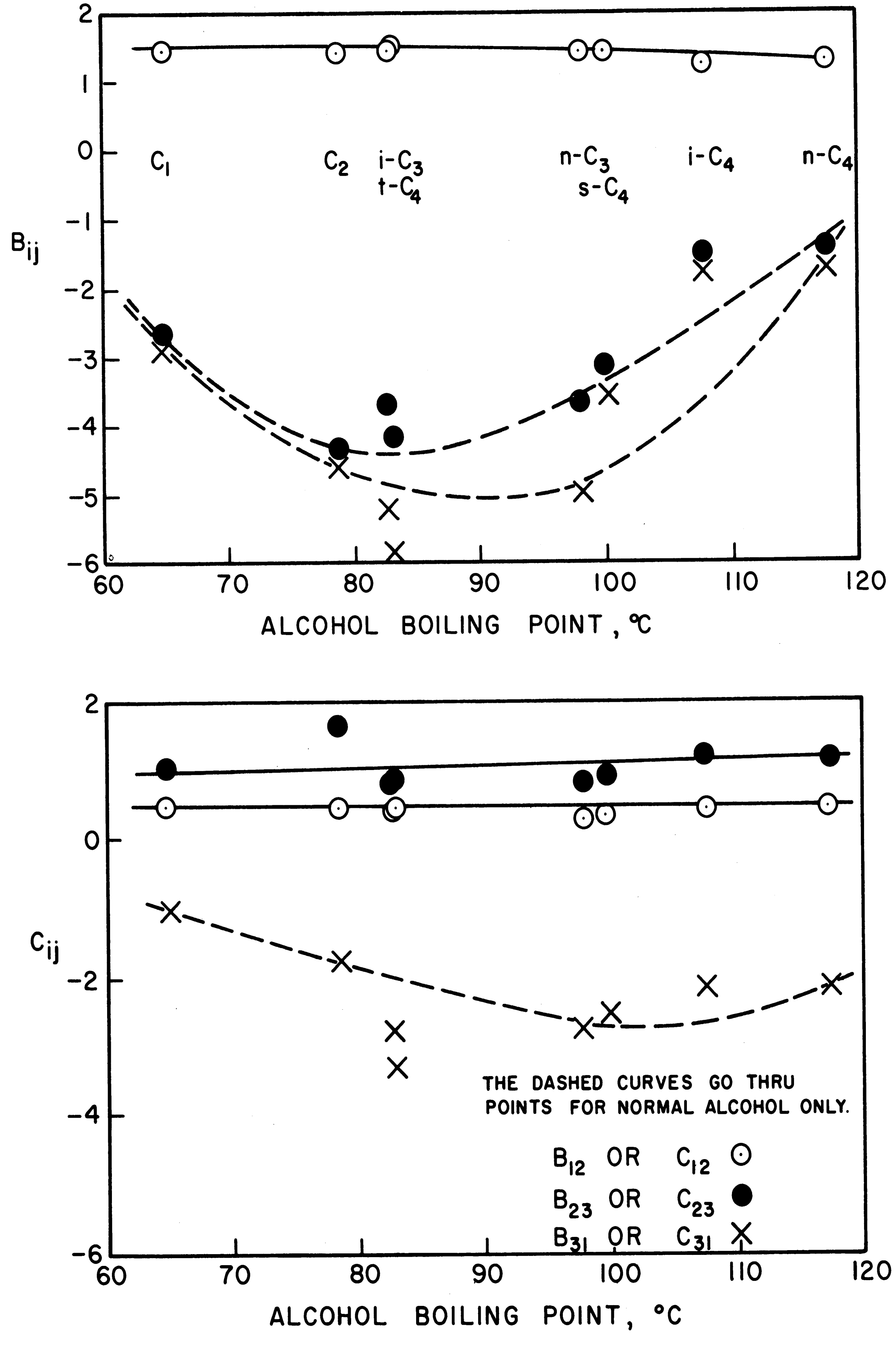


Figure 53. Binary B and C Coefficients Versus Alcohol Boiling Point for the Homologous Series of Systems H_2O (1) - Ethyl Acetate (2) - Alcohols (3) 20°C.

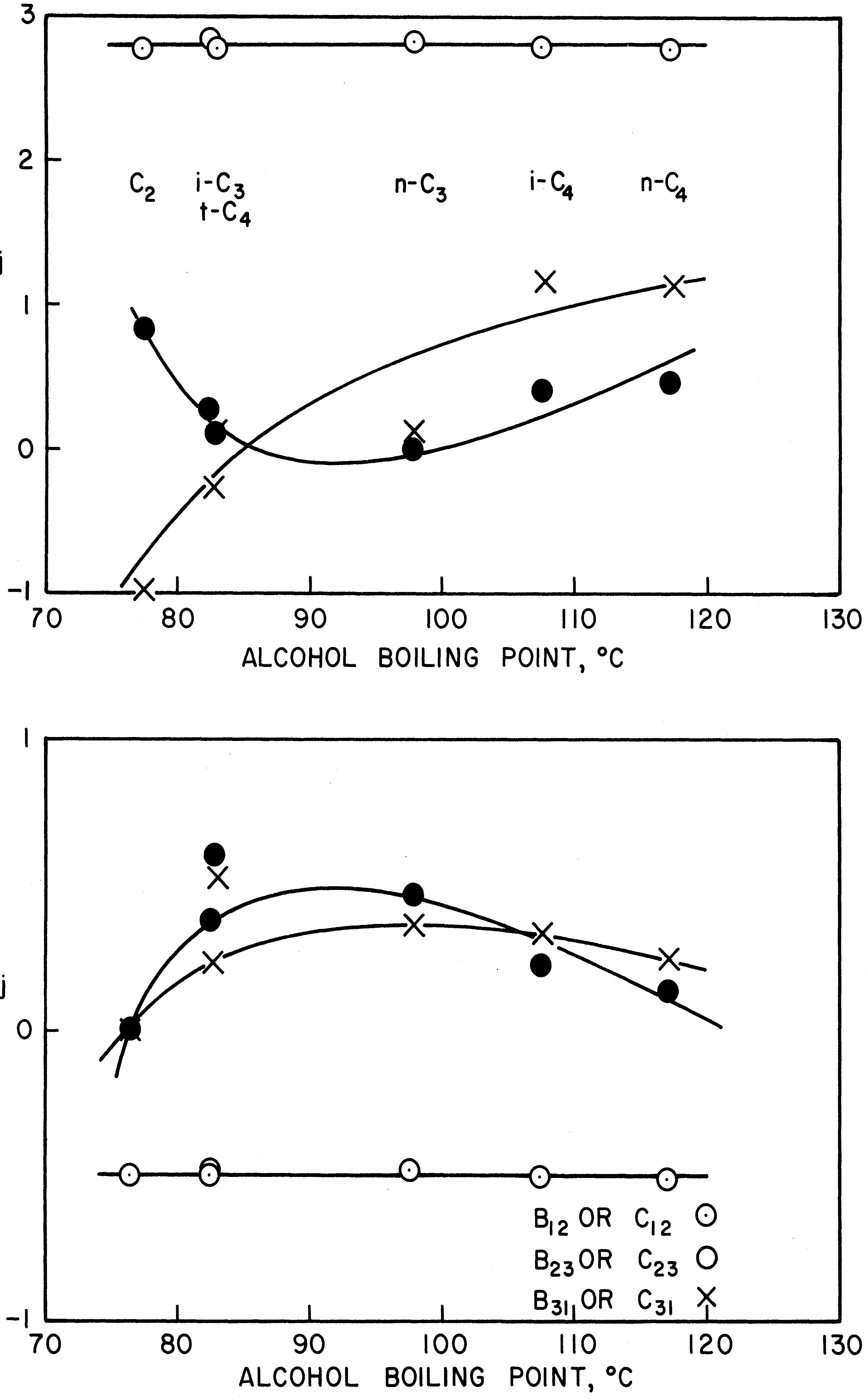


Figure 54. Binary B and C Coefficients Versus Alcohol Boiling Point for the Homologous Series of Systems $(H_2O)_8(1)$ - Benzene (2) - Alcohols (3) 25°C

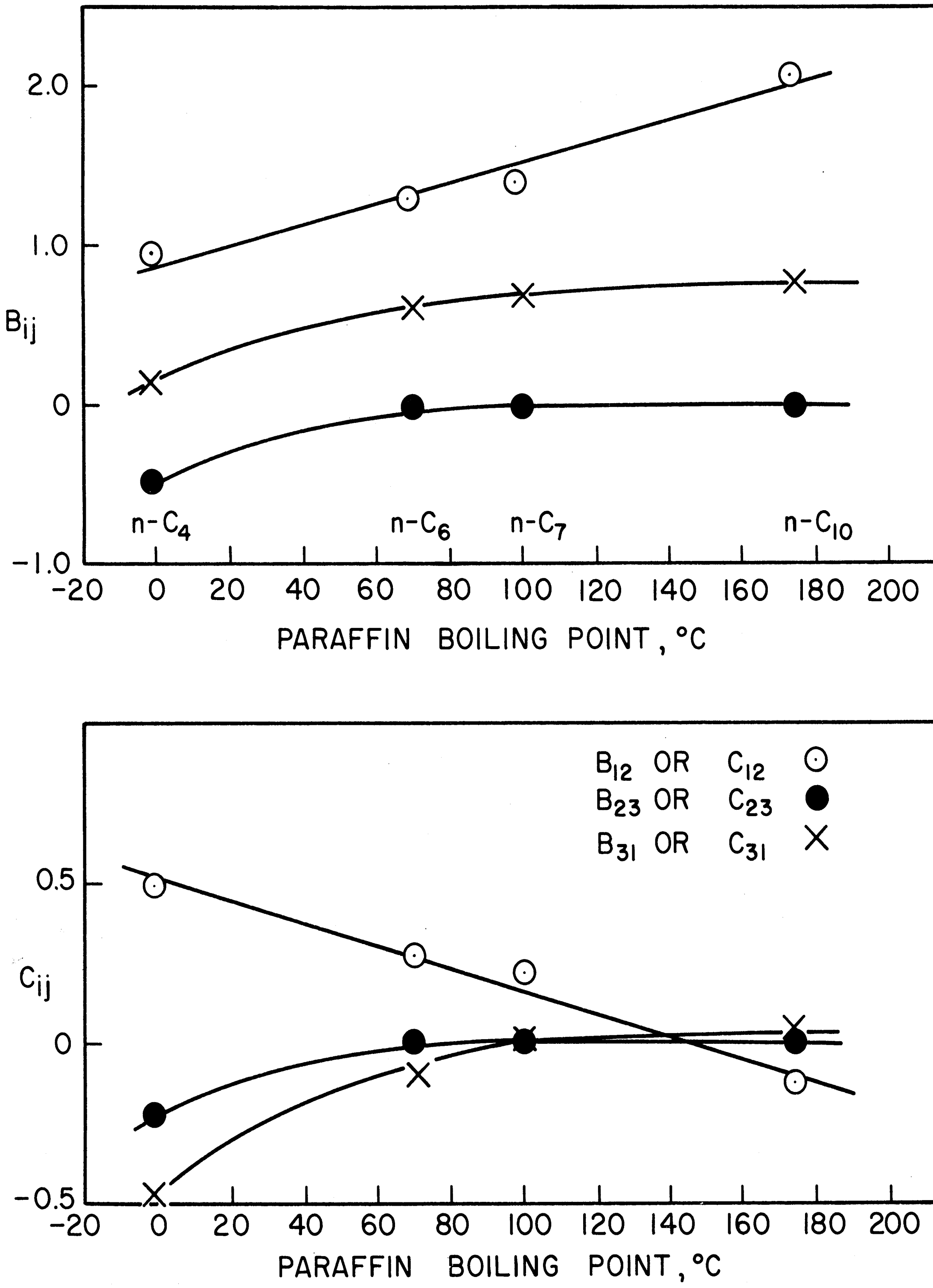


Figure 55. Binary B and C Coefficients Versus Paraffin Boiling Point for the Homologous Series of Systems N-Paraffins (1) - $(SO_2)_8$ (2) - Benzene (3).

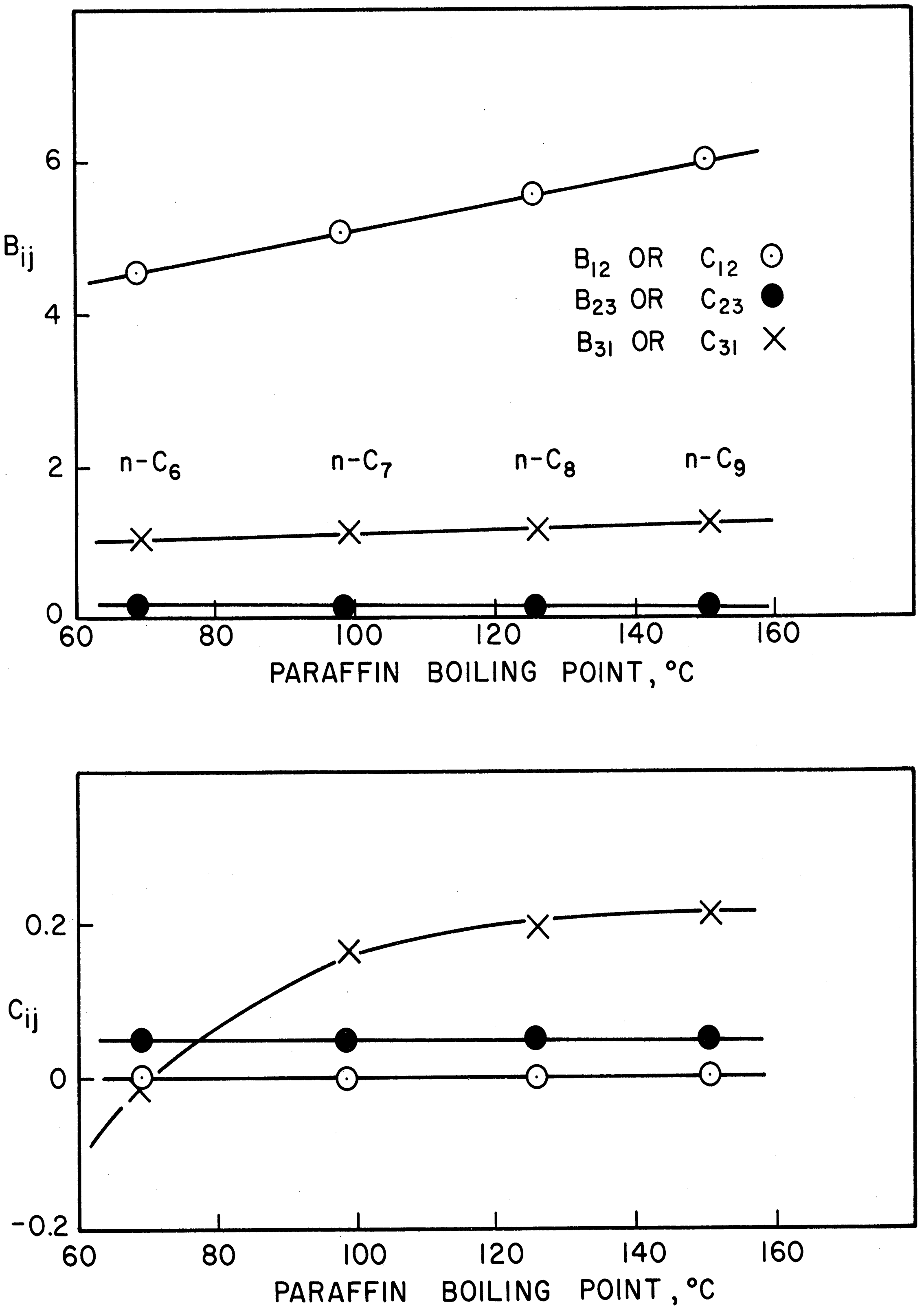


Figure 56. Binary B and C Coefficients Versus Paraffin Boiling Point for the Homologous Series of Systems N-Paraffins (1) - H_2O (2) - Methanol (3).

for thermodynamic consistency as it is in vapor-liquid equilibria determinations. However, liquid-liquid determinations appear to be less prone to experimental error than vapor-liquid determinations. In the only case found where two independent workers determined the same liquid-liquid systems at exactly the same temperature (benzene-water-ethanol at 25°C)(48,51) the data were found to be in close agreement.

Another factor which may have contributed to the scatter of the points is that for some systems as few as six experimental tie lines are available for determination of sample estimates of the coefficients. The raw experimental data were used in all cases, and no points were read from smoothed curves. In all four series of systems discussed here the precision of the data is good, and the tie lines are located so as to satisfactorily describe the equilibrium curves through out their entire ranges. In view of this it is doubtful that additional experimental data would render the sample estimates of the coefficients to be significantly different from the values already obtained.

Figure 54 for the series $(H_2O)_8$ (1)-Benzene(2)-Alcohols(3) shows that, as in the case of H_2O-Ethyl Acetate-Alcohols, the coefficients for the $(H_2O)_8$-Benzene pair (B_{12} and C_{12}) are virtually constant and have values close to those predicted from binary solubility data. The points for the 2-3 pair (benzene-alcohol) and the 3-1 pair (alcohol-$(H_2O)_8$) are scattered but have a definite trend. The shortcoming of the use of boiling point as the correlating variable is noted in the cases of two alcohols, iso-propanol and t-butanol with benzene-$(H_2O)_8$. Their boiling points being

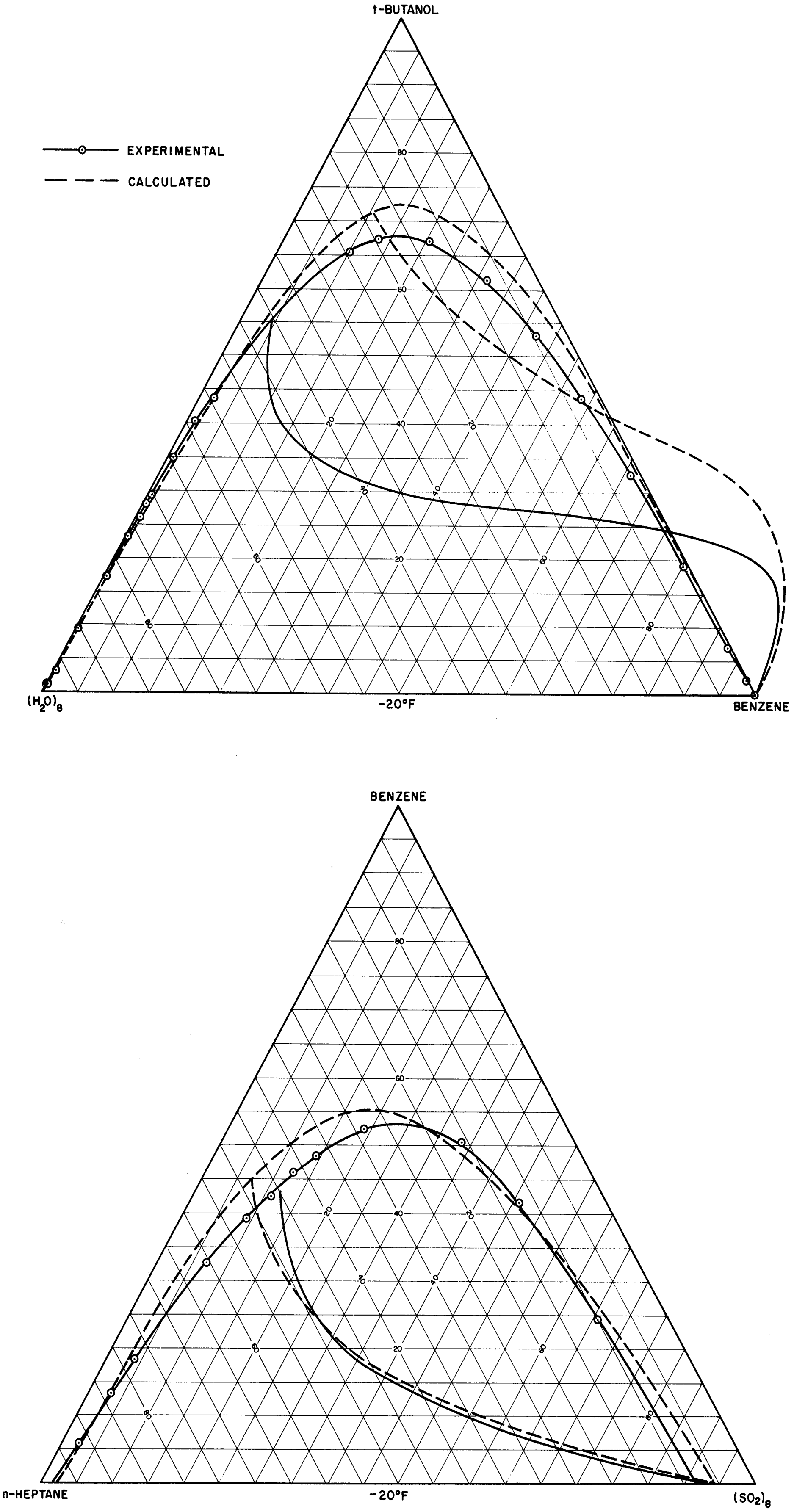


Figure 57. Comparison of Predicted and Experimental Equilibrium Curves for Two Systems Using Coefficients Taken From Homologous Series Correlation.

close together (82.5°C and 82.9°C) would cause one to predict that they have nearly identical equilibrium curves which is not the case. Their equilibrium curves are similar but by no means identical.

Far less scatter of the points is observed in Figure 55 for n-paraffins(1)-$(SO_2)_8$(2)-benzene(3) and in Figure 56 for n-paraffins(1)-H_2O(2)-methanol(3). In the case of the $(SO_2)_8$-benzene systems coefficients for the $(SO_2)_8$-benzene pair (B_{23} and C_{23}) are not constant as might be expected. On the other hand, for the methanol-water systems the coefficients for the water-methanol pair (B_{23} and C_{23}) are very nearly constant. No reason for the fact that B_{23} and C_{23} are not constant in the $(SO_2)_8$-benzene case can be given.

The use of Figures 53-56 to predict equilibrium is illustrated in Figure 57. The coefficients for the two systems given were taken from the smooth curves in Figure 54 and Figure 55. For $(H_2O)_8$(1)-Benzene(2)-t-Butanol(3) the predicted coefficients are:

$$B_{12} = 2.80, \quad B_{23} = 0.130, \quad B_{31} = -0.180$$
$$C_{12} = -0.50 \quad C_{23} = 0.38, \quad C_{31} = 0.250$$

Except near the benzene-$(H_2O)_8$ binary the calculated equilibrium curve is not in good agreement with the experimental curve as can be seen by comparison of the convolute lines. This is further evidence of the inadequacy of boiling point as the correlating property where isomers are involved.

The coefficients read from the smoothed curves through the points in Figure 55 and used to calculate the equilibria for n-heptane(1)-$(SO_2)_8$

(2)-benzene(3) are:

$$B_{12} = 1.500, \quad B_{23} = 0.000, \quad B_{31} = 0.690$$

$$C_{12} = 0.17, \quad C_{23} = 0.000, \quad C_{31} = 0.000$$

The fit of the experimental data is good.

It may be concluded that where homologous series of systems include only homologs defined in their strictest sense, boiling point is a satisfactory correlating variable to enable prediction of liquid-liquid equilibria.

VI. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. The Redlich-Kister Equations (3.10), (3.11), and (3.12) which retain only the B and C binary coefficients are capable of representing a large majority of cases of ternary liquid-liquid equilibria. Systems having one binary with a miscibility gap can be fitted more accurately than systems having two partially miscible binary systems. Systems having small miscibility gaps are better fitted than systems having large regions of immiscibility.

2. Equations of the Redlich-Kister type which are based on representation of the molar excess free energy are especially useful in predicting the location of critical solution points.

3. Binary coefficients which have been determined from binary data cannot be used to predict accurately ternary liquid-liquid equilibria except near partially miscible binary regions. If the binary B and C coefficients are determined from ternary data, Equations (3.10), (3.11), and (3.12) are capable of highly accurate representation of the data for systems where the miscibility gap is not extremely large.

4. Experimental data for a homologous series of systems i-j-k_1, i-j-k_2, ... i-j-k_N, where k_1, k_2 ... k_N are homologs (not including isomers) can be used to predict the equilibria for a system i-j-k_ℓ which has not been

determined experimentally. Redlich-Kister coefficients obtained for an homologous series of systems are simple functions of the boiling point or some other property of the variable component k. Boiling point is not a suitable correlating property to use when it is desired to predict the equilibrium of series of systems including isomers.

B. Recommendations

1. Research directed toward the prediction of solution behavior from theoretical considerations should be emphasized. Particular attention should be given to the prediction of the variation of activity coefficients with temperature.
2. The effect of additional coefficients in Equations (3.10), (3.11), and (3.12) should be studied.
3. The use of the Redlich-Kister equations to predict equilibria for systems having more than three components should be studied.
4. A study of correlating properties other than boiling point should be undertaken to permit prediction of equilibria for homologous series of systems where isomers are included.
5. A study should be undertaken to compare the effectiveness of several different representations of the molar excess free energy in representing liquid-liquid equilibria.

VII. APPENDICES

APPENDIX A

SUPPORTING DERIVATIONS AND MATHEMATICAL DETAILS

1. Expressions for $\Delta\bar{G}_{M_i}$ (see 2.61)

Consider a system composed of n_1, n_2, --- n_k moles of the various components 1, 2, --- k having molar free energies in the pure liquid states $\underline{G}_1^o$, $\underline{G}_2^o$, ... $\underline{G}_k^o$. The total free energy of mixing ΔG_M is:

$$\Delta G_M = G - \sum_{i=1}^{k} n_i \underline{G}_i^o \tag{A.1}$$

where G is the total free energy of the system after mixing. **Taking** the partial derivative of ΔG_M with respect to n_i :

$$\Delta\bar{G}_{M_i} = \bar{G}_i - \underline{G}_i^o \quad . \tag{A.2}$$

From (2.47) it follows:

$$\bar{G}_i = \underline{G} + \frac{\partial \underline{G}}{\partial x_i} - \sum_{i=1}^{k-1} x_i \frac{\partial \underline{G}}{\partial x_i} \tag{A.3}$$

From (A.1):

$$\underline{G} = \Delta \underline{G}_M + \sum_{1}^{k-1} x_i \underline{G}_i^o + x_k \underline{G}_k^o \tag{A.4}$$

Thus

$$\frac{\partial \underline{G}}{\partial x_i} = \frac{\partial \Delta \underline{G}_M}{\partial x_i} + \underline{G}_i^o - \underline{G}_k^o \tag{A.5}$$

where x_k is the mole fraction eliminated by the relation:

$$x_k = 1 - \sum_{i=1}^{k-1} x_i$$

Substituting (A.4) and (A.5) into (A.3) and simplifying:

$$\overline{G}_i = \Delta\underline{G}_M + \sum_1^{k-1} x_i \underline{G}_i^\circ + x_k \underline{G}_k^\circ + \frac{\partial \Delta \underline{G}_M}{\partial x_i} + \underline{G}_i^\circ - \underline{G}_k^\circ - \sum_1^{k-1} x_i \left(\frac{\partial \Delta \underline{G}_M}{\partial x_i} + \underline{G}_i^\circ - \underline{G}_k^\circ \right)$$

$$= \Delta\underline{G}_M + \underline{G}_i^\circ + \frac{\partial \Delta \underline{G}_M}{\partial x_i} - \sum_1^{k-1} x_i \frac{\partial \Delta \underline{G}_M}{\partial x_i} \qquad (A.6)$$

From (A.2) and (A.6):

$$\Delta\overline{G}_{M_i} = \Delta\underline{G}_M + \frac{\partial \Delta \underline{G}_M}{\partial x_i} - \sum_1^{k-1} x_i \frac{\partial \Delta \underline{G}_M}{\partial x_i} \qquad (A.7)$$

Similarly for the kth component from (2.46):

$$\Delta\overline{G}_{M_k} = \Delta\underline{G}_M - \sum_1^{k-1} x_i \frac{\partial \Delta \underline{G}_M}{\partial x_i} \qquad (A.8)$$

For a two component system (k = 2):

$$\Delta\overline{G}_{M_2} = \Delta\underline{G}_M - x_1 \frac{\partial \Delta \underline{G}_M}{\partial x_1} \qquad (A.9)$$

2. Stability Criteria for the Binary Case:(12)

The following derivation is analogous to that found in Section II, D., where $\underline{S}$ was the quantity involved.

The following phase reaction at constant T, P is proposed:

$$\mathrm{I}(n, x, \underline{G}) = \mathrm{II}(n', x + \Delta x, \underline{G} + \Delta \underline{G}) + \mathrm{III}(n'', x + \Delta x^*, \underline{G} + \Delta \underline{G}^*) \quad [T, P].$$

It follows from (2.82), (2.83), (2.84) that for I to be stable:

$$\Delta G = n'\Delta\underline{G} + n''\Delta\underline{G}^{*} > 0 \qquad (A.10)$$

$$n = n' + n'' \qquad (A.11)$$

$$n'\Delta x + n''\Delta x^{*} = 0 \qquad (A.12)$$

By Taylor-series expansion and introduction of (A.10), (A.11), (A.12):

$$\Delta\underline{G} = \frac{\partial\underline{G}}{\partial x}\Delta x + \frac{1}{2}\frac{\partial^2\underline{G}}{\partial x^2}\Delta x^2 + \cdots$$

$$\Delta\underline{G}^{*} = -\frac{n'}{n''}\frac{\partial\underline{G}}{\partial x}\Delta x + \frac{1}{2}\left(\frac{n'}{n''}\right)^2\frac{\partial^2\underline{G}}{\partial x^2}\Delta x^2 + \cdots .$$

Therefore:

$$\Delta G = \frac{n'n}{2n''}\frac{\partial^2\underline{G}}{\partial x^2}\Delta x^2 + \cdots > 0 . \qquad (A.13)$$

Since if $\Delta G > 0$ each term of a Taylor-series expansion must be greater than zero:

$$\left(\frac{\partial^2\underline{G}}{\partial x^2}\right)_{T,P} > 0 . \qquad (2.86)$$

3. <u>The Mathematic of Quadratic Forms:</u>(12)

Consider a quadratic form

$$q = ah^2 + 2bhk + ck^2$$

$$= \left[\left(h + b/a\, k\right)^2 + \left(\frac{ac - b^2}{a^2}k^2\right)\right]$$

The table gives the correspondence of the sign of quantities in q to the sign of q.

QUADRATIC FORMS

q	$ac-b^2$	a	c*
positive-definite	+	+	+
Negative-definite	+	-	-
positive-semidefinite	0	+	+
negative-semidefinite	0	-	-
indefinite	-		

4. Supporting Details of the Derivation of the Binary Redlich-Kister Critical Relations: (3.20), (3.21).

a. Taking the second partial derivative with respect to x_1 of $\frac{\Delta G_M}{RT}$ given in Equation (3.19) and applying (3.18) one obtains:

$$\frac{1}{RT}\frac{\partial^2 \Delta G_M}{\partial x_1^2} = \frac{\partial^2\left[x_1 \ln x_1 + x_2 \ln x_2 + 2.303\,Q\right]}{\partial x_1^2}$$

$$= \frac{1}{2.303\,x_1 x_2} - 2B_{12} + 6(1-2x_1)C_{12} = 0. \quad \text{(A.14)}$$

---

* c is dependent on a and $ac-b^2$

Taking the third partial derivative with respect to x_1 of $\frac{\Delta G_M}{RT}$ and applying (3.18)

$$\frac{\partial^3 \Delta G_M}{\partial x_1^3} = \frac{\partial\left[\frac{1}{2.303\, x_1 x_2} - 2B_{12} + 6(1-2x_1)C_{12}\right]}{\partial x_1}$$

$$= \frac{1}{2.303}\left[\frac{1}{x_1\, x_2^2} - \frac{1}{x_1^2 x_2}\right] - 12\, C_{12} = 0\,. \qquad (A.15)$$

From (A.15) it follows after rearranging:

$$2.303\; C_{12}^{c} = \frac{1}{12}\left[\frac{1}{(1-x_1^c)^2} - \frac{1}{x_1^{c2}}\right]. \qquad (3.21)$$

Substituting C_{12}^c from Equation (3.21) into Equation (A.14) it follows after rearrangement that:

$$2.303\; B_{12}^{c} = \frac{1}{4}\left[\frac{3-4x_1^c}{(1-x_1^c)^2} + \frac{4x_1^c - 1}{x_1^{c2}}\right]. \qquad (3.20)$$

b. The alternate derivation of Equations (3.20) and (3.21) consists of determining the following limits (see Equations (3.22)):

$$B_{12}^c = \lim_{\substack{x_1' \to x_1^c \\ x_1'' \to x_1^c}} \left[\frac{L_1 X_4 - L_2 X_3}{X_1 X_4 - X_2 X_3}\right], \quad C_{12}^c = \lim_{\substack{x_1' \to x_1^c \\ x_1'' \to x_1^c}} \left[\frac{L_2 X_1 - L_1 X_3}{X_1 X_4 - X_2 X_3}\right]. \qquad (A.16)$$

A study of Equations (3.8) and (3.9) will show that the limits in (A.16) lead to the 0/0 case which must be evaluated by l'Hospital's rule.(56)

To evaluate these limits, x_1'' was first allowed to equal x_1^c the composition at the critical point, then:

$$B_{12}^c = \lim_{x_1' \to x_1^c} \frac{\dfrac{\partial^n (L_1 X_4 - L_2 X_3)}{\partial x_1'^n}}{\dfrac{\partial^n (X_1 X_4 - X_2 X_3)}{\partial x_1'^n}} \qquad (x_1'' = x_1^c)$$

(A.17)

$$C_{12}^c = \lim_{x_1' \to x_1^c} \frac{\dfrac{\partial^n (L_2 X_1 - L_1 X_3)}{\partial x_1'^n}}{\dfrac{\partial^n (X_1 X_4 - X_2 X_3)}{\partial x_1'^n}} \qquad (x_1'' = x_1^c)$$

After taking the derivative with respect to x_1' four times of both the numerator and denominator in (A.16), that is n = 4 in (A.17), when $x_1' \rightarrow x_1^c$ both numerator and denominator are finite and non-zero, and Equations (3.20) and (3.21) are obtained. This result is also obtained by allowing $x_1' \rightarrow x_1^c$, then solving for the limit as $x_1'' \rightarrow x_1^c$ by l'Hospital's rule which indicates that the limits in (A.16) are independent of path.

5. Determination of $\frac{\partial \Delta}{\partial c_2}$ where Δ is given by (4.29)(55):

The partial derivatives of Δ with respect to the Redlich-Kister coefficients in Equations (3.10), (3.11) and (3.12) denoted here as c_ℓ , are of special importance in the determination of the coefficients that minimize Δ . Differentiating Δ (4.29) with respect to c_ℓ :

$$\frac{\partial \Delta}{\partial c_\ell} = -2 \sum_{\ell=1}^{M} \left[(x_2' - \overset{*}{x}_2{}') \frac{\partial \overset{*}{x}_2{}'}{\partial c_\ell} + (x_2'' - \overset{*}{x}_2{}'') \frac{\partial \overset{*}{x}_2{}''}{\partial c_\ell} + (x_3'' - \overset{*}{x}_3{}'') \frac{\partial \overset{*}{x}_3{}''}{\partial c_\ell} \right] . \quad \text{(A.18)}$$

The problem now is determination of $\frac{\partial \overset{*}{x}_2{}'}{\partial c_\ell}$, $\frac{\partial \overset{*}{x}_2{}''}{\partial c_\ell}$ and $\frac{\partial \overset{*}{x}_3{}''}{\partial c_\ell}$

Let us write Equations (3.10), (3.11) and (3.12) as

$$\mathcal{F} = \log_{10} x_1'/x_1'' - \sum_{\ell=1}^{6} c_\ell f_\ell = 0$$

$$\mathcal{G} = \log_{10} x_2'/x_2'' - \sum_{\ell=1}^{6} c_\ell g_\ell = 0$$

$$\mathcal{H} = \log_{10} x_3'/x_3'' - \sum_{\ell=1}^{6} c_\ell h_\ell = 0 \quad \text{(A.19)}$$

where $x_1' = 1 - x_2' - x_3'$ and $x_1'' = 1 - x_2'' - x_3''$.

By total differentiation of

$$\mathcal{F}(x_2' , x_3' , x_2'' , x_3'' , c_1 , c_2 , \cdots c_6) = 0$$

$$\mathcal{G}(x_2' , x_3' , x_2'' , x_3'' , c_1 , c_2 , \cdots c_6) = 0$$

$$\mathcal{H}(x_2' , x_3' , x_2'' , x_3'' , c_1 , c_2 \cdots c_6) = 0$$

we obtain:

$$d\mathcal{F} = \frac{\partial \mathcal{F}}{\partial x_2'} dx_2' + \frac{\partial \mathcal{F}}{\partial x_2''} dx_2'' + \frac{\partial \mathcal{F}}{\partial x_3'} dx_3' + \frac{\partial \mathcal{F}}{\partial x_3''} dx_3'' + \sum_{\ell=1}^{6} \frac{\partial \mathcal{F}}{\partial c_\ell} dc_\ell = 0 \qquad (A.20)$$

and similar expressions for $\mathcal{G}$ and $\mathcal{H}$, which form three equations from which the differentials of x_2', x_2'', and x_3'' may be eliminated. Noting that now

$$x_2' = x_2'(x_3', c_1, c_2 \cdots c_6)$$

$$x_2'' = x_2''(x_3', c_1, c_2 \cdots c_6)$$

$$x_3'' = x_3''(x_3', c_1, c_2 \cdots c_6) \qquad (A.21)$$

and thus:

$$dx_2' = \frac{\partial x_2'}{\partial x_3'} dx_3' + \sum_{\ell=1}^{6} \frac{\partial x_2'}{\partial c_\ell} dc_\ell$$

$$dx_2'' = \frac{\partial x_2''}{\partial x_3'} dx_3' + \sum_{\ell=1}^{6} \frac{\partial x_2''}{\partial c_\ell} dc_\ell$$

$$dx_3'' = \frac{\partial x_3''}{\partial x_3'} dx_3' + \sum_{\ell=1}^{6} \frac{\partial x_3''}{\partial c_\ell} dc_\ell \qquad (A.22)$$

The partial derivatives $\frac{\partial x_2'}{\partial c_\ell}$, $\frac{\partial x_2''}{\partial c_\ell}$ and $\frac{\partial x_3''}{\partial c_\ell}$ are then obtained by comparison of the terms in (A.22) with those in the expressions obtained by solving the system of Equations (A.20) for dx_2', dx_2'', dx_3''. These partial derivatives may be obtained from the matrix equation

$$\begin{pmatrix} \frac{\partial \mathcal{F}}{\partial x_2'} & \frac{\partial \mathcal{F}}{\partial x_2''} & \frac{\partial \mathcal{F}}{\partial x_3''} \\ \frac{\partial \mathcal{G}}{\partial x_2'} & \frac{\partial \mathcal{G}}{\partial x_2''} & \frac{\partial \mathcal{G}}{\partial x_3''} \\ \frac{\partial \mathcal{H}}{\partial x_2'} & \frac{\partial \mathcal{H}}{\partial x_2''} & \frac{\partial \mathcal{H}}{\partial x_3''} \end{pmatrix} \begin{pmatrix} \frac{\partial x_2'}{\partial c_\ell} \\ \frac{\partial x_2''}{\partial c_\ell} \\ \frac{\partial x_3''}{\partial c_\ell} \end{pmatrix} = \begin{pmatrix} -\frac{\partial \mathcal{F}}{\partial c_\ell} \\ -\frac{\partial \mathcal{G}}{\partial c_\ell} \\ -\frac{\partial \mathcal{H}}{\partial c_\ell} \end{pmatrix} \quad \text{(A.23)}$$

The partial derivatives $\frac{\partial \mathcal{F}}{\partial c_\ell}$, $\frac{\partial \mathcal{G}}{\partial c_\ell}$, $\frac{\partial \mathcal{H}}{\partial c_\ell}$ are simply $-f_\ell$, $-g_\ell$, and $-h_\ell$ in Equation (A.19). The partial derivatives of $\mathcal{F}$, $\mathcal{G}$, and $\mathcal{H}$ with respect to x_2', x_2'', and x_3'' are somewhat lengthy algebraically. They are written out in Fortran compiler notation in the program listing of Program 8. See the Correspondence of Variables section for the compiler statements.

It is understood that to obtain $\frac{\partial \overset{*}{x}{}_2'}{\partial c_\ell}$, $\frac{\partial \overset{*}{x}{}_2''}{\partial c_\ell}$, $\frac{\partial \overset{*}{x}{}_3''}{\partial c_\ell}$ the values of $\overset{*}{x}{}_2'$, $\overset{*}{x}{}_2''$, and $\overset{*}{x}{}_3''$ (predicted from the equations, not experimental data) are used in the algebraic expression obtained from (A.23).

APPENDIX B

DESCRIPTION OF COMPUTER PROGRAMS

In the course of this research a number of computer programs have been written for the IBM 650 and the IBM 704. Programs for the 650 were written in the Generalized Algebraic Translator Language(10) by B. Arden and R. Graham of the University of Michigan computer research staff. The language adheres to the rules of algebra in arithmetic statements. The reader is referred to Reference (10) for details of the language and of input-output format.

Programs for the 704 were written in the Fortran language which is described in detail in References (15) and (16). Subroutines used were those available at the University of Michigan Computer Center, September 1959. Input and output format is controlled by the FORMAT statements found in the Fortran program listings. These statements are described in detail in References (15) and (16).

The eight programs described here were not the only ones written during this research. A number of other programs were written but were found to be less satisfactory than those presented here.

PROGRAM 1:

Title: Binary Vapor-Liquid Least Squares Program, Constant Temperature.

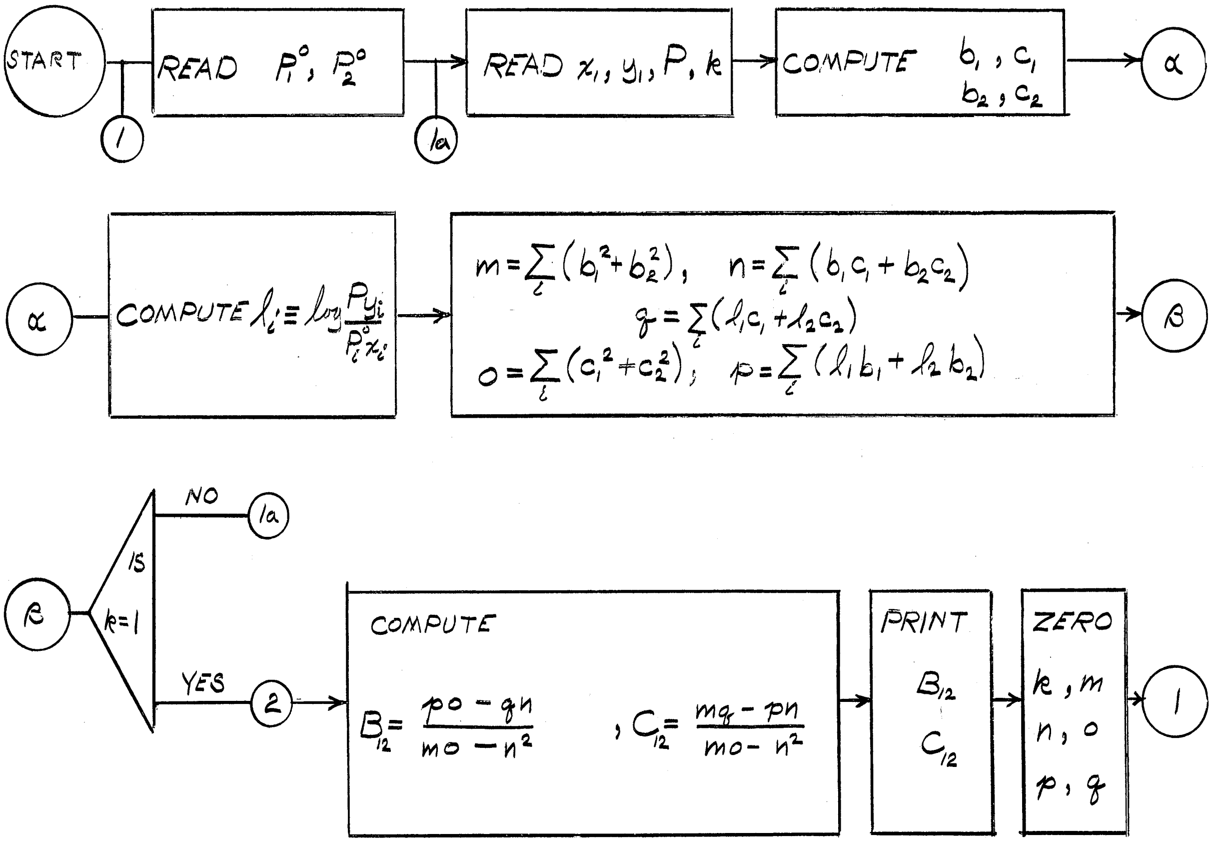
Language and Computer: GAT - IBM 650

Function: Accepts x, y, P data and determines B_{12} and C_{12} in Equations (2.53), (2.59) by minimization of Δ where Δ is:

$$\Delta = \sum_{i=1}^{N}\left[\left(\log_{10}\frac{Py_1}{P_1^0 x_1} - \log_{10}\gamma_1'\right)^2 + \left(\log_{10}\frac{Py_2}{P_2^0 x_2} - \log_{10}\gamma_2'\right)^2\right]_i \qquad (4.10)$$

where $\log_{10}\gamma'$ is the binary Redlich-Kister expression for $\log_{10}\gamma$ using the B_{12} and C_{12} binary coefficients.

Flow Sheet:



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* b_1, c_1, b_2, c_2 are the multiplyers of B_{12} & C_{12} in $\log\gamma_1'$, $\log\gamma_2'$ respectively.

Correspondence of Variables:

x_1 = Y1

x_2 = Y2

y_1 = Y3

y_2 = Y4

b_1 = Y11

b_2 = Y12

c_1 = Y9

c_2 = Y10

P = Y8

P_1^o = Y5

P_2^o = Y6

l_1 = Y18

l_2 = Y19

m = Y13

n = Y14

o = Y16

p = Y15

q = Y17

k = I0

B_{12} = C1

C_{12} = C2

Input: Y5, Y6; then Y1, Y3, Y8 with I0 = 1 on last data point.

Subroutines: READ, PUNCH, FIX, FLOAT, LOGIO.

GAT Compiler Statements:

```
            2 IS HIGHEST STATEMENT NUMBER
            300 USED IN SUBROUTINES
            DIMENSION Y(20) C(2)
1           READ
            Y2=1.-Y1
            Y4=1.-Y3
            Y11=Y2*Y2
            Y12=Y1*Y1
            Y9=Y11*(-Y2+3.*Y1)
            Y10=Y12*(Y1-3.*Y2)
            Y18=LOG10.((Y8*Y3)/(Y5*Y1))
            Y19=LOG10.((Y8*Y4)/(Y6*Y2))
            Y13=Y13+(Y11*Y11)+Y12*Y12
            Y14=Y14+(Y9*Y11)+Y10*Y12
            Y15=Y15+(Y11*Y18)+Y12*Y19
            Y16=Y16+(Y9*Y9)+Y10*Y10
            Y17=Y17+(Y9*Y18)-Y10*Y19
            GO TO 1 IF I0U0
            Y20=(Y13*Y16)-Y14*Y14
            C1=((Y15*Y16)-Y14*Y17)/Y20
            C2=((Y13*Y17)-Y15*Y14)/Y20
2           TC1 TC2
            Y13=0.
            Y14=Y13
            Y15=Y13
            Y16=Y13
            Y17=Y13
            I0=0
            GO TO 1
            END
```

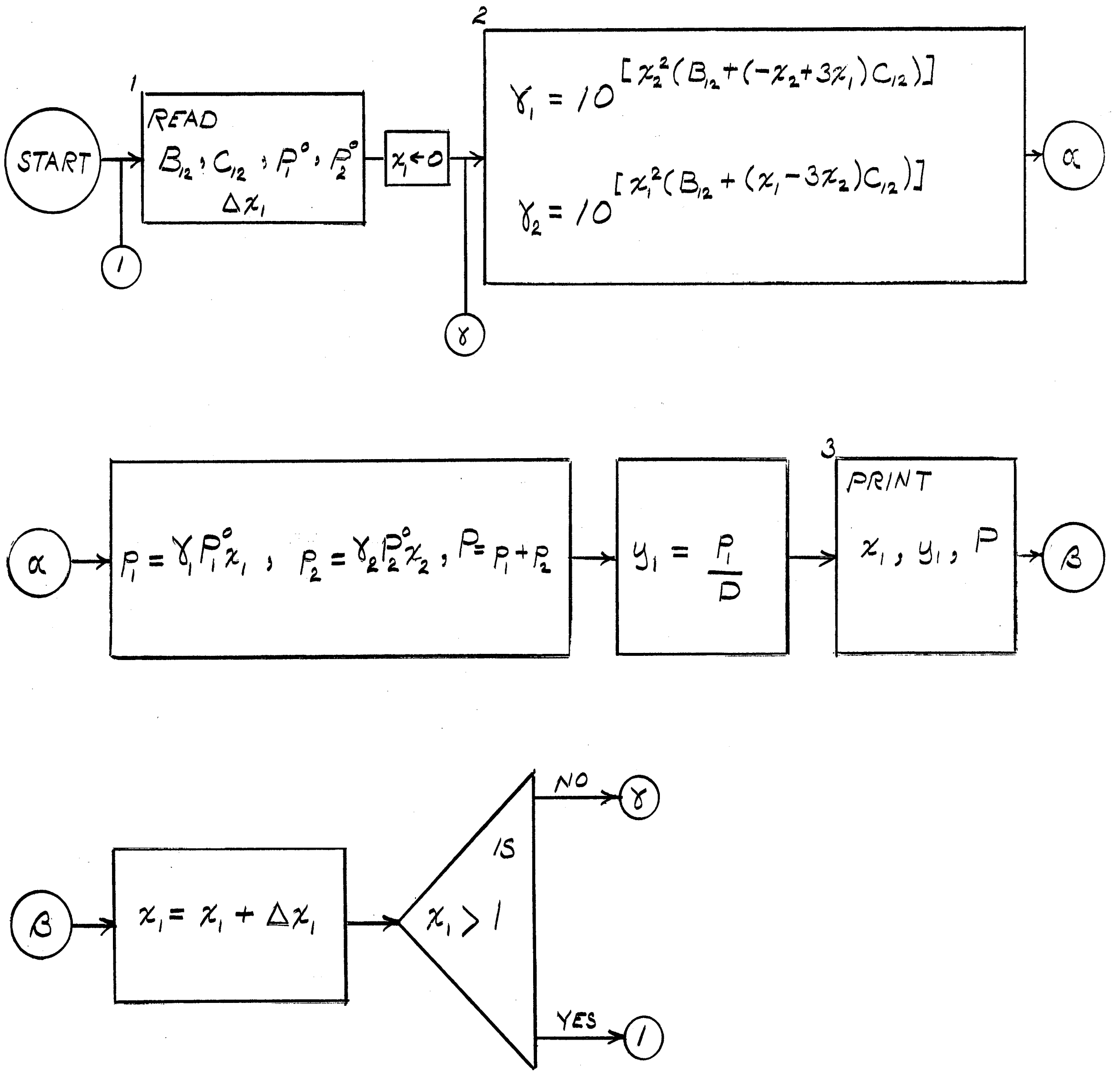
PROGRAM 2:

Title: Binary Vapor-Liquid Back Calculation Program, Constant Temperature.

Language and Computer: GAT - IBM 650

Function: Given B_{12}, C_{12}, P , P_2^o, this program computes x_1, y_1, P in steps of any specified Δx_1 by solving the Redlich-Kister equations for the binary vapor - liquid case.

Flow Sheet:



Correspondence of Variables:

(same as previous program except as follows)

γ_1 = Y9

γ_2 = Y10

P_1 = Y11

P_2 = Y12

Δx_1 = Y0

Input: C1, C2, Y5, Y6, Y0

Subroutines: READ, PUNCH, FIX, FLOAT, GENERAL EXPONENTATION

GAT Compiler Statements:

```
           3 IS HIGHEST STATEMENT NUMBER
           400 USED IN SUBROUTINES
           DIMENSION Y(12) C(2)
1          READ
           3,Y1,0.,Y0,1.0,
2          Y2=1.-Y1
           Y9=10.P(Y2*Y2*(C1+C2*(-Y2   N
           +3.*Y1)))
           Y10=10.P(Y1*Y1*(C1+C2*(Y1-   N
           3.*Y2)))
           Y11=Y9*Y5*Y1
           Y12=Y10*Y6*Y2
           Y8=Y11+Y12
           Y3=Y11/Y8
           Y4=Y12/Y8
3           TY1 TY3 TY8
           GO TO 1
           END
```

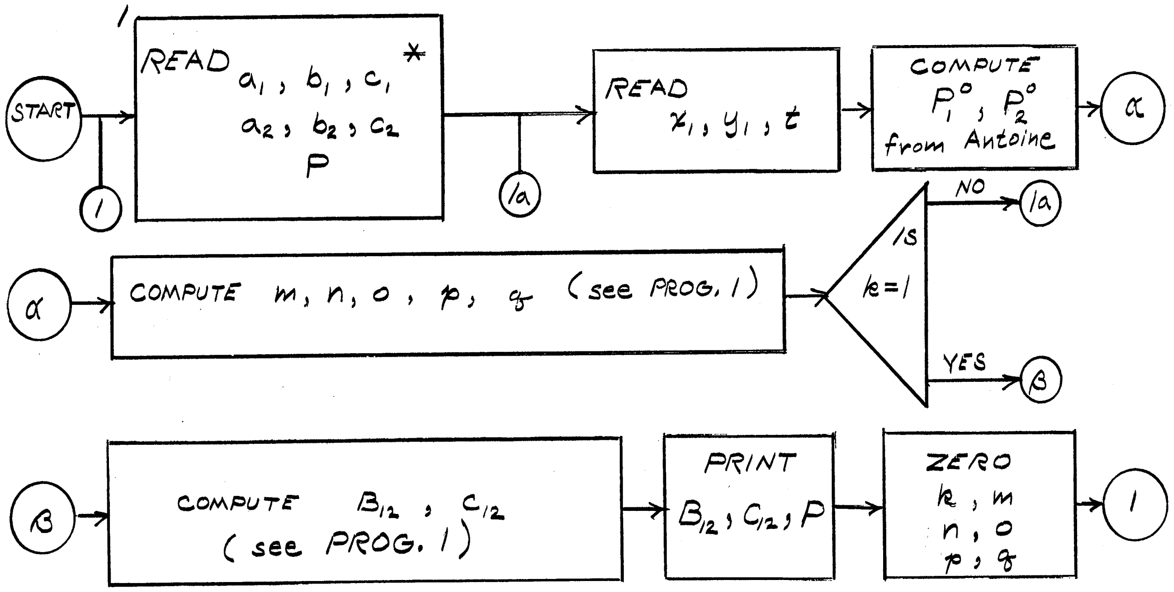
PROGRAM 3:

Title: Binary Vapor-Liquid Least Squares Program, Constant Pressure.

Language and Computer: GAT - IBM 650

Function: Accepts x_1, y_1, T data and determines B_{12} and C_{12} in Equations (2.55), (2.56) by minimization of Δ given in Equation (4.10).

Flow Sheet:



Correspondence of Variables:

(same as program 1 except as follows)

a_1 = D1 a_2 = D4

b_1 = D2 b_2 = D5

c_1 = D3 c_2 = D6

t = X1

Input: D1 - D6; Y1, Y3, X1; I0 = 1 (last data card)

Subroutines: READ, PUNCH, FIX, FLOAT, GEN. EXPONENTIATION, LOGIO.

---

* a_i, b_i, c_i are the coefficients in the Antoine equation.

$$\log_{10} P_i^o = a_i - \frac{b_i}{t + c_i}$$

GAT Compiler Statements:

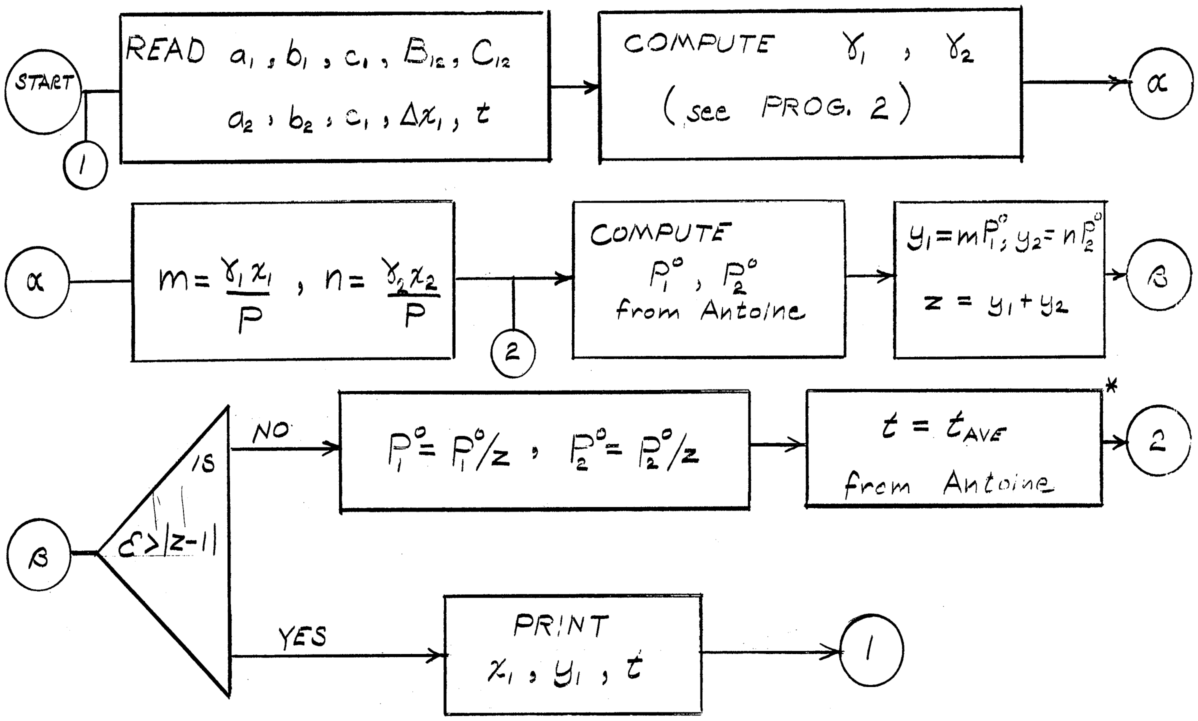
```
           2 IS HIGHEST STATEMENT NUMBER
           645 USED IN SUBROUTINES
           DIMENSION C(2)X(1)Y(20)D(6)  N
           I(1)
1          READ
           Y2=1.-Y1
           Y4=1.-Y3
           Y5=10.P(D1-D2/(X1+D3))
           Y6=10.P(D4-D5/(X1+D6))
           Y11=Y2*Y2
           Y12=Y1*Y1
           Y9=Y11*(-Y2+3.*Y1)
           Y10=Y12*(Y1-3.*Y2)
           Y18=LOG10.(Y8*Y3/(Y5*Y1))
           Y19=LOG10.(Y8*Y4/(Y6*Y2))
           Y13=Y13+Y11*Y11+Y12*Y12
           Y14=Y14+Y9*Y11+Y10*Y12
           Y15=Y15+Y11*Y18+Y12*Y19
           Y16=Y16+Y9*Y9+Y10*Y10
           Y17=Y17+Y9*Y18+Y10*Y19
           GO TO 1 IF I0U0
           Y20=Y13*Y16-Y14*Y14
           C1=(Y15*Y16-Y14*Y17)/Y2
           C2=(Y13*Y17-Y15*Y14)/Y2
2          TC1TC2TY8
           Y13=0.
           Y14=Y13
           Y15=Y13
           Y16=Y13
           Y17=Y13
           I0=0
           GO TO 1
           END
```

PROGRAM 4:

Title: Binary Vapor-Liquid Back Calculation Program, Constant Pressure.

Function: Given B_{12}, C_{12}, P, x_1 and vapor pressure data in the form of Antoine equation coefficients, Program 4 solves the Redlich-Kister equations in B & C binary coefficients for y_1 and t in steps of any specified Δx_1, from x = 0 to 1.

Flow Sheet:



Correspondence of Variables:

x_1 = X1

Δx_1 = X0

x_2 = X2

γ_1 = Y3

P_2^o = X4

a_1 = D3

b_1 = -D1

c_1 = D2

Z = Y9

t = Y5

P = Y10

---

* Solving the Antoine equations for each component for t and taking the average

B_{12} = C1

C_{12} = C2

γ_2 = Y4

m = Y6

n = Y7

P = X3

a_2 = Z3

b_2 = -Z1

c_2 = Z2

ε = Y0

y_1 = Y1

y_2 = Y2

Input: D1, D2, D3, Z1, Z2, Z3, C1, C2, X0, Y5

Subroutines: READ, PUNCH, FIX, FLOAT, 10EXP., LOG10.

GAT Compiler Statements:

```
            349 USED IN SUBROUTINES
            3 IS HIGHEST STATEMENT NUMBER
            DIMENSION Y(10)X(4)D(3)Z(3)   N
            C(2)
1           READ
            3,X1,0.,X0,1.0,
            X2=1.-X1
            Y3=10EXP.(X2*X2*(C1+C2*(-X2+ N
            3.*X1)))
            Y4=10EXP.(X1*X1*(C1+C2*(X1-3.N
            *X2)))
            Y6=Y3*X1/Y1
            Y7=Y4*X2/Y1
2           X3=10EXP.(D1/(Y5+D2)+D3)
            X4=10EXP.(Z1/(Y5+Z2)+Z3)
            Y1=Y6*X3
            Y2=Y7*X4
            Y9=Y1+Y2
            GO TO 3 IF YOV(A(Y9-1.))
            X3=X3/Y9
            X4=X4/Y9
            Y5=(D1/(LOG10.(X3)-D3)-D2+   N
            Z1/(LOG10.(X4)-Z3)-Z2)/2.
            GO TO 2
3           TX1TY1TY5
            GO TO 1
            END
```

PROGRAM 5:

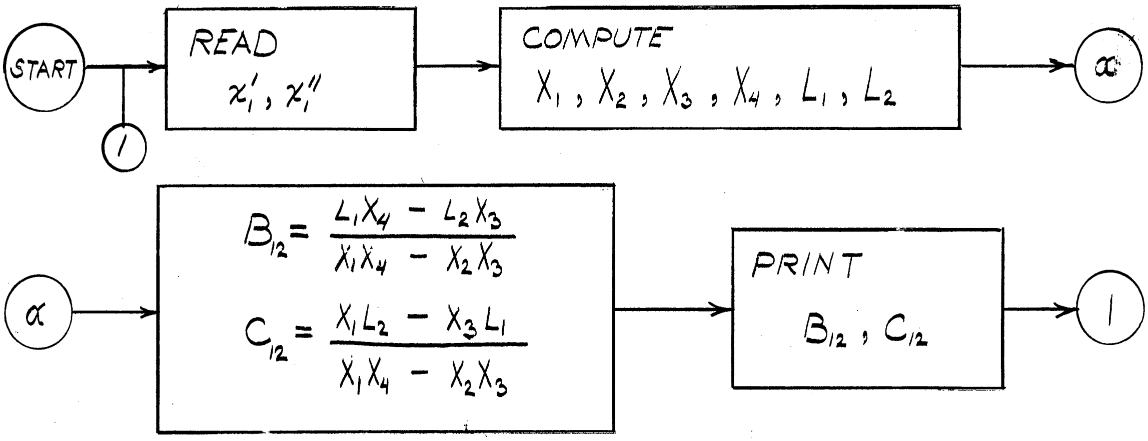
Title: Program for Computing B_{12} and C_{12} from Binary Solubility Data.

Function: Given x_1' , x_1'' Program 5 computes B_{12} and C_{12} in the Redlich-Kister equations for a partially miscible binary by solving Equations (3.8), (3.9), written as

$$L_1 = X_1 B_{12} + X_2 C_{12}$$

$$L_2 = X_3 B_{12} + X_4 C_{12}$$

Flow Sheet:



Correspondence of Variables:

x_1' = Y1

x_2' = Y2

x_1'' = Y5

x_2'' = Y6

X_1 = Y3

X_3 = Y8

L_1 = Y10

L_2 = Y11

B_{12} = C21

C_{12} = C22

X = Y4

X = Y9

X_2 = Y4

Y_2 = Y9

Input: Y1, Y5

Subroutines: READ, PUNCH, FIX, FLOAT, LOG10.

GAT Compiler Statements:

```
         2 IS HIGHEST STATEMENT NUMBER
         645 USED IN SUBROUTINES
         DIMENSION Y(14)C(22)
1        READ
         Y2=1.-Y1
         Y6=1.-Y5
         Y3=(Y6*Y6)-Y2*Y2
         Y8=(Y5*Y5)-Y1*Y1
         Y4=(Y6*Y6*(-1.+4.*Y5))-Y2*Y2*N
         (-1.+4.*Y1)
         Y9=(Y5*Y5*(-3.+4.*Y5))-Y1*Y1*N
         (-3.+4.*Y1)
         Y10=LOG10.(Y1/Y5)
         Y11=LOG10.(Y2/Y6)
         Y12=(Y3*Y9)-Y4*Y8
         Y13=(Y10*Y9)-Y4*Y11
         Y14=(Y3*Y11)-Y10*Y8
         C21=Y13/Y12
         C22=Y14/Y12
2        TC21TC22
         GO TO 1
         END
```

PROGRAM 6:

Title: Solution Program for the Three Component Redlich-Kister Liquid-Liquid Equations.

Language and Computer: GAT - IBM 650 or Fortran II - IBM 704.

Function: Program 6 solves Equations (3.10), (3.11), (3.12) for values of x_3' in steps of any specified $\Delta x_3'$ up to a specified final value of x_3'. Program 6 begins by solving a point low on the binodal curve where x_3 is very small. An initial guess of x_1', x_1'', x_2'' is read in initially for this first point. The iteration then begins and solution is assumed when

$$\mathcal{E} > \sum_{i=1}^{3} \left| \log_{10} x_i'/x_i'' - \phi_i \right| ,$$

$\mathcal{E}$ being arbitrarily chosen to give the desired accuracy. For the second point:

$$x_3'^{[2]} = x_3'^{[1]} + \Delta x_3' , \quad x_1'^{[2]} = x_1'^{[1]} \qquad x_2''^{[2]} = x_2''^{[1]}$$

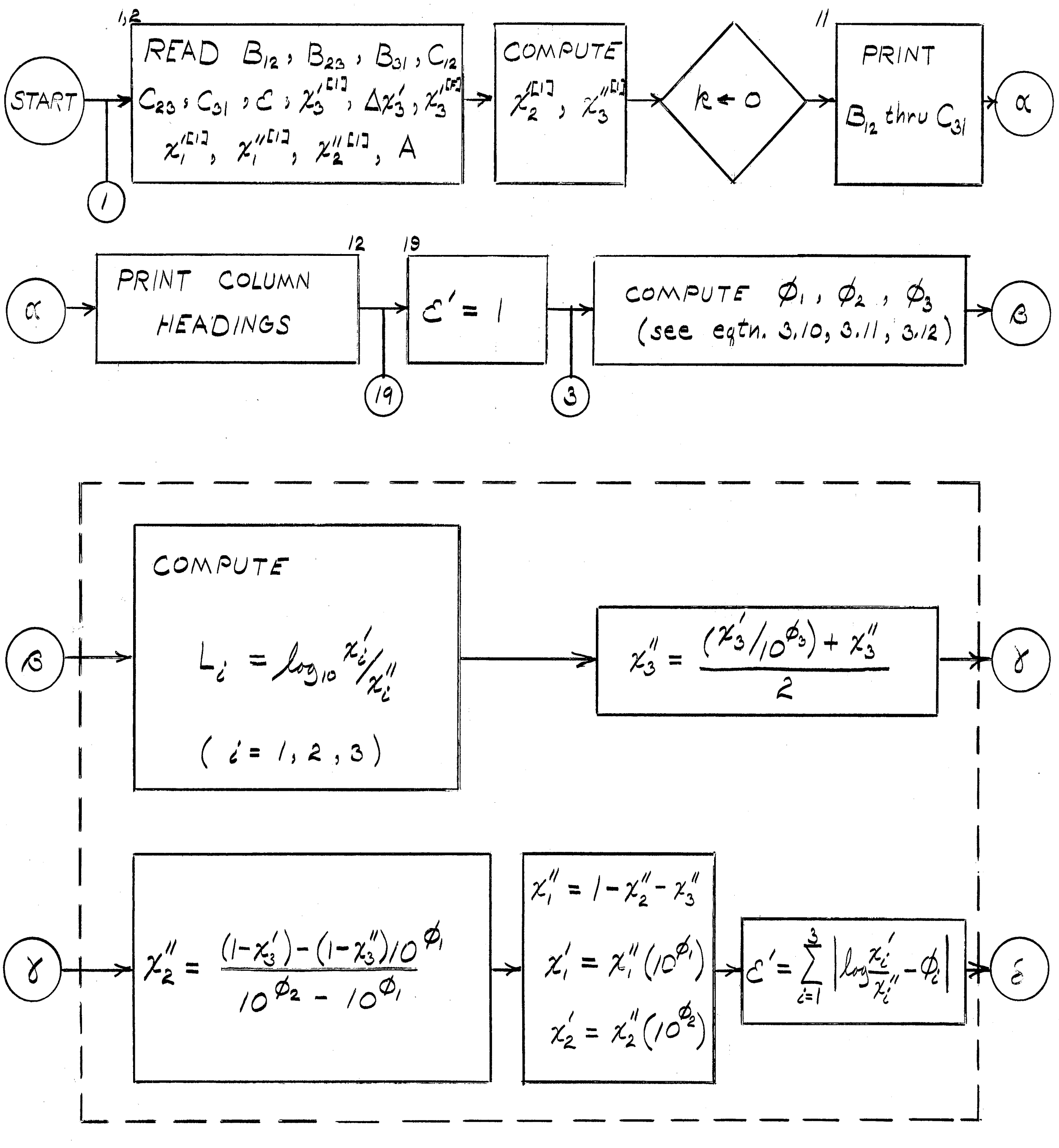
$$x_2'^{[2]} = 1 - x_1'^{[1]} - x_3'^{[1]} , \quad x_1''^{[2]} = x_1''^{[1]}$$

(where $[n]$ refers to the point number) are taken as initial guesses and the iteration starts again. In order to insure convergence $\Delta x_3'$ should be 0.01 or smaller in almost all cases. For the third point and all successive points, initial guesses are made by linear extrapolation from the last two points:

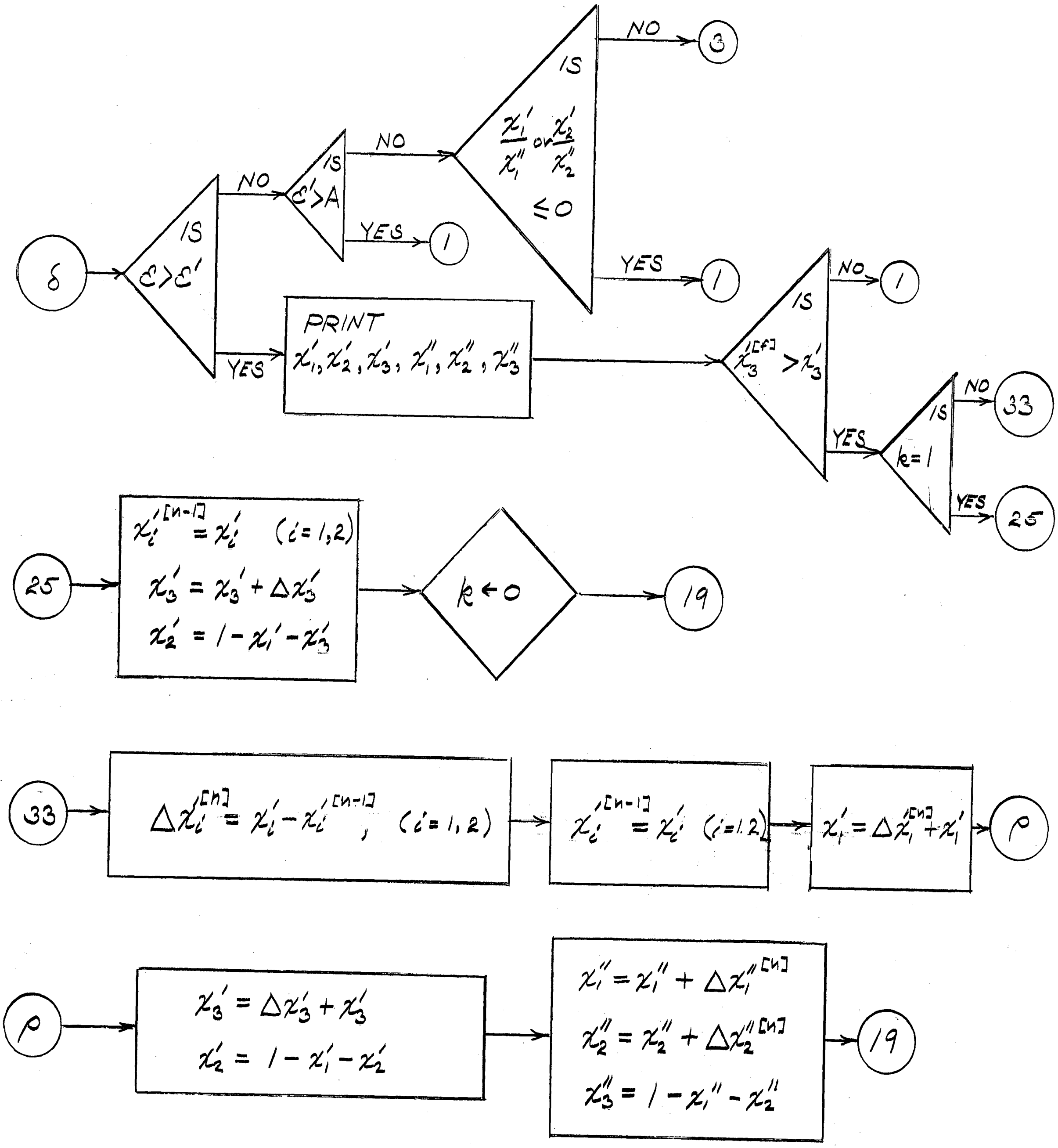
$$x_i^{[n+1]} = x_i^{[n]} + x_i^{[n]} - x_i^{[n-1]} \qquad (i = 1, 2)$$

Program 6 converges rapidly near a partially miscible binary region, more slowly near a plait point. For a given $\mathcal{E}$ the accuracy of solution is lowest near a plait point. For an average case less than one minute is required to compute a complete binodal curve on the IBM 704. If divergence occurs or if the logarithm of a negative number is taken during computation, a new set of Redlich-Kister coefficients is read in and computation proceeds.

Flow Sheet:



Note: Dashed lines enclose solution routine used in Program 8


δ
IS $\mathcal{E} > \mathcal{E}'$
NO
YES
IS $\mathcal{E}' > A$
NO
YES
1
IS $\frac{x_1'}{x_1''}$ or $\frac{x_2'}{x_2''}$ ≤ 0
NO
3
YES
1
PRINT $x_1', x_2', x_3', x_1'', x_2'', x_3''$
IS $x_3'^{[f]} > x_3'$
NO
1
YES
IS $k=1$
NO
33
YES
25
25
$x_i'^{[n-1]} = x_i' \quad (i=1,2)$
$x_3' = x_3' + \Delta x_3'$
$x_2' = 1 - x_1' - x_3'$
$k \leftarrow 0$
19
33
$\Delta x_i'^{[n]} = x_i' - x_i'^{[n-1]}, \quad (i=1,2)$
$x_i'^{[n-1]} = x_i' \quad (i=1,2)$
$x_1' = \Delta x_1'^{[n]} + x_1'$
ρ
ρ
$x_3' = \Delta x_3' + x_3'$
$x_2' = 1 - x_1' - x_2'$
$x_1'' = x_1'' + \Delta x_1''^{[n]}$
$x_2'' = x_2'' + \Delta x_2''^{[n]}$
$x_3'' = 1 - x_1'' - x_2''$
19

Correspondence of Variables:

B_{12} = C1

B_{23} = C2

B_{31} = C3

C_{12} = C4

C_{23} = C5

C_{31} = C6

x_1' = Y1

x_2' = Y2

x_3' = Y3

x_1'' = Y5

x_2'' = Y6

x_3'' = Y7

$\mathcal{E}'$ = Y8

ϕ_1 = Z17

ϕ_2 = Z18

ϕ_3 = Z19

L_1 = D8

L_2 = D9

L_3 = D10

f_j = F(J)

g_j = G(J)

h_j = H(J)

$\mathcal{E}$ = Y

$\Delta x_3'$ = X

$x_3^{[F]}$ = FY3

$\Delta x_1'^{[n]}$ = X21

$\Delta x_2'^{[n]}$ = X22

$\Delta x_1''^{[n]}$ = X23

$\Delta x_2''^{[n]}$ = X24

$x_1'^{[n-1]}$ = X17

$x_2'^{[n-1]}$ = X18

$x_1''^{[n-1]}$ = X19

$x_2''^{[n-1]}$ = X20

A = A

$\mathcal{E}'$ = Y8

Input: See READ INPUT TAPE Statement in program below. Format is in accordance with FORMAT statement 2. A is a divergence test constant normally set greater than one.

Subroutines Used: LOG (natural log), general exponentation plus the usual Fortran system routines.

Fortran Compiler Statements:

```
      DIMENSION C(6),F(6),G(6),H(6)
    1 READ INPUT TAPE 7,2,(C(I),I=1,6),Y,Y3,X,FY3,Y1,Y5,Y6,A
    2 FORMAT (6E12.4/4E10.2/4E12.4)
      E=0.43429448
      Y2=1.-Y1-Y3
      Y7=1.-Y5-Y6
      K=1
      WRITE OUTPUT TAPE 6,11,(C(I),I=1,6)
   11 FORMAT (4H1C1=E12.4,4H C2=E12.4,4H C3=E12.4,4H C4=E12.4,4H C5=E12
     X .4,4H C6=E12.4)
      WRITE OUTPUT TAPE 6,12
   12 FORMAT (68H       Y1            Y2            Y3            Y5            Y
     X6          Y7)
   19 Y8=1.
      C26=1.-Y3
      C27=1.-Y7
    3 C16=1.-Y1
      C17=1.-Y2
      C18=1.-Y5
      C19=1.-Y6
      C20=2.*Y1
      C21=2.*Y2
      C22=2.*Y3
      C23=2.*Y5
      C24=2.*Y6
      C25=2.*Y7
      Y10=Y2-Y1
      X10=Y6-Y5
      Z10=Y5-Y7
      F(1)=Y6*C18-Y2*C16
      F(2)=Y2*Y3-Y6*Y7
      F(3)=Y7*C18-Y3*C16
      F(4)=Y6*(C23*(X10+1.)-Y6)-Y2*(C20*(Y2+C16)-Y2)
      F(5)=C24*Y7*(Y7-Y6)-C21*Y3*(Y3-Y2)
      F(6)=Y7*(C23*(Z10-1.)+Y7)-Y3*(C20*(-Y3-C16)+Y3)
      G(1)=Y5*C19-Y1*C17
      G(2)=Y7*C19-Y3*C17
      G(3)=Y1*Y3-Y5*Y7
      G(4)=Y5*(C24*(X10-1.)+Y5)-Y1*(C21*(Y10-1.)+Y1)
      G(5)=Y7*(C24*(C19+Y7)-Y7)-Y3*(C21*(C17+Y3)-Y3)
      G(6)=C23*Y7*Z10-C20*Y3*(Y1-Y3)
      H(1)=Y1*Y2-Y5*Y6
      H(2)=Y6*C27-Y2*C26
      H(3)=Y5*C27-Y1*C26
      H(4)=C23*Y6*X10-C20*Y2*Y10
      H(5)=Y6*(C25*(-C27-Y6)+Y6)+Y2*(C22*(C26+Y2)-Y2)
      H(6)=Y5*(C25*(Z10+1.)-Y5)-Y1*(C22*(C26+Y1)-Y1)
   31 Z17=C(1)*F(1)+C(2)*F(2)+C(3)*F(3)+C(4)*F(4)+C(5)*F(5)+C(6)*F(6)
      Z18=C(1)*G(1)+C(2)*G(2)+C(3)*G(3)+C(4)*G(4)+C(5)*G(5)+C(6)*G(6)
      Z19=C(1)*H(1)+C(2)*H(2)+C(3)*H(3)+C(4)*H(4)+C(5)*H(5)+C(6)*H(6)
      D8=E*LOGF(Y1/Y5)
      D9=E*LOGF(Y2/Y6)
      D10=E*LOGF(Y3/Y7)
      Y7=((Y3/(10.**Z19))+Y7)/2.
      X8=10.**Z17
      X9=10.**Z18
      C26=1.-Y3
      C27=1.-Y7
      Y6=(C26-C27*X8)/(X9-X8)
      Y5=1.-Y6-Y7
      Y1=X8*Y5
```

Fortran Compiler Statements:

```
      Y2=X9*Y6
      Y8=ABSF(D8-Z17)+ABSF(D9-Z18)+ABSF(D10-Z19)
      IF(Y8-Y)4,4,32
   32 IF(Y8- A )10,1,1
   10 IF(Y1/Y5)1,1,14
   14 IF (Y2/Y6)1,1,3
    4 WRITE OUTPUT TAPE6,8,Y1,Y2,Y3,Y5,Y6,Y7
    8 FORMAT (1H 6E12.4)
      IF (FY3-Y3)1,13,13
   13 IF (K-1)33,25,33
   33 X21=Y1-X17
      X22=Y2-X18
      X23=Y5-X19
      X24=Y6-X20
      X17=Y1
      X18=Y2
      X19=Y5
      X20=Y6
      Y1=X17+X21
      Y3=X+Y3
      Y2=1.-Y1-Y3
      Y5=X19+X23
      Y6=X20+X24
      Y7=1.-Y5-Y6
      GO TO 19
   25 X17=Y1
      X18=Y2
      X19=Y5
      X20=Y6
      Y3=X+Y3
      Y2=1.-Y1-Y3
      K=0
      GO TO 19
```

PROGRAM 7:

Title: Linearized Ternary Liquid-Liquid Least Squares Program.

Language and Computer: GAT - IBM 650

Function: Program 7 determines the coefficients in Equations (3.10), (3.11), (3.12) from ternary liquid-liquid equilibrium tie line data for three cases:

1. Where Equations (3.10), (3.11), (3.12) retain all six coefficients.
2. Where Equations (3.10), (3.11), (3.12) retain only B_{12}, B_{23}, B_{31}, and C_{12}.
3. Where Equations (3.10), (3.11), (3.12) retain only B_{12}, C_{12}, C_{23}, and C_{31}.

In order that Equations (4.5) be linear in the coefficients the following Δ is minimized:

$$\Delta = \sum_{i=1}^{M}\left[\left(\log_{10} x_1'/x_1'' - \phi_1\right)^2 + \left(\log_{10} x_2'/x_2'' - \phi_1\right)^2 + \left(\log_{10} x_3'/x_3'' - \phi_3\right)^2\right]_i$$

The method used in solving the linear simultaneous equations is that of Jordan Elimination and the routine used here was written by Professor B. A. Galler and is described in Reference (8).

For reasons discussed earlier, Program 7 does not always give satisfactory estimates of the coefficients. Because of its speed however it is always advisable to try Program 7 and see if it gives good estimates of the coefficients for a given set of data.

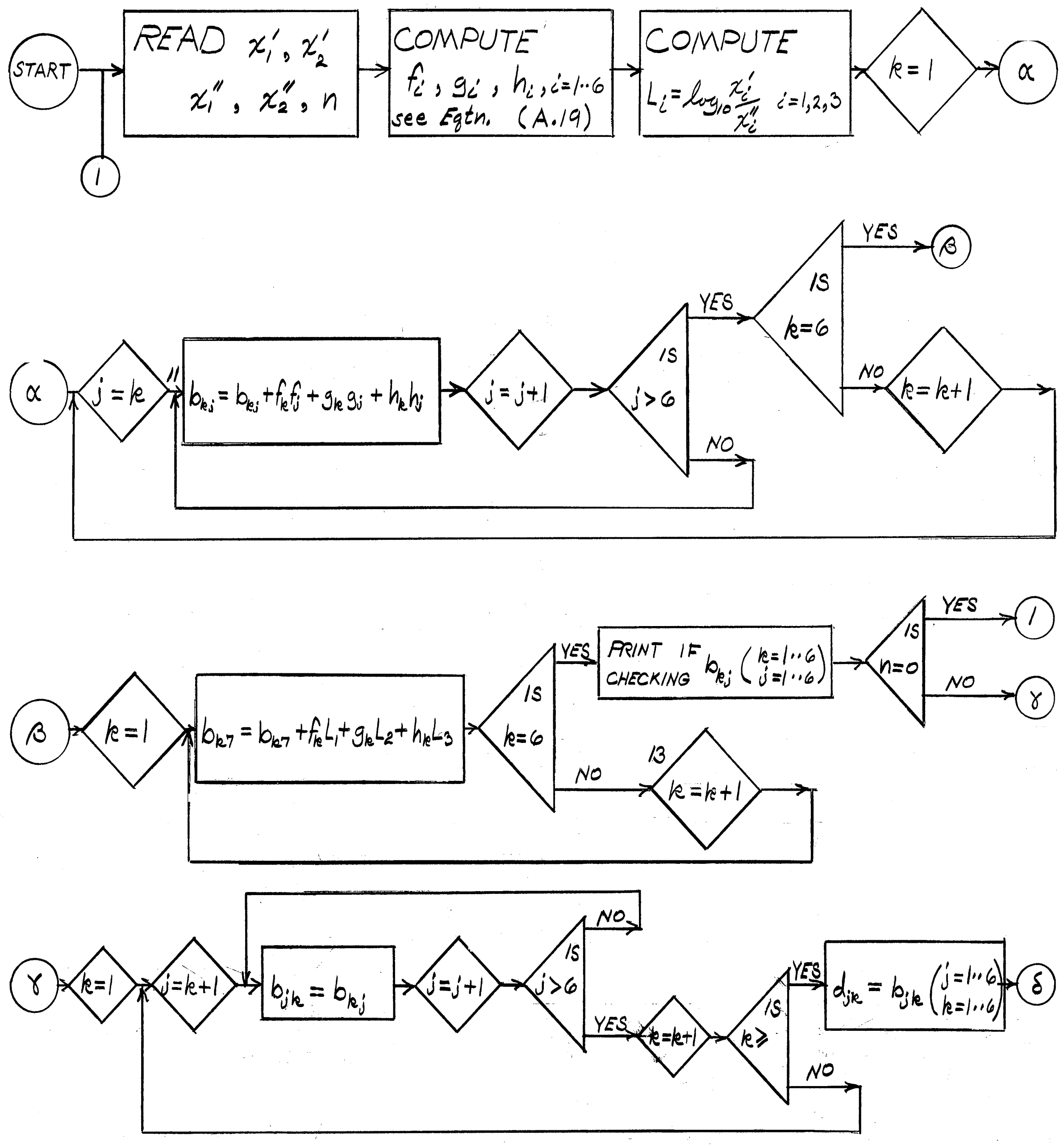
In comparing the flow sheet to the compiler statements it will be recognized that GAT stores:

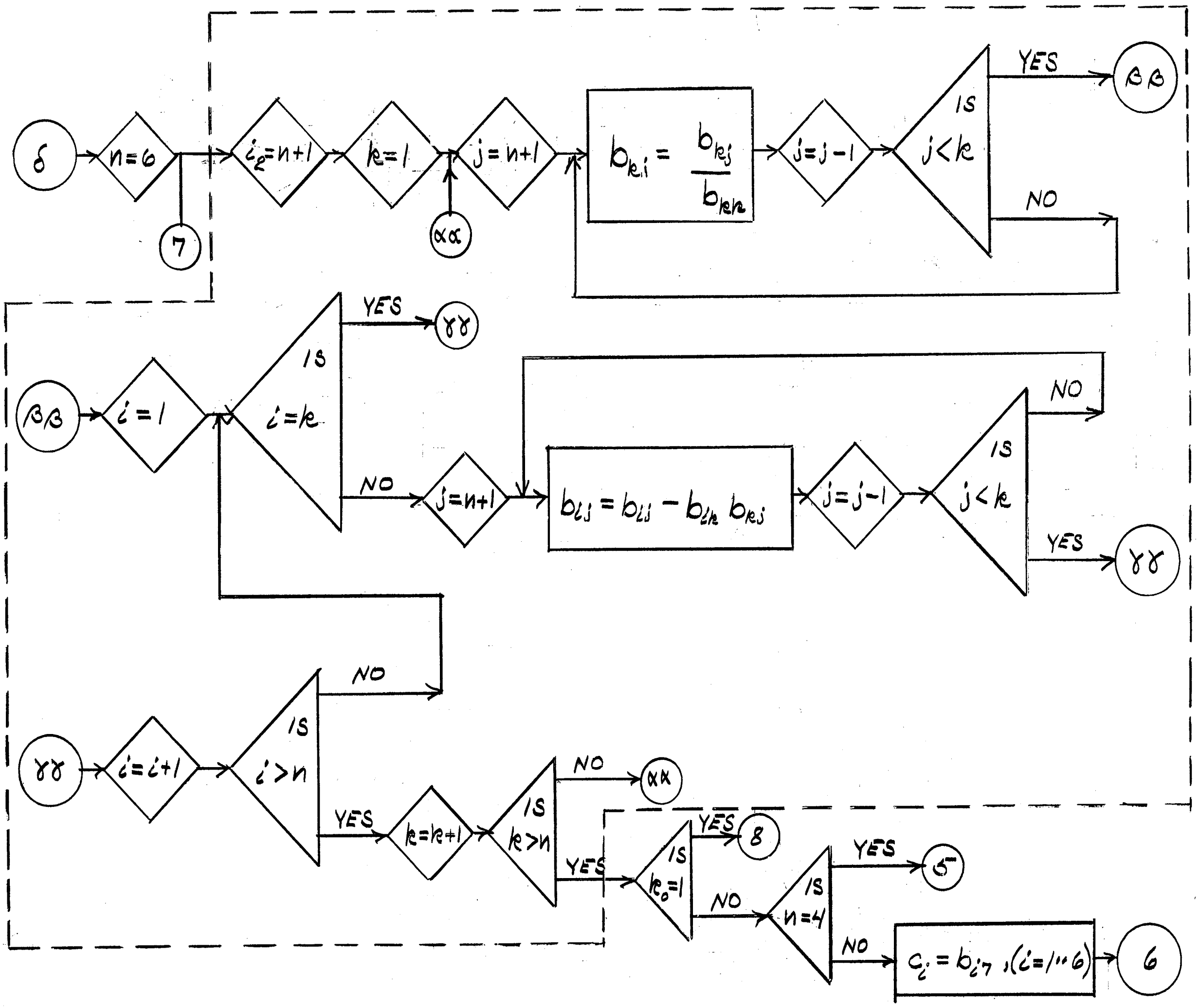
$$C1 = C(1,1),\quad C2 = C(1,2) \text{ ---- } Cn = C(1,n)$$

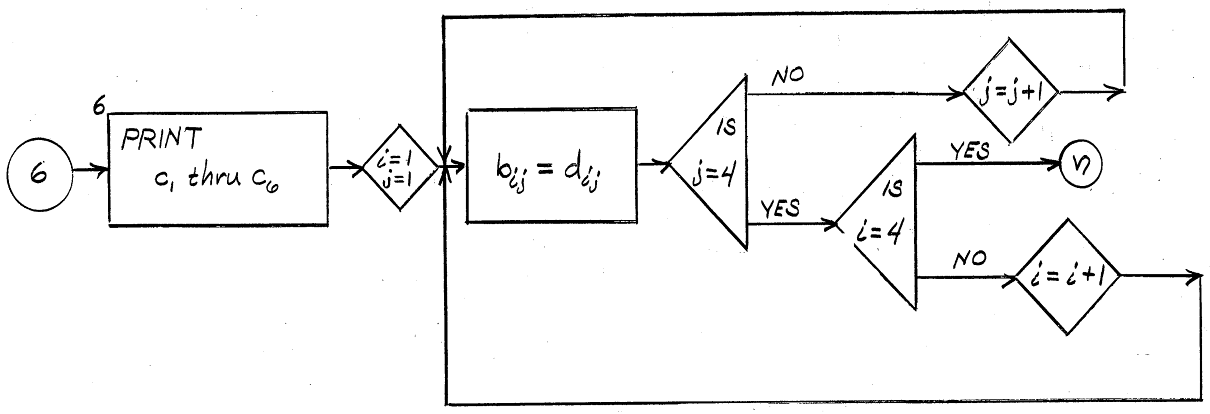
$$C(n+1) = C(2,1),\quad C(n+2) = C(2,2) \text{ ---- } C(2n) = C(2,n) \text{ etc.}$$

when in the DIMENSION statement $C(n_1, n_2, n_3)$, $n_3 = 1$.

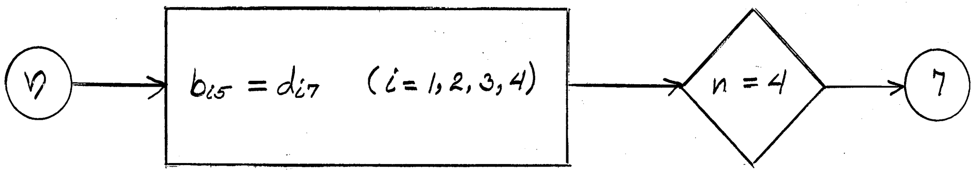
Flow Sheet:

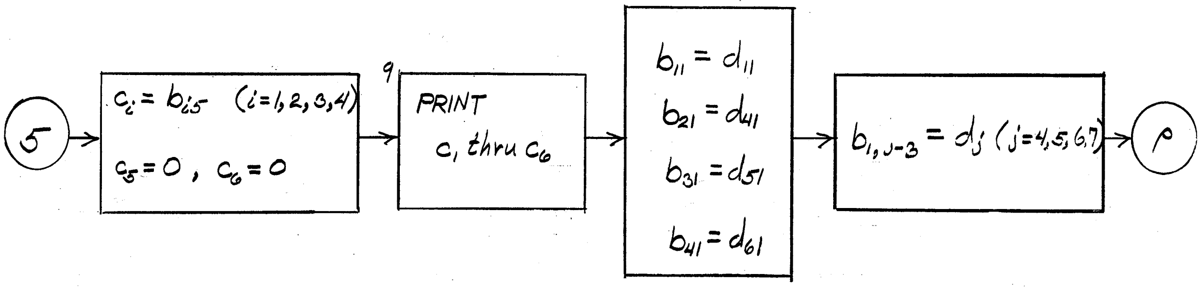


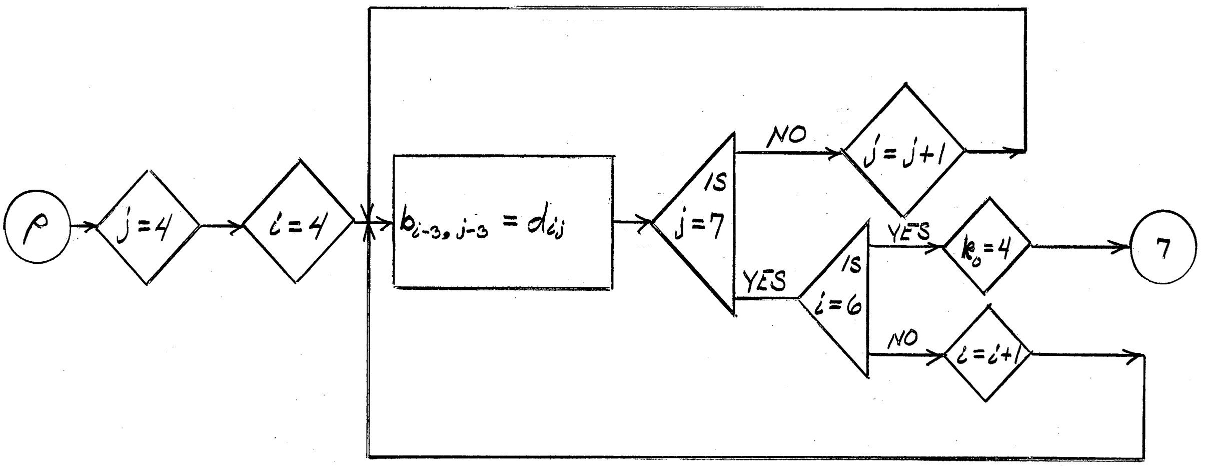


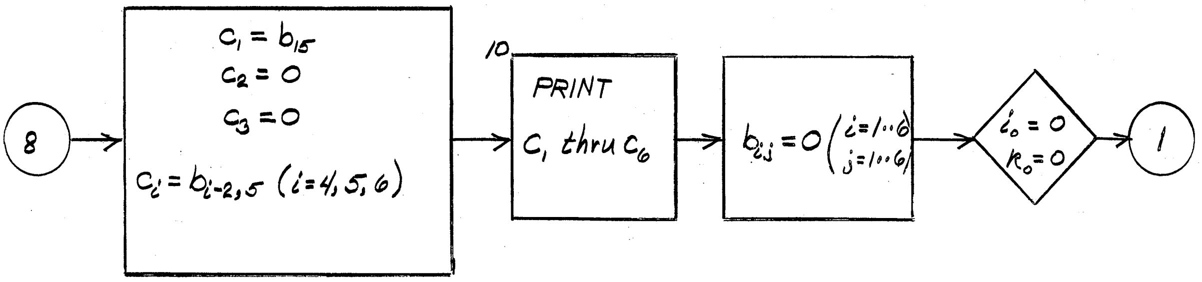


Note: The dashed lines enclosed the Jordan Elimination Routine; on exit the coefficients B_{12} , B_{23} , B_{31} , C_{12} , C_{23} , C_{31} are in location b_{17} , b_{27} , b_{37} --- etc.


η
$b_{i5} = d_{i7}$ $(i = 1, 2, 3, 4)$
$n = 4$
7


5
$c_i = b_{i5}$ $(i=1,2,3,4)$
$c_5 = 0$, $c_6 = 0$
9
PRINT
c_1 thru c_6
$b_{11} = d_{11}$
$b_{21} = d_{41}$
$b_{31} = d_{51}$
$b_{41} = d_{61}$
$b_{1, j-3} = d_j$ $(j=4,5,6,7)$
ρ


ρ
$j = 4$
$i = 4$
$b_{i-3, j-3} = d_{ij}$
IS $j = 7$
NO
$j = j+1$
YES
IS $i = 6$
YES
$k_o = 4$
7
NO
$i = i+1$


8
$c_1 = b_{15}$
$c_2 = 0$
$c_3 = 0$
$c_i = b_{i-2, 5}$ $(i=4,5,6)$
10
PRINT
c_1 thru c_6
$b_{ij} = 0$ $\left(\begin{smallmatrix} i=1 \cdots 6 \\ j=1 \cdots 6 \end{smallmatrix}\right)$
$i_o = 0$
$k_o = 0$
1

Correspondence of Variables:

(same as Program 6 except as follows)

f_1 to f_6 = X1 to X6

g_1 to g_6 = Y11 to Y16

h_1 to h_6 = Z1 to Z6

L_1 to L_3 = D1 to D3

n = I0

b_{ij} = C(I1, J1)

d_{ij} = Y(I1, J1)

Input: Y1, Y2, Y5, Y6 with I0 = 1 on last data point.

Subroutines: READ, PUNCH, FIX, FLOAT, LOG10., MATRIX SUBSCRIPTION

GAT Compiler Statements:

```
              15 IS HIGHEST STATEMENTNUMBER
              645 USED IN SUBROUTINES
              DIMENSION C(42,I2,1)Y(42)I(4)N
              J(1)K(1)Z(6)X(6)D(3)
 1            READ
              Y3=1.-Y1-Y2
              Y7=1.-Y5-Y6
              Y8=1.-Y5
              Y9=1.-Y1
              X1=Y6*Y8-Y2*Y9
              X2=Y2*Y3-Y6*Y7
              X3=Y7*Y8-Y3*Y9
              X4=Y6*(2.*Y5*(Y6+Y8)-Y6)-   N
              Y2*(2.*Y1*(Y2+Y9)-Y2)
              X5=2.*(Y6*Y7*(Y7-Y6)-Y2*Y3   N
              *(Y3-Y2))
              X6=Y7*(Y7-2.*Y5*(Y7+Y8))-   N
              Y3*(Y3-2.*Y1*    (Y3+Y9))
              Y8=1.-Y6
              Y9=1.-Y2
              Y11=Y5*Y8-Y1*Y9
              Y12=Y7*Y8-Y3*Y9
              Y13=Y1*Y3-Y5*Y7
              Y14=Y5*(Y5-2.*Y6*(Y5+Y8))-   N
              Y1*(Y1-2.*Y2*(Y1+Y9))
              Y15=Y7*(2.*Y6*(Y7+Y8)-Y7)-   N
              Y3*(2.*Y2*(Y3+Y9)-Y3)
              Y16=2.*(Y5*Y7*(Y5-Y7)-   N
              Y1*Y3*(Y1-Y3) )
              Y8=1.-Y7
              Y9=1.-Y3
              Z1=Y1*Y2-Y5*Y6
              Z2=Y6*Y8-Y2*Y9
              Z3=Y5*Y8-Y1*Y9
              Z4=2.*(Y5*Y6*(Y6-Y5)-   N
              Y1*Y2*(Y2-Y1))
              Z5=Y6*(Y6-2.*Y7*(Y6+Y8))-Y2 N
              *(Y2-2.*Y3*(Y2+Y9))
              Z6=Y5*(2.*Y7*(Y5+Y8)-Y5)-Y1 N
              *(2.*Y3*(Y1+Y9)-Y1)
              D1=LOG10.(Y1/Y5)
              D2=LOG10.(Y2/Y6)
              D3=LOG10.(Y3/Y7)
              I1=1
              I4=2
              12,K1,1,1,6,
              I2=K1
              I3=K1
 11           CI1=CI1+XI2*XI3+Y(I2+10)*Y(I3N
              +10)+ZI2*ZI3
              I3=I3+1
              I1=I1+1
              GO TO 11IF 6WI3
              I1=I1+I4
 12           I4=I4+1
              I1=7
              13,I2,1,1,6,
              CI1=CI1+XI2*D1+Y(I2+10)*D2+ZIN
              2*D3
```

GAT Compiler Statements:(Cont'd)

```
        TC1...C42
        GO TO 1 IF I0U0
        C8=C2
        C15=C3
        C22=C4
        C29=C5
        C36=C6
        C16=C10
        C23=C11
        C30=C12
        C24=C18
        C37=C13
        C38=C20
        C39=C27
        C40=C34
        C31=C19
        C32=C26
        14,I1,1,1,42,
14      YI1=CI1
        I0=6
 7      I2=I0+1
        4,K1,1,1,I0,
        2,J1,I2,-1,K1,
 2      C(K1,J1)=C(K1,J1)/C(K1,K1)
        4,I1,1,1,I0,
        GO TO 4IF I1UK1
        3,J1,I2,-1,K1,
 3      C(I1,J1)=C(I1,J1)-C(I1,K1)* N
          C(K1,J1)
 4      I0=I0
        GO TO 8 IF K0U1
        GO TO 5 IF I0U4
        C1=C7
        C2=C14
        C3=C21
        C4=C28
        C5=C35
        C6=C42
 6      TC1TC2TC3TC4TC5TC6
        C1=Y1
        C2=Y2
        C3=Y3
        C4=Y4
        C5=Y7
        C6=Y8
        C7=Y9
        C8=Y10
        C9=Y11
        C10=Y14
        C11=Y15
        C12=Y16
        C13=Y17
        C14=Y18
        C15=Y21
        C16=Y22
        C17=Y23
        C18=Y24
        C19=Y25
        C20=Y28
```

GAT Compiler Statements (Cont'd)

```
                   I0=4
                   GO TO 7
        5          C1=C5
                   C2=C10
                   C3=C15
                   C4=C20
                   C5=0.
                   C6=0.
        9          TC1TC2TC3TC4TC5TC6
                   C1=Y1
                   C2=Y4
                   C3=Y5
                   C4=Y6
                   C5=Y7
                   C6=Y22
                   C7=Y25
                   C8=Y26
                   C9=Y27
                   C10=Y28
                   C11=Y29
                   C12=Y32
                   C13=Y33
                   C14=Y34
                   C15=Y35
                   C16=Y36
                   C17=Y39
                   C18=Y40
                   C19=Y41
                   C20=Y42
                   K0=4
                   GO TO 7
        8          C1=C5
                   C2=0.
                   C3=0.
                   C4=C10
                   C5=C15
                   C6=C20
       10          TC1TC2TC3TC4TC5TC6
                   15,I1,1,1,42,
       15          CI1=0.
                   I0=0
                   K0=0
                   GO TO 1
                   END
```

PROGRAM 8:

Title: Non-Linear Ternary Liquid-Liquid Least Squares Program

Language and Computer: Fortran II - IBM 704

Function: Program 8 determines the six coefficients in Equations (3.10), (3.11), (3.12) from ternary liquid-liquid equilibrium tie line data by minimization of Δ defined as:

$$\Delta = \sum_{i=1}^{M} \left[(x_2' - \overset{*}{x}_2')^2 \omega_1 + (x_2'' - \overset{*}{x}_2'')^2 \omega_2 + (x_3'' - \overset{*}{x}_3'')^2 \omega_3 \right]_i$$

The method of steepest descent described by Marquardt(21) is used to approach the minimum until a good approximation is obtained after which the truncated Taylor series method is used which near the minimum Δ converges more rapidly than the steepest descent method.

Very generally the following steps take place:

1. The experimental data and the initial guess of the coefficients are read in.

2. Equations (3.10), (3.11), (3.12) are solved for $\overset{*}{x}_3'$ equal to the x_3' of each experimental point starting with the lowest value of x_3' by the method of Program 6.

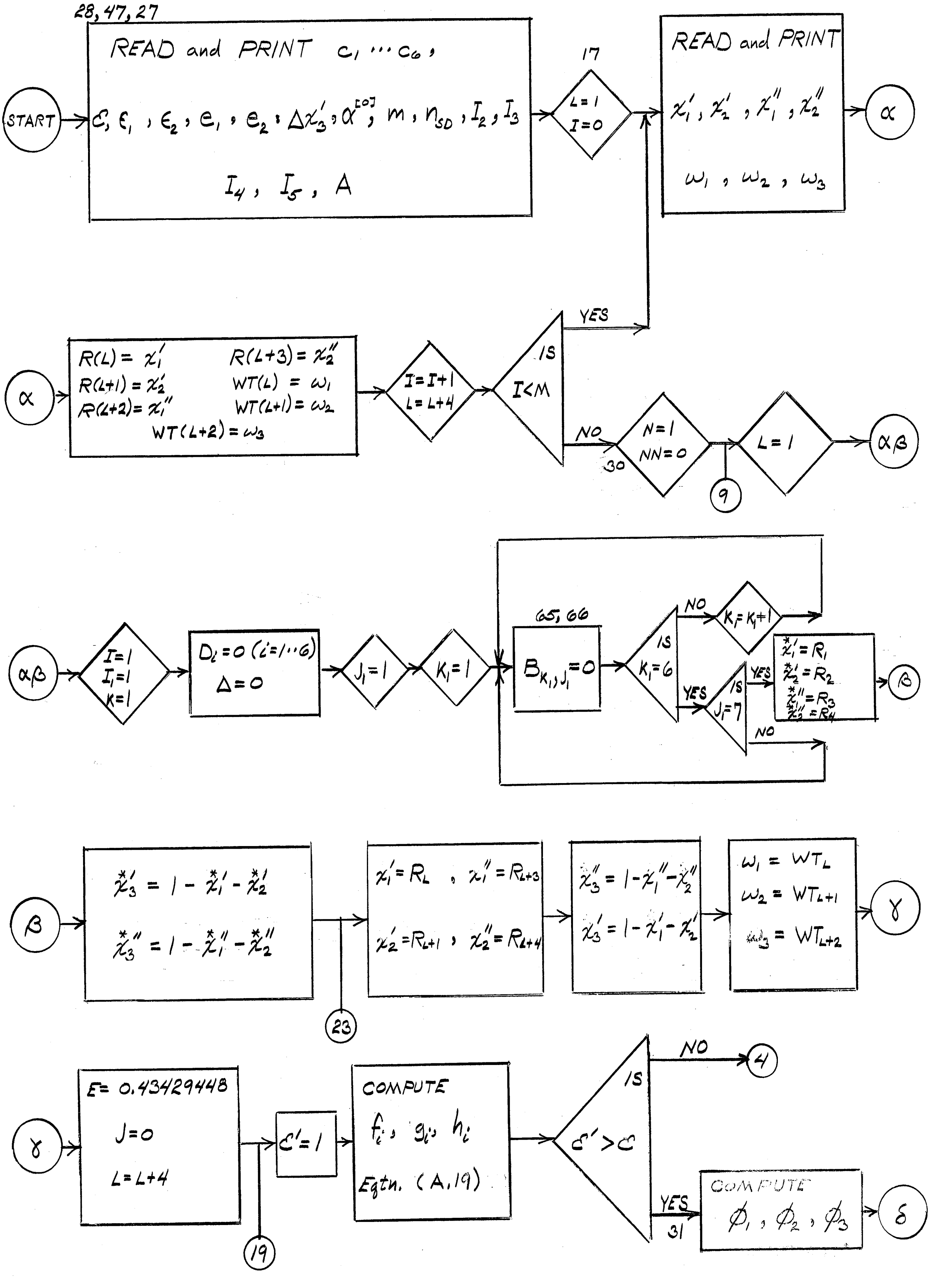
3. Δ and the partial derivatives $\frac{\partial \overset{*}{x}_2'}{\partial c_i}$, $\frac{\partial \overset{*}{x}_2''}{\partial c_i}$, $\frac{\partial \overset{*}{x}_3''}{\partial c_i}$ and $\frac{\partial \Delta}{\partial c_i}$ are computed.

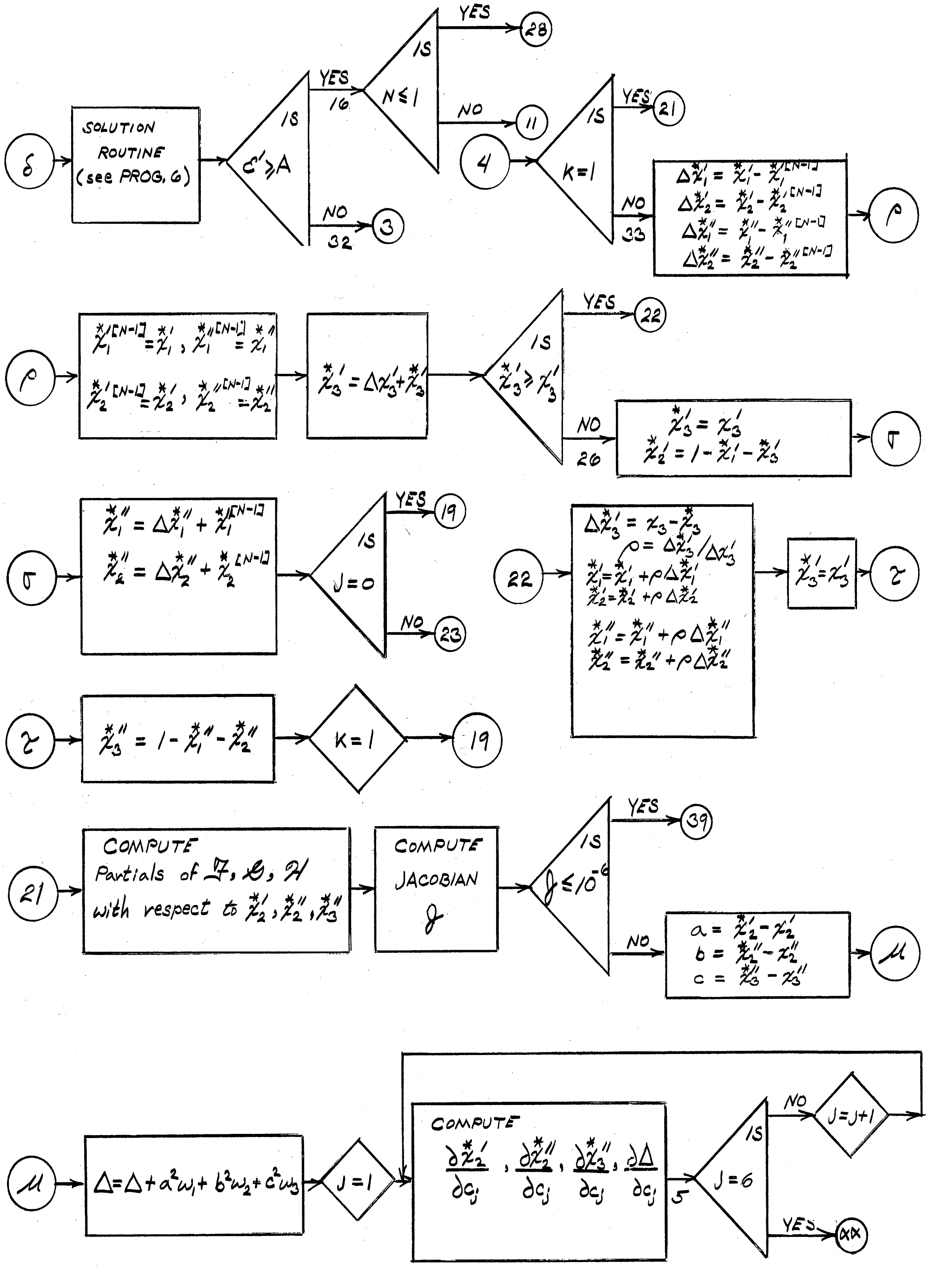
4. Corrections to the coefficients are computed either by steepest descent or by the truncated Taylor series method.

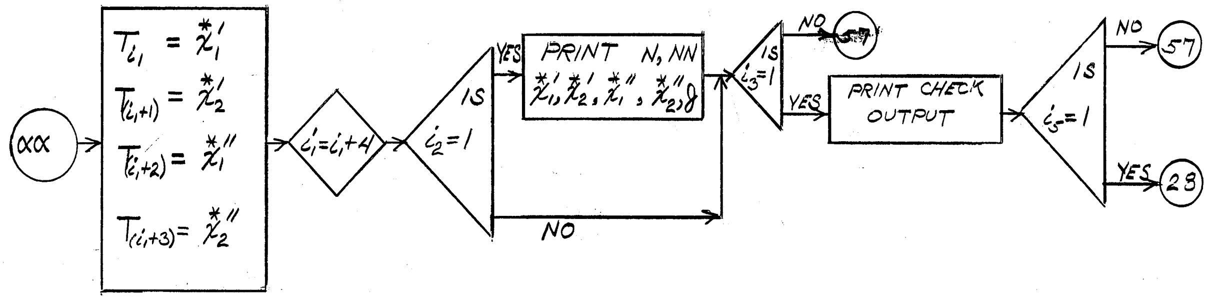
5. The process is repeated starting with step 2 until

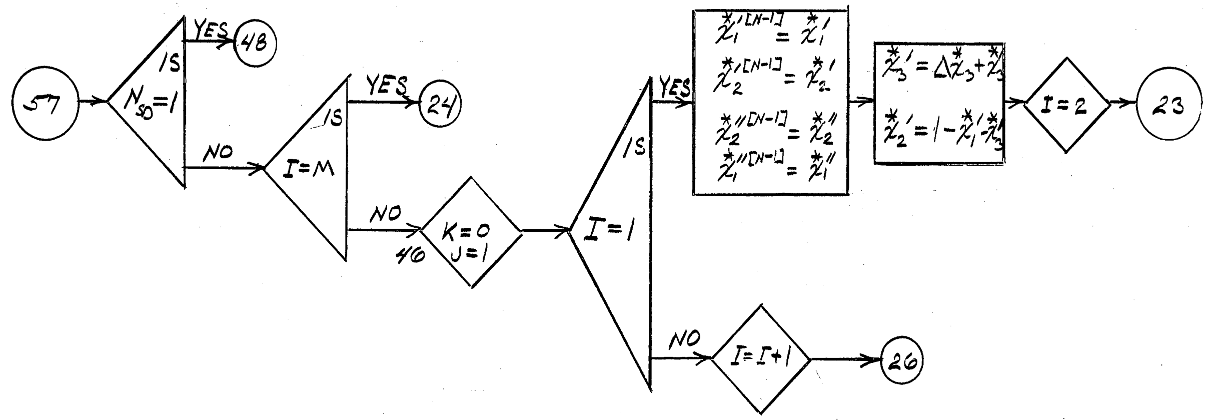
$$\varepsilon > \sum_{i=1}^{6} \left(c_i^{[n]} - c_i^{[n-1]} \right)^2 , \qquad \varepsilon \text{ being arbitrarily small.}$$

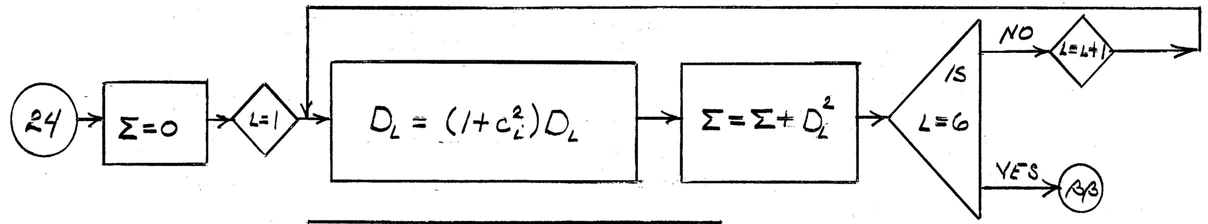
Flow Sheet:

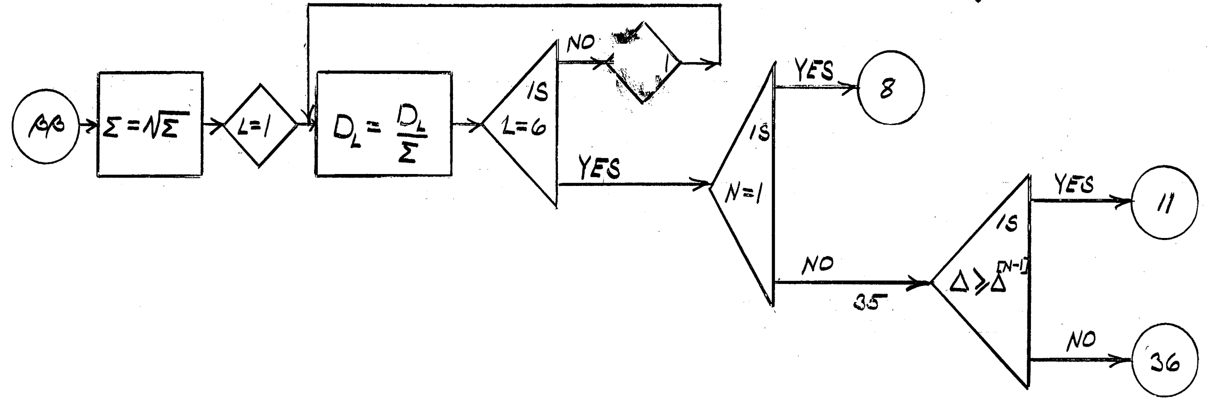

START
28, 47, 27
READ and PRINT $c_1 \cdots c_6$,
$\mathcal{E}, \epsilon_1, \epsilon_2, e_1, e_2, \Delta x_3', \alpha^{[0]}, m, n_{SD}, I_2, I_3$
I_4, I_5, A
17
$L=1$
$I=0$
READ and PRINT
x_1', x_2', x_1'', x_2''
$\omega_1, \omega_2, \omega_3$
α
α
$R(L) = x_1'$
$R(L+1) = x_2'$
$R(L+2) = x_1''$
$R(L+3) = x_2''$
$WT(L) = \omega_1$
$WT(L+1) = \omega_2$
$WT(L+2) = \omega_3$
$I=I+1$
$L=L+4$
IS
$I<M$
YES
NO
30
$N=1$
$NN=0$
9
$L=1$
$\alpha\beta$
$\alpha\beta$
$I=1$
$I_1=1$
$K=1$
$D_i=0\ (i=1\cdots6)$
$\Delta=0$
$J_1=1$
$K_1=1$
65, 66
$B_{K_1,J_1}=0$
IS
$K_1=6$
NO
$K_1=K_1+1$
YES
IS
$J_1=7$
YES
NO
$\overset{*}{x}_1'=R_1$
$\overset{*}{x}_2'=R_2$
$\overset{*}{x}_1''=R_3$
$\overset{*}{x}_2''=R_4$
β
β
$\overset{*}{x}_3' = 1 - \overset{*}{x}_1' - \overset{*}{x}_2'$
$\overset{*}{x}_3'' = 1 - \overset{*}{x}_1'' - \overset{*}{x}_2''$
23
$x_1' = R_L$, $x_1'' = R_{L+3}$
$x_2' = R_{L+1}$, $x_2'' = R_{L+4}$
$x_3'' = 1 - x_1'' - x_2''$
$x_3' = 1 - x_1' - x_2'$
$\omega_1 = WT_L$
$\omega_2 = WT_{L+1}$
$\omega_3 = WT_{L+2}$
γ
γ
$E = 0.434294448$
$J=0$
$L=L+4$
19
$\mathcal{E}'=1$
COMPUTE
f_i, g_i, h_i
Eqtn. (A.19)
IS
$\mathcal{E}' > \mathcal{E}$
NO
4
YES
31
COMPUTE
ϕ_1, ϕ_2, ϕ_3
δ

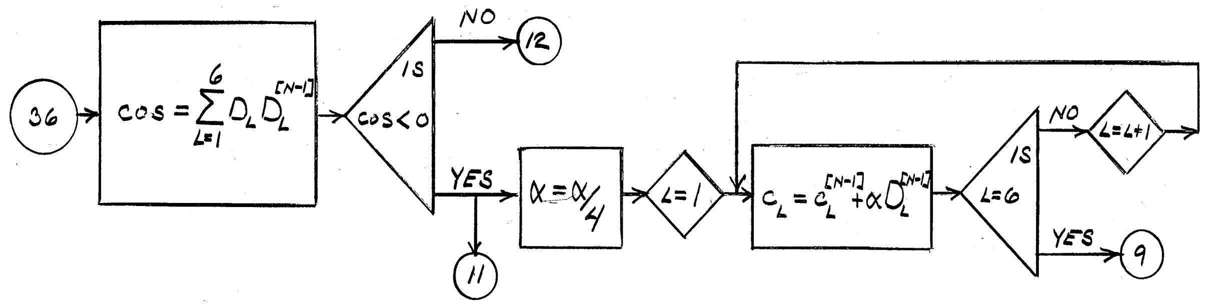

δ
SOLUTION ROUTINE (see PROG. 6)
IS $\varepsilon' \geq A$
YES 16
NO 32
3
IS $N \leq 1$
YES 28
NO 11
4
IS $K=1$
YES 21
NO 33
$\Delta\overset{*}{x}_1' = \overset{*}{x}_1' - \overset{*}{x}_1'^{[N-1]}$
$\Delta\overset{*}{x}_2' = \overset{*}{x}_2' - \overset{*}{x}_2'^{[N-1]}$
$\Delta\overset{*}{x}_1'' = \overset{*}{x}_1'' - \overset{*}{x}_1''^{[N-1]}$
$\Delta\overset{*}{x}_2'' = \overset{*}{x}_2'' - \overset{*}{x}_2''^{[N-1]}$
ρ
ρ
$\overset{*}{x}_1'^{[N-1]} = \overset{*}{x}_1'$, $\overset{*}{x}_1''^{[N-1]} = \overset{*}{x}_1''$
$\overset{*}{x}_2'^{[N-1]} = \overset{*}{x}_2'$, $\overset{*}{x}_2''^{[N-1]} = \overset{*}{x}_2''$
$\overset{*}{x}_3' = \Delta x_3' + \overset{*}{x}_3'$
IS $\overset{*}{x}_3' \geq x_3'$
YES 22
NO 26
$\overset{*}{x}_3' = x_3'$
$\overset{*}{x}_2' = 1 - \overset{*}{x}_1' - \overset{*}{x}_3'$
σ
σ
$\overset{*}{x}_1'' = \Delta\overset{*}{x}_1'' + \overset{*}{x}_1''^{[N-1]}$
$\overset{*}{x}_2'' = \Delta\overset{*}{x}_2'' + \overset{*}{x}_2''^{[N-1]}$
IS $J=0$
YES 19
NO 23
22
$\Delta\overset{*}{x}_3' = x_3 - \overset{*}{x}_3$
$\rho = \Delta\overset{*}{x}_3' / \Delta x_3'$
$\overset{*}{x}_1' = \overset{*}{x}_1' + \rho\Delta\overset{*}{x}_1'$
$\overset{*}{x}_2' = \overset{*}{x}_2' + \rho\Delta\overset{*}{x}_2'$
$\overset{*}{x}_1'' = \overset{*}{x}_1'' + \rho\Delta\overset{*}{x}_1''$
$\overset{*}{x}_2'' = \overset{*}{x}_2'' + \rho\Delta\overset{*}{x}_2''$
$\overset{*}{x}_3' = x_3'$
τ
τ
$\overset{*}{x}_3'' = 1 - \overset{*}{x}_1'' - \overset{*}{x}_2''$
K = 1
19
21
COMPUTE Partials of $\mathcal{F}, \mathcal{G}, \mathcal{H}$ with respect to $\overset{*}{x}_2', \overset{*}{x}_2'', \overset{*}{x}_3''$
COMPUTE JACOBIAN $\mathcal{J}$
IS $\mathcal{J} \leq 10^{-6}$
YES 39
NO
$a = \overset{*}{x}_2' - x_2'$
$b = \overset{*}{x}_2'' - x_2''$
$c = \overset{*}{x}_3'' - x_3''$
μ
μ
$\Delta = \Delta + a^2 w_1 + b^2 w_2 + c^2 w_3$
J = 1
COMPUTE
$\frac{\partial\overset{*}{x}_2'}{\partial c_j}, \frac{\partial\overset{*}{x}_2''}{\partial c_j}, \frac{\partial\overset{*}{x}_3''}{\partial c_j}, \frac{\partial\Delta}{\partial c_j}$
5
IS $J=6$
NO
J=J+1
YES
αα

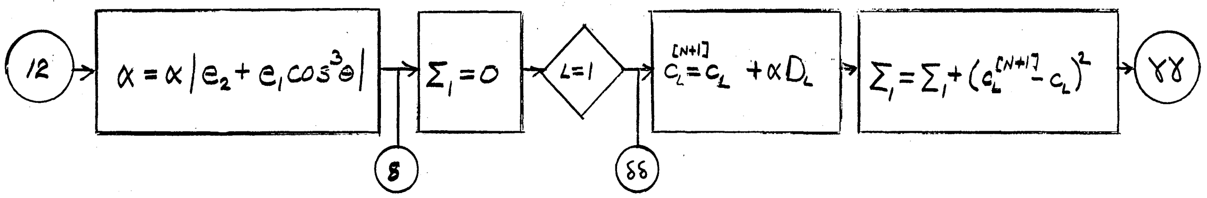

αα
$T_{i_1} = \overset{*}{\chi}_1'$
$T_{(i_1+1)} = \overset{*}{\chi}_2'$
$T_{(i_1+2)} = \overset{*}{\chi}_1''$
$T_{(i_1+3)} = \overset{*}{\chi}_2''$
$i_1 = i_1+4$
IS $i_2=1$
YES
PRINT N, NN $\overset{*}{\chi}_1', \overset{*}{\chi}_2', \overset{*}{\chi}_1'', \overset{*}{\chi}_2'', \delta$
NO
IS $i_3=1$
NO
57
YES
PRINT CHECK OUTPUT
IS $i_5=1$
NO
57
YES
23

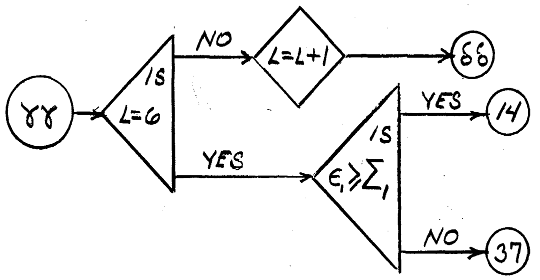

57
IS $N_{SD}=1$
YES
48
NO
IS I=M
YES
24
NO
46
K=0 J=1
IS I=1
YES
$\overset{*}{\chi}_1'^{[N-1]} = \overset{*}{\chi}_1'$
$\overset{*}{\chi}_2'^{[N-1]} = \overset{*}{\chi}_2'$
$\overset{*}{\chi}_2''^{[N-1]} = \overset{*}{\chi}_2''$
$\overset{*}{\chi}_1''^{[N-1]} = \overset{*}{\chi}_1''$
$\overset{*}{\chi}_3' = \Delta\overset{*}{\chi}_3 + \overset{*}{\chi}_3$
$\overset{*}{\chi}_2' = 1 - \overset{*}{\chi}_1' - \overset{*}{\chi}_3'$
I=2
23
NO
I=I+1
26

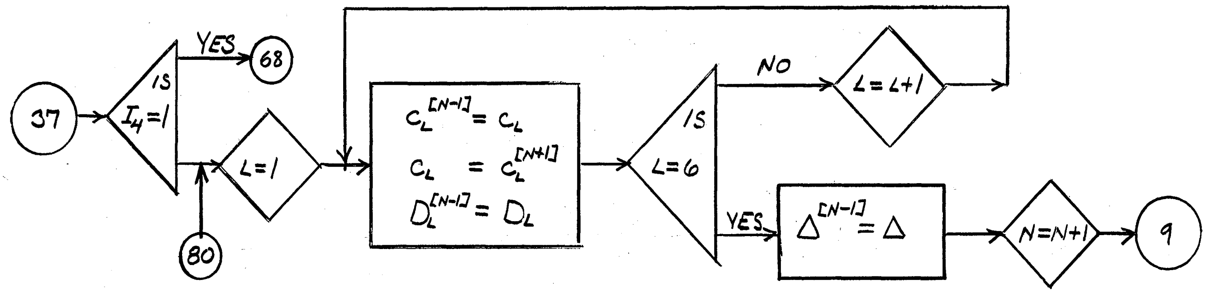

24
Σ=0
L=1
$D_L = (1+c_L^2)D_L$
$\Sigma = \Sigma + D_L^2$
IS L=6
NO
L=L+1
YES
ββ

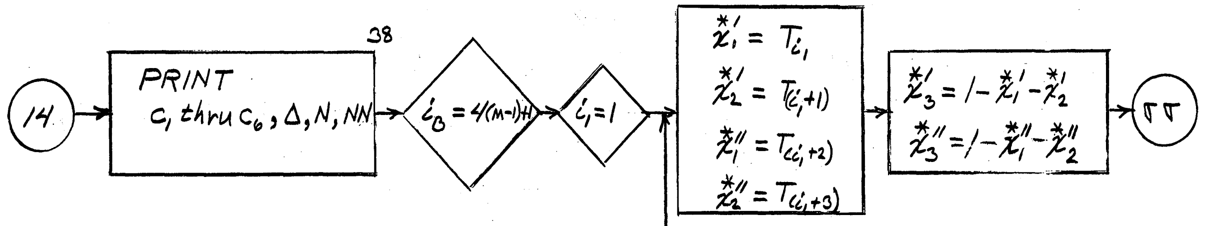

ββ
$\Sigma = \sqrt{\Sigma}$
L=1
$D_L = \frac{D_L}{\Sigma}$
IS L=6
NO
YES
IS N=1
YES
8
NO
35
IS $\Delta \geq \Delta^{[N-1]}$
YES
11
NO
36

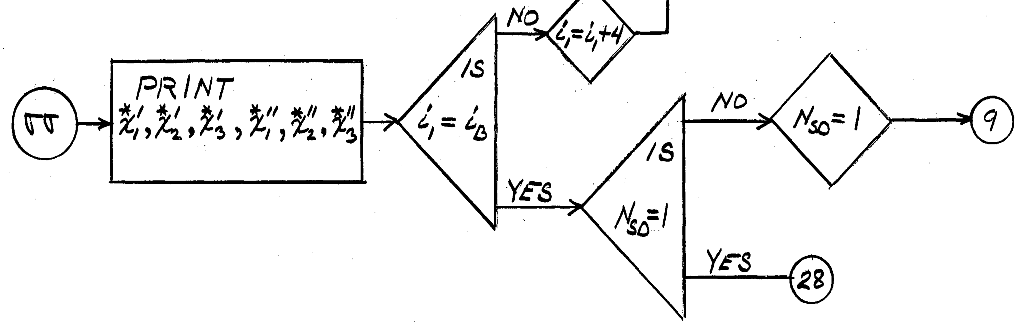

36
$\cos = \sum_{L=1}^{6} D_L D_L^{[N-1]}$
IS cos<0
NO
12
YES
11
$\alpha = \alpha/4$
L=1
$c_L = c_L^{[N-1]} + \alpha D_L^{[N-1]}$
IS L=6
NO
L=L+1
YES
9

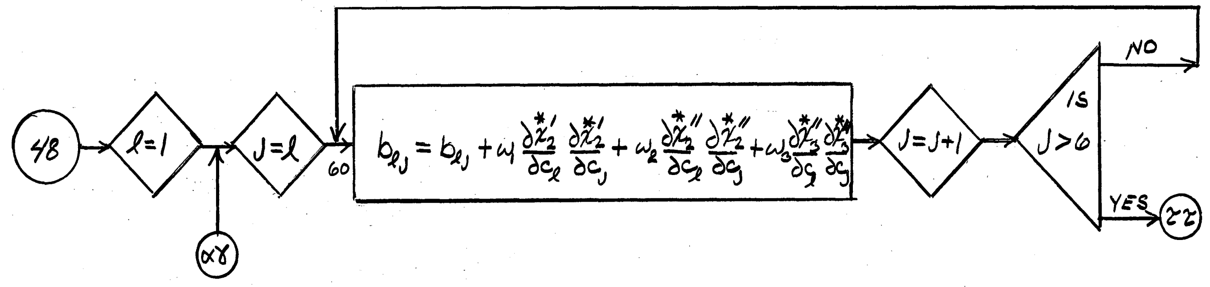

12
$\alpha = \alpha |e_2 + e_1 \cos^3\theta|$
$\Sigma_1 = 0$
$L=1$
$C_L^{[N+1]} = C_L + \alpha D_L$
$\Sigma_1 = \Sigma_1 + (C_L^{[N+1]} - C_L)^2$
γγ
8
δδ

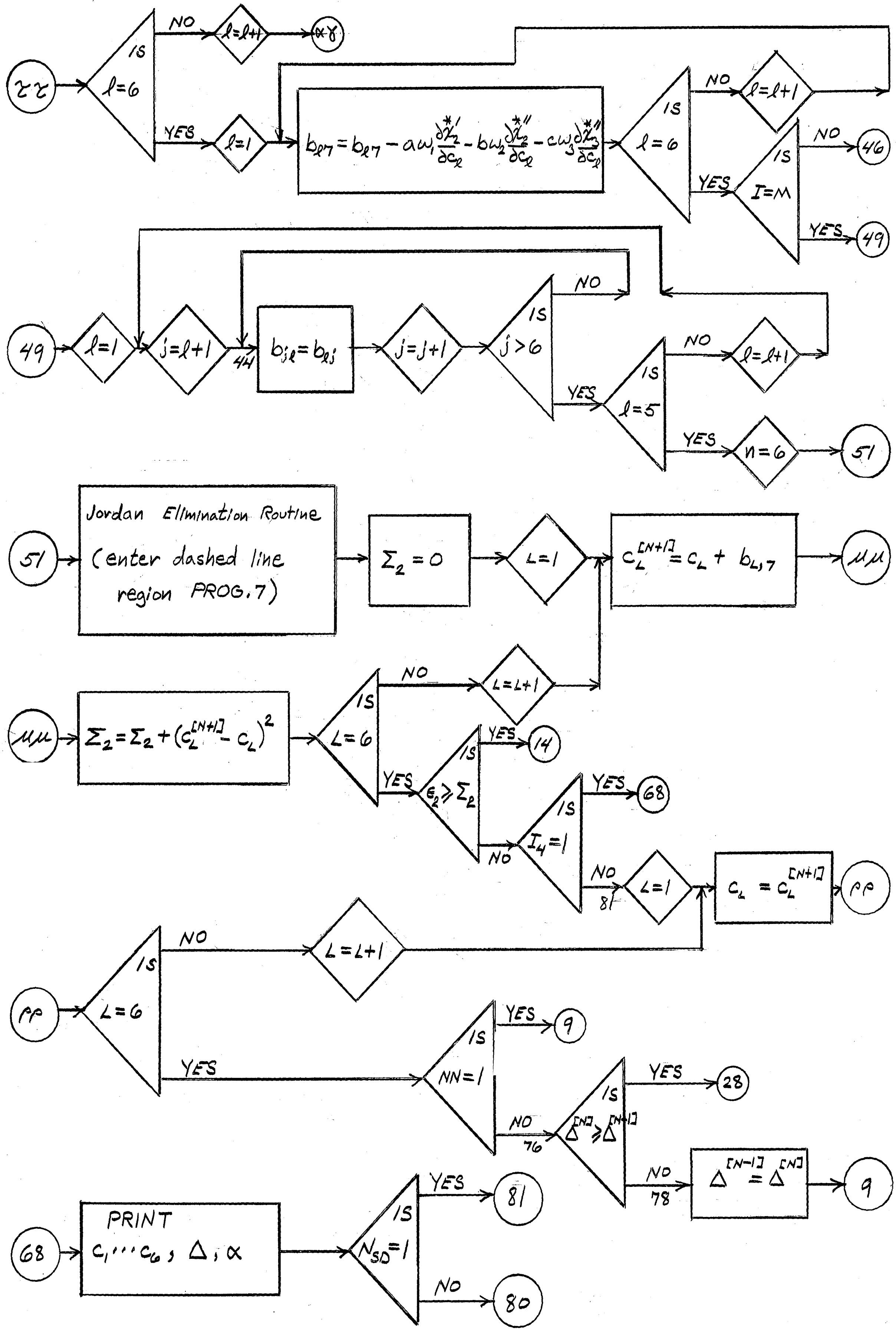

γγ
IS
$L=6$
NO
$L=L+1$
δδ
YES
IS
$\epsilon_1 \geq \Sigma_1$
YES
14
NO
37


37
IS
$I_4=1$
YES
68
$L=1$
80
$C_L^{[N-1]} = C_L$
$C_L = C_L^{[N+1]}$
$D_L^{[N-1]} = D_L$
IS
$L=6$
NO
$L=L+1$
YES
$\Delta^{[N-1]} = \Delta$
$N=N+1$
9


14
PRINT
c_1 thru c_6, Δ, N, NN
38
$i_B = 4(M-1)+1$
$i_1=1$
$\overset{*}{x}{}'_1 = T_{i_1}$
$\overset{*}{x}{}'_2 = T_{(i_1+1)}$
$\overset{*}{x}{}''_1 = T_{(i_1+2)}$
$\overset{*}{x}{}''_2 = T_{(i_1+3)}$
$\overset{*}{x}{}'_3 = 1 - \overset{*}{x}{}'_1 - \overset{*}{x}{}'_2$
$\overset{*}{x}{}''_3 = 1 - \overset{*}{x}{}''_1 - \overset{*}{x}{}''_2$
σσ


σσ
PRINT
$\overset{*}{x}{}'_1, \overset{*}{x}{}'_2, \overset{*}{x}{}'_3, \overset{*}{x}{}''_1, \overset{*}{x}{}''_2, \overset{*}{x}{}''_3$
IS
$i_1 = i_B$
NO
$i_1=i_1+4$
YES
IS
$N_{SO}=1$
NO
$N_{SO}=1$
9
YES
28


48
$l=1$
$J=l$
αγ
60
$b_{lJ} = b_{lJ} + \omega_1 \frac{\partial \overset{*}{x}{}'_2}{\partial c_l} \frac{\partial \overset{*}{x}{}'_2}{\partial c_J} + \omega_2 \frac{\partial \overset{*}{x}{}''_2}{\partial c_l} \frac{\partial \overset{*}{x}{}''_2}{\partial c_J} + \omega_3 \frac{\partial \overset{*}{x}{}''_3}{\partial c_l} \frac{\partial \overset{*}{x}{}''_3}{\partial c_J}$
$J=J+1$
IS
$J>6$
NO
YES
ZZ


γγ
IS $l=6$
NO
$l=l+1$
αγ
YES
$l=1$
$b_{l7}=b_{l7}-a\omega_1\frac{\partial\chi_2^{*\prime}}{\partial c_l}-b\omega_2\frac{\partial\chi_2^{*\prime\prime}}{\partial c_l}-c\omega_3\frac{\partial\chi_3^{*\prime\prime}}{\partial c_l}$
IS $l=6$
NO
$l=l+1$
YES
IS $I=M$
NO
46
YES
49
49
$l=1$
$j=l+1$
44
$b_{jl}=b_{lj}$
$j=j+1$
IS $j>6$
NO
YES
IS $l=5$
NO
$l=l+1$
YES
$n=6$
51
51
Jordan Elimination Routine (enter dashed line region PROG.7)
$\Sigma_2=0$
$L=1$
$c_L^{[N+1]}=c_L+b_{L,7}$
μμ
μμ
$\Sigma_2=\Sigma_2+(c_L^{[N+1]}-c_L)^2$
IS $L=6$
NO
$L=L+1$
YES
IS $\epsilon_2\geqslant\Sigma_2$
YES
14
NO
IS $I_4=1$
YES
68
NO
81
$L=1$
$c_L=c_L^{[N+1]}$
ρρ
ρρ
IS $L=6$
NO
$L=L+1$
YES
IS $NN=1$
YES
9
NO
76
IS $\Delta^{[N]}\geqslant\Delta^{[N+1]}$
YES
28
NO
78
$\Delta^{[N-1]}=\Delta^{[N]}$
9
68
PRINT $c_1\cdots c_6$, Δ, α
IS $N_{SD}=1$
YES
81
NO
80

Correspondence of Variables:*

(same as Program 6 for B_{12} through C_{31}, $\overset{*}{x}_1'$, $\overset{*}{x}_2'$, $\overset{*}{x}_3'$, $\overset{*}{x}_1''$, $\overset{*}{x}_2''$, $\overset{*}{x}_3''$.

$\mathcal{E}$ = Y

ϵ_1 = Z

ϵ_2 = EPS

$\Delta x_3'$ = X

α = Z20

ϕ_1 = Z17

ϕ_2 = Z18

ϕ_3 = Z19

$\Delta \overset{*}{x}_1'$ = X21

$\Delta \overset{*}{x}_2'$ = X22

$\Delta \overset{*}{x}_1''$ = X23

$\Delta \overset{*}{x}_2''$ = X24

Σ = Z13

f_j = F(J)

$\overset{*}{x}_1'^{[n-1]}$ = X17

$\overset{*}{x}_2'^{[n-1]}$ = X18

$\overset{*}{x}_1''^{[n-1]}$ = X19

$\overset{*}{x}_2''^{[n-1]}$ = X20

x_3' = X28

x_1' = X1

x_2' = X2

x_3' = X3

x_1'' = X5

x_2'' = X6

x_3'' = X7

$\Delta \overset{*}{x}_3'$ = X26

Σ_1, Σ_2 = Z11

$D_\ell^{[n-1]}$ = DL(L)

g_j = G(J)

ρ = X27

$\frac{\partial \overset{*}{\mathcal{F}}}{\partial x_2'}$ = C7

$\frac{\partial \overset{*}{\mathcal{G}}}{\partial x_2'}$ = C8

$\frac{\partial \overset{*}{\mathcal{H}}}{\partial x_2'}$ = C9

$\frac{\partial \overset{*}{\mathcal{F}}}{\partial x_2''}$ = C10

$\frac{\partial \overset{*}{\mathcal{G}}}{\partial x_2''}$ = C11

$\frac{\partial \overset{*}{\mathcal{H}}}{\partial x_2''}$ = C12

$\frac{\partial \overset{*}{\mathcal{F}}}{\partial x_3''}$ = C13

$c_\ell^{[n-1]}$ = CL(L)

h_j = H(J)

$\frac{\partial \overset{*}{\mathcal{G}}}{\partial x_3''}$ = C14

$\frac{\partial \overset{*}{\mathcal{H}}}{\partial x_3''}$ = C15

$\mathcal{J}$ = Y10

a = Z4

b = Z5

c = Z6

Δ = DEL

$\Delta^{[n-1]}$ = DELL

$\frac{\partial \overset{*}{x}_2'}{\partial c_j}$ = P2(J)

$\frac{\partial \overset{*}{x}_2''}{\partial c_j}$ = PB2(J)

$\frac{\partial \overset{*}{x}_3''}{\partial c_j}$ = PB3(J)

$c_\ell^{[n+1]}$ = CN(L)

Input:

1. C(1), C(2), C(3), C(4), C(5), C(6) equal to initial guesses of B_{12}, B_{23}, B_{31}, C_{12}, C_{23}, C_{31}.

2. Y $\equiv \mathcal{E}$ which is greater than $\sum_{i=1}^{3} \left| \log_{10} x_i'/x_i'' - \phi_i \right|$ when Equations (3.10), (3.11), (3.12) are solved.

---

*Those cases where correspondence is obvious are not included.

3. Z ≡ ϵ_1 which is greater than $\sum_{l=1}^{6}\left(C_l^{[n]} - C_l^{[n-1]}\right)^2$ when the program leaves the steepest descent routine to begin the truncated Taylor series routine.

4. EPS ≡ ϵ_2 which is greater than $\sum_{l=1}^{6}\left(C_l^{[n]} - C_l^{[n-1]}\right)^2$ when the minimum Δ has been reached by the truncated Taylor series method.

5. E1, E2 = e_1, e_2 in the expression $\left| e_2 + e_1 (\cos)^3 \right|$.

6. X = Δx_3, should be less than 0.01 and may be as low as 0.0005 in some cases to insure convergence.

7. Z20 = α ; should always be negative, -0.2 say.

8. M; the number of tie lines for a given system.

9. NSD; if set equal to 1, causes the steepest descent method to be skipped - uses the truncated Taylor series method only.

10. I2; if set equal to 1, causes printing of Y1, Y2, Y3, Y5, Y6, Y7 equal $x_1^{*\prime}$, $x_2^{*\prime}$, $x_3^{*\prime}$, $x_1^{*\prime\prime}$, $x_2^{*\prime\prime}$, $x_3^{*\prime\prime}$, corresponding to every experimental tie line, for every trial of C(1) through C(6).

11. I3; if set equal to 1, causes printing of C7 - C15; F(J), G(J), H(J), P2(J), PB2(J), PB3(J), D(J), (J = 1 through 6); DEL.

12. I4; if set equal to 1, causes printing of C(1) through C(6), DEL, Z20 for every trial of the coefficients.

13. I5; if set equal to 1 causes program to read in new data immediately after printing information caused by setting I3 = 1.

14. A; solution routine divergence control constant. Set equal one or greater.

15. x_1', x_2', x_1'', x_2'', w_1, w_2, w_3, are read in as Y1, Y2, Y5, Y6, W1, W2, W3, in order of increasing x_3'.

Subroutines: LOGF (natural log), SQRTF. (square root), along with the normal FORTRAN, MICHIGAN EXECUTIVE SYSTEM routines.

Fortran II Compiler Statements:

```
      DIMENSION  CN(6), C(6), CL(6),F(6), G(6), H(6), DL(6), R(120),D(6)
     X, WT(120), T(120),P2(6), PB2(6), PB3(6), B(6,7)
 28   READ INPUT TAPE 7,47,(C(I),I=1,6),Y,Z,EP,E1,E2,X,Z20,M,NSD,I2,I3,
     X  I4,I5,A
 47  FORMAT (6E12.4/7E10.2/6I4,E10.2)
 27  FORMAT (1H1 6E12.4/7E10.2/6I4,E10.2)
      WRITE OUTPUT TAPE 6,27,(C(I),I=1,6),Y,Z,EP,E1,E2,X,Z20,M,NSD,I2,I3
     X  ,I4,I5  ,A
 17   L=1
      I=0
  1   READ INPUT TAPE 7,29,Y1,Y2,Y5,Y6,W1,W2,W3
      WRITE OUTPUT TAPE 6,69,Y1,Y2,Y5,Y6,W1,W2,W3
 29  FORMAT( 4E12.4,3F6.0 )
 69  FORMAT (1H  4E12.4,3F6.0)
      R(L)=Y1
      R(L+1)=Y2
      R(L+2)=Y5
      R(L+3)=Y6
      WT( L)=W1
      WT(L+1)=W2
      WT(L+2)=W3
      I=I+1
      L=L+4
      IF(I-M) 1,30,30
 30   N=1
      NN=0
  9   L=1
      I=1
      I1=1
      K=1
      D(1)=0.
      D(2)=0.
      D(3)=0.
      D(4)=0.
      D(5)=0.
      D(6)=0.
      DEL=0.
      DO 66 JI=1,7
      DO 65 KI=1,6
 65   B(KI,JI)=0.
 66   CONTINUE
      Y1=R(1)
      Y2=R(2)
      Y5=R(3)
      Y6=R(4)
      Y3=1.-Y2-Y1
      Y7=1.-Y6-Y5
 23   X1=R(L)
      X2=R(L+1)
      X5=R(L+2)
      X6=R(L+3)
      X7=1.-X5-X6
      X3=1.-X1-X2
      W1=WT(L)
      W2=WT(L+1)
      W3=WT(L+2)
      J=0
      E=0.43429448
      L=L+4
 19   Y8=1.
```

Fortran II Compiler Statements: (Cont'd)

```
   C27=1.-Y7
 3 C16=1.-Y1
   C17=1.-Y2
   C18=1.-Y5
   C19=1.-Y6
   C20=2.*Y1
   C21=2.*Y2
   C22=2.*Y3
   C23=2.*Y5
   C24=2.*Y6
   C25=2.*Y7
   Y10=Y2-Y1
   X10=Y6-Y5
   Z10=Y5-Y7
   F(1)=Y6*C18-Y2*C16
   F(2)=Y2*Y3-Y6*Y7
   F(3)=Y7*C18-Y3*C16
   F(4)=Y6*(C23*(X10+1.)-Y6)-Y2*(C20*(Y2+C16)-Y2)
   F(5)=C24*Y7*(Y7-Y6)-C21*Y3*(Y3-Y2)
   F(6)=Y7*(C23*(Z10-1.)+Y7)-Y3*(C20*(-Y3-C16)+Y3)
   G(1)=Y5*C19-Y1*C17
   G(2)=Y7*C19-Y3*C17
   G(3)=Y1*Y3-Y5*Y7
   G(4)=Y5*(C24*(X10-1.)+Y5)-Y1*(C21*(Y10-1.)+Y1)
   G(5)=Y7*(C24*(C19+Y7)-Y7)-Y3*(C21*(C17+Y3)-Y3)
   G(6)=C23*Y7*Z10-C20*Y3*(Y1-Y3)
   H(1)=Y1*Y2-Y5*Y6
   H(2)=Y6*C27-Y2*C26
   H(3)=Y5*C27-Y1*C26
   H(4)=C23*Y6*X10-C20*Y2*Y10
   H(5)=Y6*(C25*(-C27-Y6)+Y6)+Y2*(C22*(C26+Y2)-Y2)
   H(6)=Y5*(C25*(Z10+1.)-Y5)-Y1*(C22*(C26+Y1)-Y1)
   IF(Y8-Y)4,4,31
31 Z17=C(1)*F(1)+C(2)*F(2)+C(3)*F(3)+C(4)*F(4)+C(5)*F(5)+C(6)*F(6)
   Z18=C(1)*G(1)+C(2)*G(2)+C(3)*G(3)+C(4)*G(4)+C(5)*G(5)+C(6)*G(6)
   Z19=C(1)*H(1)+C(2)*H(2)+C(3)*H(3)+C(4)*H(4)+C(5)*H(5)+C(6)*H(6)
   D8=E*LOGF(Y1/Y5)
   D9=E*LOGF(Y2/Y6)
   D10=E*LOGF(Y3/Y7)
   Y7=((Y3/(10.**Z19))+Y7)/2.
   X8=10.**Z17
   X9=10.**Z18
   C26=1.-Y3
   C27=1.-Y7
   Y6=(C26-C27*X8)/(X9-X8)
   Y5=1.-Y6-Y7
   Y1=X8*Y5
   Y2=X9*Y6
   Y8=ABSF(D8-Z17)+ABSF(D9-Z18)+ABSF(D10-Z19)
   IF (Y8-A ) 32,16,16
16 IF (N-1) 28,28,11
32 GO TO 3
 4 IF (K-1)33,21,33
33 X21=Y1-X17
   X22=Y2-X18
   X23=Y5-X19
   X24=Y6-X20
   X17=Y1
   X18=Y2
```

Fortran II Compiler Statements: (Cont'd)

```
   X19=Y5
   X20=Y6
   X28=X+Y3
   IF(X28-X3)26,22,22
26 Y1=X17+X21
   Y3=X28
   Y2=1.-Y1-Y3
   Y5=X19+X23
   Y6=X20+X24
   Y7=1.-Y5-Y6
   IF ( J ) 23,19,23
22 X26=X3-Y3
   X27=X26/X
   Y1=Y1+X27*X21
   Y2=Y2+X27*X22
   Y5=Y5+X27*X23
   Y6=Y6+X27*X24
   Y3=X3
   Y7=1.-Y5-Y6
   K=1
   GO TO 19
21 C16=C(1)-C(2)
   C18=C(3)-C(2)
   X9=0.43429448
   Y4=X9/Y5
   C7=(-X9/Y1)+C(1)*(Y10+1.)+Y3*C18+2.*(C(4)*((-Y10)*(Y10+1.)
  X+(C20-1.)*Y2)+Y3*(C(5)*(-C21+Y3)+C(6)*(-C20+Y3+1.)))
   C8=Y4-C(1)*(X10+1.)-Y7*C18-2.*(C(4)*((-X10)*(X10+1.)+(C23-1.)*Y6)
  X+Y7*(C(5)*(-C24+Y7)+C(6)*(Y7-C23+1.)))
   C9=Y4-Y6*C16-C(3)*(1.-Z10)-2.*(Y6*(C(4)*(C23-Y6-1.)+C(5)*(C25
  X-Y6))+C(6)*(Z10*(Z10-1.)+Y7*(1.-C23)))
   C10=X9/Y2+C(1)*(Y10-1.)+Y3*C18+2.*(C(4)*((-Y10)*(Y10-1.)+Y1
  X*(C21-1.))+Y3*(C(5)*(Y3-C21+1.)+C(6)*(Y3-C20)))
   C11=(-X9/Y6)-C(1)*(X10-1.)-Y7*C18-2.*(C(4)*((-X10)*(X10-1.)+Y5*(
  XC24-1.))+Y7*(C(5)*(Y7-C24+1.)+C(6)*(Y7-C23)))
   C12=C16*C19+C(3)*Z10-2.*(C(4)*(Y5*(-C19)-Y6*(X10-1.))+C(5)*(Y7
  X*(-C19)+Y6*(Y7+C19))+C(6)*(Z10*Z10-C23*Y7))
   C13=C(1)*Y10-C18*C26+2.*(C(4)*(C20*Y2-Y10*Y10)+C(5)*(Y2
  X*C26+Y3*(-Y2-C26))+C(6)*(Y1*C26-Y3*(Y1+C26)))
   C14=C(1)*(-X10)+C18*C27-2.*(C(4)*(C23*Y6-X10*X10)+C(5)*(Y6*C27
  X-Y7*(C27+Y6))+C(6)*(Y5*C27-Y7*(Y5+C27)))
   C15=(-X9/Y7)-Y6*C16+C(3)*(Z10+1.)-2.*(Y6*(C(4)*(C23-Y6)+C(5)*
  X(C25-Y6-1.))+C(6)*(Z10*(Z10+1.)+Y5*(1.-C25)))
   C16=C9*C11-C12*C8
   C17=C12*C14-C11*C15
   C18=C15*C8-C14*C9
   C19=C12*C7-C10*C9
   C20=C10*C15-C13*C12
   C21=C9*C13-C7*C15
   C22=C10*C8-C7*C11
   C23=C13*C11-C10*C14
   C24=C14*C7-C13*C8
   Y10=(C15*C22)+C9*C23+C12*C24
   IF (ABSF(Y10)-0.000001) 39,39,72
72 Z4=Y2-X2
   Z5=Y6-X6
   Z6=Y7-X7
   DEL=DEL+Z4*Z4*W1+Z5*Z5*W2+Z6*Z6*W3
   DO 5 J=1,6
```

Fortran II Compiler Statements: (Cont'd)

```
      P2(J)=(H(J)*C16+F(J)*C17+G(J)*C18)/Y10
      PB2(J)=(H(J)*C19+F(J)*C20+G(J)*C21)/Y10
      PB3(J)=(H(J)*C22+F(J)*C23+G(J)*C24)/Y10
    5 D(J)=D(J)+2.*(Z4*P2(J)*W1+Z5*PB2(J)*W2+Z6*PB3(J)*W3)
      T(I1)=Y1
      T(I1+1)=Y2
      T(I1+2)=Y5
      T(I1+3)=Y6
      I1=I1+4
      IF(I2-1) 41,39,41
   39 WRITE OUTPUT TAPE 6,40,Y1,Y2,Y3,Y5,Y6,Y7,N,NN,Y10
   40 FORMAT (4H Y1=E11.4,4H Y2=E11.4,4H Y3=E11.4,4H Y5=E11.4,
     X 4H Y6=E11.4,4H Y7=E11.4,4H  N=I3,4H NN=I3,5H Y10=E11.4 )
   41 IF (I3-1) 57,42,57
   42 WRITE OUTPUT TAPE 6,43,C7,C8,C9,C10,C11,C12,C13,C14,
     X  C15,(F(IA),IA=1,6),(G(IA),IA=1,6),(H(IA),IA=1,6)
     X ,(P2(IA),IA=1,6),(PB2(IA),IA=1,6),   (PB3(IA),IA=1,6)
     X  ,(D(IA),IA=1,6),DEL
   43 FORMAT (1H  9E12.5)
      IF (I5-1) 57,28,57
   57 IF (NSD-1)18,48,18
   18 IF (I-M)46,24,46
   46 K=0
      J=1
      IF (I-1) 34,25,34
   34 I=I+1
      GO TO 26
   25 X17=Y1
      X18=Y2
      X19=Y5
      X20=Y6
      Y3=X+Y3
      Y2=1.-Y1-Y3
      I=2
      GO TO 23
   24 Z13=0.
      DO 6 L=1,6
      Z14=(1.+C(L)*C(L))*D(L)
      Z13=Z13+Z14*Z14
    6 D(L)=Z14
      Z13=SQRTF(Z13)
      DO 7 L=1,6
    7 D(L)=D(L)/Z13
      IF (N-1) 35,8,35
   35 IF (DEL-DELL) 36,11,11
   11 Z20=Z20/4.
      DO 10 L=1,6
   10 C(L)=CL(L) +Z20*DL(L)
      GO TO 9
   36 COS=D(1)*DL(1)+D(2)*DL(2)+D(3)*DL(3)+D(4)*DL(4)+D(5)*DL(5)+D(6)
     X  *DL(6)
   12 Z20=Z20*ABSF(E2+E1*COS*COS*COS)
    8 Z11=0.
      DO 13 L=1,6
      CN(L)=C(L)+Z20*D(L)
      Z10=CN(L)-C(L)
   13 Z11=Z11+Z10*Z10
      IF (Z-Z11) 37,14,14
   37 IF(I4-1) 80,68,80
```

Fortran II Compiler Statements: (Cont'd)

```
80 DO 15L=1,6
   CL(L)=C(L)
   C(L)=CN(L)
15 DL(L)=D(L)
   DELL=DEL
   N=N+1
   GO TO 9
14 WRITE OUTPUT TAPE 6,38,(C(IA),IA=1,6),DEL,N,NN
38 FORMAT (4H C1=E11.4,4H C2=E11.4,4H C3=E11.4,4H C4=E11.4,
  X 4H C5=E11.4,4H C6=E11.4,5H DEL=E11.4,3H N=I3,4H NN=I3)
   IB=4*(M-1)+1
   DO 70 I1=1,IB,4
   Y1=T(I1)
   Y2=T(I1+1)
   Y5=T(I1+2)
   Y6=T(I1+3)
   Y3=1.-Y1-Y2
   Y7=1.-Y5-Y6
45 FORMAT(4H Y1=E12.4,4H Y2=E12.4,4H Y3=E12.4,4H Y5=E12.4,
  X   4H Y6=E12.4,4H Y7=E12.4)
70 WRITE OUTPUT TAPE 6,45,Y1,Y2,Y3,Y5,Y6,Y7
   IF (NSD-1) 56,28,28
56 NSD=1
   GO TO 9
48 DO 61 KI=1,6
   J=KI
60 B(KI,J)=B(KI,J)+P2(KI)*P2(J)*W1+PB2(KI)*PB2(J)*W2+PB3(KI)*PB3(J)*
  X   W3
   J=J+1
   IF (J-6) 60,60,61
61 CONTINUE
   DO 62 KI=1,6
62 B(KI,7)=B(KI,7)-Z4*P2(KI)*W1-Z5*PB2(KI)*W2-Z6*PB3(KI)*W3
   IF (I-M) 46,49,46
49 DO 63 KI=1,5
   J=KI+1
44 B(J,KI)=B(KI,J)
   J=J+1
   IF (J-6) 44,44,63
63 CONTINUE
   DO 50  KI=1,6
   JI=7
51 B(KI,JI)=B(KI,JI)/B(KI,KI)
   JI=JI-1
   IF (JI-KI) 64,51,51
64 DO 50 II=1,6
   IF (II-KI) 53,50,53
53 JI=7
52 B(II,JI)=B(II,JI)-B(II,KI)*B(KI,JI)
   JI=JI-1
   IF (JI-KI) 50,52,52
50 CONTINUE
   Z11=0.
   DO 54 L=1,6
   CN(L)=C(L)+B(L,7)
   Z10=CN(L)-C(L)
54 Z11=Z11+Z10*Z10
   NN=NN+1
   IF (EP-Z11) 55,14,14
```

Fortran II Compiler Statements: (Cont'd)

```
55 IF(I4-1) 81,68,81
81 DO 71 L=1,6
71 C(L)=CN(L)
   IF (NN-1) 76,9,76
76 IF (DEL-DELL) 78,28,28
78 DELL=DEL
   GO TO 9
68 WRITE OUTPUT TAPE 6, 75,(C(IZ), IZ=1,6),DEL,Z20
75 FORMAT (4H C1=E11.4,4H C2=E11.4,4H C3=E11.4,4H C4=E11.4,
  X   4H C5=E11.4,4H C6=E11.4,5H DEL=E11.4,5H Z20=E9.2)
   IF(NSD-1)80,81,80
```

APPENDIX C

TABLES OF CALCULATED VALUES APPEARING IN FIGURES

For readers desiring to reproduce calculated plots appearing in this thesis with high accurracy, the following tables of calculated values follow. Concentrations (x's) are in mol fraction.

TABLE VIII*

LINES OF CONSTANT $\frac{\Delta G_M}{2.303RT}$ FOR THE SYSTEM

$B_{12} = 1.3$, $B_{23} = 0$, $B_{31} = 0.5$, $C_{12} = 0$, $C_{23} = 0$, $C_{31} = 0$

$\frac{\Delta G_M}{2.303RT}$ = -0.133		-0.20		-0.24		-0.28		-0.32	
X_1	X_2	X_1	X_2	X_1	X_2	X_1	X_2	X_1	X_2
0.100	0.822	0.100	0.750	0.100	0.710	0.100	0.636	0.100	0.520
0.200	0.720	0.200	0.647	0.200	0.590	0.200	0.518	0.200	0.360
0.300	0.610	0.300	0.540	0.300	0.476	0.300	0.373	0.200	0.290
0.400	0.493	0.400	0.416	0.400	0.340	0.300	0.150	0.100	0.300
0.500	0.386	0.500	0.311	0.500	0.210	0.200	0.155		
0.600	0.290	0.600	0.185	0.500	0.020	0.100	0.185		
0.700	0.195	0.650	0.070	0.300	0.057				
0.800	0.100			0.200	0.084				
				0.100	0.121				

*Reference Figure 15.

TABLE IX*

FICTITIOUS SYSTEMS $B_{12} = 1.3$, $B_{23} = C_{12} = C_{23} = C_{31} = 0$

$B_{31} = -2$

X_1'	X_2'	X_1''	X_2''
0.920	0.069	0.070	0.929
0.779	0.059	0.049	0.941
0.595	0.071	0.033	0.907
0.422	0.107	0.033	0.787
0.290	0.167	0.049	0.626
0.218	0.223	0.070	0.515
0.150	0.309	0.100	0.410

$B_{31} = -1$

X_1'	X_2'	X_1''	X_2''
0.873	0.076	0.069	0.922
0.806	0.083	0.067	0.909
0.712	0.096	0.066	0.876
0.553	0.135	0.076	0.783
0.491	0.157	0.082	0.731
0.416	0.193	0.097	0.657

$B_{31} = 0$

X_1'	X_2'	X_1''	X_2''
0.865	0.083	0.083	0.865
0.761	0.107	0.107	0.761
0.676	0.133	0.133	0.676
0.579	0.170	0.170	0.579
0.449	0.239	0.239	0.449
0.378	0.290	0.290	0.378

$B_{31} = 0.5$

X_1'	X_2'	X_1''	X_2''
0.871	0.078	0.096	0.781
0.777	0.092	0.146	0.560
0.703	0.106	0.192	0.473
0.624	0.125	0.250	0.373
0.535	0.154	0.329	0.282
0.487	0.171	0.403	0.221

$B_{31} = 0.87$

X_1'	X_2'	X_1''	X_2''
0.885	0.063	0.101	0.656
0.777	0.041	0.202	0.229
0.728	0.031	0.257	0.126
0.679	0.020	0.318	0.059
0.628	0.011	0.382	0.022
0.604	0.005	0.421	0.009

$B_{31} = 1.0$

X_1'	X_2'	X_1''	X_2''
0.925	0.075	0.075	0.925
0.895	0.054	0.099	0.584
0.862	0.037	0.130	0.326
0.836	0.022	0.158	0.170
0.817	0.011	0.180	0.077
0.805	0.004	0.195	0.025

*Reference Figures 16-21.

TABLE X*

FICTITIOUS SYSTEMS $B_{12} = 1.3$, $B_{31} = 1.0$, $C_{12} = C_{23} = C_{31} = 0$

$B_{23} = 0.87$				$B_{23} = 1.0$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.905	0.075	0.075	0.895	0.905	0.075	0.075	0.905
0.776	0.102	0.121	0.700	0.775	0.105	0.105	0.775
0.686	0.120	0.310	0.295	0.596	0.160	0.160	0.596
0.666	0.104	0.320	0.204	0.596	0.160	0.325	0.325
0.689	0.076	0.285	0.140	0.585	0.140	0.415	0.190
0.732	0.045	0.250	0.080	0.640	0.096	0.340	0.152
0.780	0.010	0.214	0.018	0.734	0.040	0.242	0.062
				0.780	0.010	0.210	0.016

*Reference Figures 22-23.

TABLE XI*

FICTITIOUS SYSTEMS $B_{12} = 1.3$, $B_{23} = B_{31} = 0.5$, $C_{12} = 0.2$

$C_{23} = C_{31} = 0.3$				$C_{23} = C_{31} = 0.5$			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.935	0.042	0.110	0.882	0.935	0.045	0.110	0.885
0.816	0.061	0.120	0.815	0.815	0.060	0.105	0.858
0.725	0.085	0.145	0.710	0.655	0.110	0.183	0.599
0.634	0.116	0.224	0.494	0.550	0.133	0.285	0.314
0.543	0.145	0.325	0.301	0.494	0.130	0.257	0.258
0.492	0.165	0.406	0.229	0.480	0.085	0.180	0.191
				0.470	0.035	0.136	0.092
				0.420	0.000	0.132	0.000

*Reference Figures 24-25

TABLE XII*

CRITICAL VALUES OF THE B AND C COEFFICIENTS

x_1	B^c	C^c	x_1	B^c	C^c	x_1	B^c	C^c
0.02	- 249.40	- 90.44	0.34	0.747	- 0.229	0.66	0.747	0.229
0.04	- 56.67	- 22.58	0.36	0.782	- 0.181	0.68	0.701	0.276
0.06	- 22.58	- 10.12	0.38	0.809	- 0.156	0.70	0.640	0.328
0.08	- 11.19	- 5.61	0.40	0.829	- 0.125	0.72	0.560	0.392
0.10	- 6.17	- 3.57	0.42	0.845	- 0.097	0.74	0.453	0.469
0.12	- 3.58	- 2.46						
0.14	- 2.08	- 1.80	0.44	0.856	- 0.071	0.76	0.308	0.565
0.16	- 1.16	- 1.36	0.46	0.863	- 0.047	0.78	0.109	0.688
0.18	- 0.570	- 1.062	0.48	0.867	- 0.022	0.80	- 0.170	0.848
0.20	- 0.170	- 0.848	0.50	0.869	0.000	0.82	- 0.570	1.062
0.22	0.109	- 0.688	0.52	0.867	0.022	0.84	- 1.16	1.36
0.24	0.308	- 0.565	0.54	0.863	0.047	0.86	- 2.08	1.80
0.26	0.453	0.469	0.56	0.856	0.071	0.88	- 3.58	2.46
0.28	0.560	0.392	0.58	0.845	0.097	0.90	- 6.17	3.57
0.30	0.640	0.328	0.60	0.829	0.125	0.92	- 11.19	5.61
0.32	0.701	- 0.276	0.62	0.809	0.156	0.94	- 22.58	10.12
			0.64	0.782	0.181	0.96	- 56.67	22.58
						0.98	- 249.40	90.44

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*Reference Figures 26-27.

TABLE XIII*

EXAMPLES OF FITS OBTAINED USING APPROXIMATE LINEARIZATIONS**

H_2O (1) - ETHYL ACETATE (2) - i-Propanol (3) 20°C

x_1'	x_2'	x_1''	x_2''
0.9829	0.0161	0.1147	0.8807
0.9639	0.0191	0.1958	0.7335
0.9342	0.0248	0.3639	0.4880
0.9027	0.0323	0.5412	0.2785
0.8683	0.0427	0.6850	0.1470
0.8502	0.0487	0.7594	0.0948

H_2O (1) - ETHYL ACETATE (2) - Acetone (3) 31°C

x_1'	x_2'	x_1''	x_2''
0.8083	0.1044	0.0638	0.8727
0.6669	0.1557	0.0591	0.8955
0.5792	0.1835	0.0591	0.9055
0.5052	0.1975	0.0620	0.9059
0.4541	0.1886	0.0647	0.9043
0.3630	0.1697	0.0677	0.9018

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* Reference Figure 28.

* Calculated points only, mole fraction.

TABLE XIV*

B_{ij} - C_{ij} FIT OF BINARY X-Y DATA**

Ethanol (1) - H_2O (2) 74.79°C		Ethanol (1) - Ethyl Acetate (2) 1 atm		H_2O (1) - Dioxane (2) 25°C		Benzene (1) - Dioxane (2) 25°C	
0.050	0.329	0.050	0.0895	0.050	0.166	0.050	0.140
0.100	0.451	0.100	0.160	0.100	0.253	0.100	0.255
0.150	0.513	0.150	0.217	0.150	0.303	0.150	0.350
0.200	0.549	0.200	0.266	0.200	0.333	0.200	0.430
0.250	0.573	0.250	0.308	0.250	0.352	0.250	0.498
0.300	0.591	0.300	0.345	0.300	0.364	0.300	0.557
0.400	0.620	0.400	0.409	0.400	0.377	0.400	0.654
0.500	0.651	0.500	0.468	0.500	0.385	0.500	0.730
0.600	0.691	0.600	0.528	0.600	0.397	0.600	0.794
0.700	0.744	0.700	0.595	0.700	0.421	0.700	0.849
0.800	0.814	0.800	0.680	0.800	0.474	0.800	0.899
0.900	0.901	0.900	0.794	0.900	0.599	0.900	0.949

*Reference Figure 29.

TABLE XV*

COMPARISON OF FITS OBTAINED USING COEFFICIENTS DETERMINED FROM BINARY VERSUS TERNARY DATA

H_2O (1) - Ethyl Acetate (2) - Ethanol (3) 70°C

Experimental				Calc. from Binary				Calc. from Ternary			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.9760	0.0150	0.2520	0.7330	0.9734	0.0146	0.2296	0.7447	0.9644	0.0186	0.2805	0.6793
0.9640	0.0170	0.2980	0.6580	0.9234	0.0186	0.2409	0.6369	0.9448	0.0232	0.3559	0.5667
0.9400	0.0220	0.3940	0.5070	0.8701	0.0239	0.2612	0.5232	0.9169	0.0311	0.4501	0.4365
0.9170	0.0300	0.4650	0.4150	0.8151	0.0309	0.2928	0.4118	0.8861	0.0419	0.5241	0.3431
0.8990	0.0380	0.5230	0.3440	0.7701	0.0379	0.3278	0.3289	0.8600	0.0530	0.5715	0.2880
0.8840	0.0460	0.5550	0.3100	0.7282	0.0458	0.3674	0.2615	0.8301	0.0679	0.6168	0.2391
				0.6788	0.0572	0.4212	0.1961	0.8070	0.0810	0.6502	0.2056
				0.6199	0.0741	0.4999	0.1315	0.7797	0.0983	0.6903	0.1685

Benzene (1) - Water (2) - Dioxane (3) 25°C

Experimental				Calc. from Binary				Calc. from Ternary			
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
0.9500	0.0043	0.0002	0.9900	0.9602	0.00065	0.0016	0.9884	0.9386	0.00161	0.00358	0.9867
0.7890	0.0088	0.0003	0.9550	0.7235	0.00280	0.0019	0.9281	0.7568	0.00445	0.00374	0.9515
0.6860	0.0265	0.0003	0.9360	0.5179	0.00922	0.0023	0.8677	0.6747	0.00703	0.00385	0.9324
0.6170	0.0312	0.0006	0.9200	0.3583	0.02287	0.0026	0.8074	0.6137	0.00989	0.00397	0.9166
0.4600	0.0658	0.0010	0.8750	0.2380	0.04655	0.0030	0.7470	0.4660	0.02274	0.00437	0.8717
0.3690	0.0990	0.0022	0.8450	0.1491	0.08312	0.0035	0.6865	0.3857	0.03605	0.00472	0.8425
0.3220	0.1190	0.0027	0.8270	0.0865	0.1348	0.0041	0.6259	0.3409	0.04682	0.00496	0.8247
0.2900	0.1420	0.0031	0.8220	0.0640	0.1663	0.0045	0.5955	0.3298	0.04999	0.00503	0.8201
0.2382	0.1821	0.0064	0.7820	0.0468	0.2007	0.0049	0.5651	0.2433	0.08422	0.00565	0.7828
0.1388	0.3084	0.0130	0.7190	0.0340	0.2371	0.0053	0.5347	0.1059	0.2102	0.00681	0.7252
0.1054	0.3930	0.0209	0.6720	0.0209	0.2946	0.0062	0.4888	0.0439	0.3701	0.00752	0.6854

*Reference Figure 30.

TABLE XVI*

H_2O (1) - ETHYL ACETATE (2) - ALCOHOLS (3)

Methanol

Experimental				Calculated			
x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9564	0.0178	0.1446	0.8315	0.9569	0.0174	0.1433	0.8225
0.9268	0.0192	0.1721	0.7581	0.9232	0.0228	0.1759	0.7491
0.9030	0.0217	0.2151	0.6744	0.8968	0.0279	0.2045	0.6899
0.8763	0.0252	0.2273	0.6449	0.8667	0.0348	0.2380	0.6254
0.8192	0.0373	0.3173	0.5077	0.8028	0.0537	0.3069	0.5065
0.7579	0.0602	0.4022	0.3911	0.7386	0.0795	0.3730	0.4076
				0.6538	0.1262	0.4581	0.2997
				0.5795	0.1785	0.5492	0.2049

Ethanol

x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9652	0.0177	0.1520	0.8150	0.9635	0.0194	0.1585	0.8081
0.9471	0.0194	0.2062	0.7100	0.9428	0.0237	0.2164	0.7075
0.9311	0.0218	0.2547	0.6342	0.9252	0.0277	0.2728	0.6168
0.9092	0.0263	0.2945	0.5688	0.9019	0.0336	0.3341	0.5248
0.8855	0.0334	0.3962	0.4360	0.8785	0.0404	0.3823	0.4572
0.8472	0.0496	0.5219	0.3027	0.8448	0.0520	0.4386	0.3839
				0.8131	0.0649	0.4827	0.3308
				0.6988	0.1292	0.6317	0.1814

i-Propanol

x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9711	0.0177	0.1736	0.7755	0.9705	0.0183	0.1672	0.7828
0.9577	0.0196	0.2249	0.6867	0.9566	0.0207	0.2365	0.6708
0.9477	0.0218	0.2972	0.5775	0.9468	0.0227	0.2927	0.5883
0.9333	0.0244	0.3867	0.4586	0.9319	0.0258	0.3921	0.4555
0.9168	0.0289	0.5015	0.3241	0.9162	0.0295	0.5050	0.3219
0.8986	0.0362	0.6044	0.2245	0.9016	0.0332	0.5969	0.2267
				0.8820	0.0371	0.6791	0.1502
				0.8500	0.0495	0.7741	0.0872

i-Butanol

x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9736	0.0170	0.2027	0.7372	0.9770	0.0137	0.1988	0.7295
0.9674	0.0171	0.2844	0.5998	0.9702	0.0144	0.2748	0.6117
0.9598	0.0172	0.3760	0.4587	0.9619	0.0151	0.3881	0.4546
0.9510	0.0184	0.4916	0.3132	0.9535	0.0158	0.5078	0.3077
0.9454	0.0189	0.5698	0.2346	0.9481	0.0162	0.5765	0.2326
0.9307	0.0222	0.7117	0.1244	0.9360	0.0168	0.6882	0.1279
				0.9299	0.0171	0.7284	0.0966
				0.9195	0.0175	0.7790	0.0634

TABLE XVI* (CONT'D)

H_2O (1) - ETHYL ACETATE (2) - ALCOHOLS (3)

n-Propanol

Experimental				Calculated			
x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9710	0.0175	0.1728	0.7606	0.9679	0.0205	0.1620	0.7640
0.9612	0.0183	0.2749	0.5949	0.9574	0.0221	0.2736	0.5966
0.9545	0.0193	0.3635	0.4705	0.9508	0.0230	0.3743	0.4635
0.9448	0.0214	0.4844	0.3232	0.9423	0.0239	0.4893	0.3267
0.9363	0.0235	0.5662	0.2424	0.9353	0.0246	0.5598	0.2510
0.9114	0.0313	0.6830	0.1469	0.9164	0.0263	0.6882	0.1336
				0.9030	0.0280	0.7395	0.0958
				0.8912	0.0298	0.7748	0.0738

s-Butanol

x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9840	0.0150	0.1350	0.8600	0.9819	0.0171	0.1094	0.8749
0.9761	0.0160	0.2075	0.6750	0.9760	0.0161	0.2466	0.6150
0.9733	0.0152	0.3163	0.4974	0.9733	0.0153	0.3319	0.4803
0.9720	0.0146	0.4085	0.3572	0.9718	0.0148	0.3728	0.4205
0.9656	0.0121	0.4911	0.2457	0.9655	0.0122	0.5190	0.2310
0.9618	0.0097	0.5746	0.1434	0.9611	0.0104	0.5956	0.1486
0.9559	0.0061	0.6503	0.0571	0.9545	0.0075	0.6830	0.0707
0.9500	0.0001	0.7800	0.0020	0.9468	0.0042	0.7494	0.0252

i-Butanol

x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9840	0.0150	0.1350	0.8600	0.9761	0.0229	0.1770	0.8143
0.9789	0.0161	0.2484	0.6206	0.9724	0.0226	0.2624	0.6443
0.9782	0.0152	0.3279	0.4631	0.9720	0.0214	0.3343	0.4903
0.9760	0.0140	0.3708	0.3792	0.9736	0.0164	0.4173	0.3062
0.9756	0.0106	0.4249	0.2614	0.9756	0.0107	0.4840	0.1845
0.9760	0.0080	0.4574	0.1738	0.9764	0.0076	0.5230	0.1262
0.9776	0.0044	0.4766	0.0826	0.9768	0.0052	0.5566	0.0823
0.9780	0.0001	0.4500	0.0010	0.9772	0.0018	0.6064	0.0262

n-Butanol

x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9840	0.0150	0.1350	0.8600	0.9768	0.0222	0.1719	0.8181
0.9818	0.0138	0.2634	0.6049	0.9740	0.0216	0.2813	0.5987
0.9816	0.0127	0.3570	0.4327	0.9745	0.0198	0.3535	0.4358
0.9817	0.0116	0.4118	0.3420	0.9755	0.0177	0.3855	0.3601
0.9815	0.0091	0.4632	0.2427	0.9787	0.0119	0.4501	0.2230
0.9817	0.0074	0.4937	0.1578	0.9804	0.0087	0.4857	0.1602
0.9827	0.0039	0.5077	0.0758	0.9824	0.0042	0.5435	0.0748
0.9830	0.0005	0.5100	0.0010	0.9840	0.0000	0.6147	0.0000

*Reference Figures 31-38.

TABLE XVII*

$(H_2O)_8$ (1) - BENZENE (2) - ALCOHOLS (3)

Ethanol

Experimental				Calculated			
x_1'	x_2'	x_1''	x_2''	$\overset{*}{x}{}_1'$	$\overset{*}{x}{}_2'$	$\overset{*}{x}{}_1''$	$\overset{*}{x}{}_2''$
0.6311	0.0026	0.0007	0.9681	0.5737	0.0097	0.0003	0.9685
0.4214	0.0073	0.0017	0.9346	0.4345	0.0155	0.0003	0.9361
0.3259	0.0172	0.0024	0.8964	0.3329	0.0239	0.0002	0.8986
0.2708	0.0271	0.0043	0.8681	0.2794	0.0311	0.0003	0.8722
0.1934	0.0774	0.0060	0.8198	0.2062	0.0471	0.0003	0.8255
0.1450	0.1252	0.0090	0.7634	0.1437	0.0714	0.0003	0.7721
0.1114	0.1829	0.0128	0.7101	0.0995	0.1011	0.0004	0.7225
0.0906	0.2326	0.0176	0.6502	0.0614	0.1457	0.0006	0.6672
0.0835	0.2545	0.0190	0.6320	0.0518	0.1625	0.0007	0.6503
0.0598	0.3461	0.0327	0.5247	0.0144	0.2941	0.0013	0.5562

i-Propanol

x_1'	x_2'	x_1''	x_2''	$\overset{*}{x}{}_1'$	$\overset{*}{x}{}_2'$	$\overset{*}{x}{}_1''$	$\overset{*}{x}{}_2''$
0.9294	0.0040	0.0004	0.9892	0.9277	0.0057	0.0005	0.9933
0.8664	0.0051	0.0004	0.9802	0.8646	0.0068	0.0005	0.9836
0.8064	0.0061	0.0004	0.9699	0.8041	0.0084	0.0005	0.9696
0.7649	0.0070	0.0004	0.9571	0.7620	0.0099	0.0005	0.9560
0.7106	0.0078	0.0004	0.9368	0.7059	0.0125	0.0007	0.9308
0.6491	0.0089	0.0003	0.8870	0.6412	0.0168	0.0009	0.8835
0.6040	0.0097	0.0018	0.8112	0.5924	0.0213	0.0016	0.8164
0.5770	0.0102	0.0046	0.7515	0.5626	0.0246	0.0031	0.7419
0.5498	0.0105	0.0101	0.6725	0.5320	0.0283	0.0067	0.6399
0.5391	0.0108	0.0151	0.6214	0.5201	0.0298	0.0089	0.6020
0.5241	0.0120	0.0200	0.5635	0.5042	0.0320	0.0120	0.5581
0.5082	0.0132	0.0253	0.5154	0.4870	0.0344	0.0159	0.5165
0.4999	0.0144	0.0321	0.4708	0.4787	0.0356	0.0178	0.4983
0.4836	0.0168	0.0406	0.4337	0.4624	0.0381	0.0222	0.4645
0.4738	0.0218	0.0445	0.4175	0.4567	0.0390	0.0237	0.4539
				0.4012	0.0488	0.0413	0.3628
				0.2783	0.0817	0.1001	0.2175
				0.2159	0.1091	0.1500	0.1569

t-Butanol

x_1'	x_2'	x_1''	x_2''	$\overset{*}{x}{}_1'$	$\overset{*}{x}{}_2'$	$\overset{*}{x}{}_1''$	$\overset{*}{x}{}_2''$
0.9659	0.0031	0.0007	0.9924	0.9634	0.0056	0.00057	0.9958
0.9052	0.0039	0.0016	0.9758	0.9024	0.0067	0.00060	0.9832
0.8278	0.0046	0.0019	0.9276	0.8233	0.0091	0.00078	0.9458
0.7673	0.0054	0.0066	0.8046	0.7607	0.0120	0.00233	0.8089
0.7378	0.0061	0.0180	0.6605	0.7309	0.0131	0.00980	0.5762
0.7187	0.0064	0.0333	0.5345	0.7117	0.0134	0.01368	0.5046
0.7028	0.0068	0.0536	0.4245	0.6960	0.0136	0.01664	0.4590
0.6862	0.0074	0.0836	0.3138	0.6798	0.0137	0.01956	0.4191
0.6482	0.0092	0.1352	0.2050	0.6437	0.0137	0.02610	0.3453
0.5902	0.0160	0.2028	0.1333	0.5928	0.0134	0.03579	0.2643
0.5423	0.0236	0.2514	0.1048	0.5529	0.0130	0.04433	0.2127

TABLE XVII*(CONT'D)

$(H_2O)_8$ (1) - BENZENE (2) - ALCOHOLS (3)

n-Propanol

Experimental				Calculated			
x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.8624	0.0051	0.0016	0.9482	0.8596	0.0079	0.0008	0.9440
0.8201	0.0099	0.0048	0.8796	0.8208	0.0092	0.0010	0.9048
0.7978	0.0114	0.0042	0.8938	0.7992	0.0101	0.0014	0.8706
0.7720	0.0112	0.0073	0.8049	0.7720	0.0112	0.0023	0.8040
0.7057	0.0153	0.0273	0.5822	0.7071	0.0139	0.0096	0.5835
0.6656	0.0149	0.0439	0.4521	0.6650	0.0155	0.0168	0.4809
				0.5192	0.0208	0.0506	0.2620
				0.3528	0.0322	0.1174	0.1232
				0.2707	0.0443	0.1798	0.0756

i-Butanol

Experimental				Calculated			
x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9784	0.00365	0.00038	0.9899	0.9762	0.00585	0.00063	0.9724
0.9507	0.00505	0.00103	0.9610	0.9495	0.00629	0.00095	0.9152
0.9272	0.00481	0.00173	0.9054	0.9254	0.00663	0.00181	0.8175
0.9152	0.00460	0.00571	0.7861	0.9131	0.00672	0.00330	0.7134
0.9069	0.00353	0.01109	0.6792	0.9037	0.00668	0.00586	0.5976
0.9000	0.00316	0.01798	0.5674	0.8966	0.00654	0.00844	0.5132
0.8919	0.00245	0.02641	0.4445	0.8881	0.00628	0.01158	0.4307
0.8867	0.00227	0.03535	0.3391	0.8829	0.00606	0.01346	0.3880
0.8802	0.00191	0.04819	0.2355	0.8764	0.00575	0.01581	0.3401
0.8661	0.00069	0.06590	0.1155	0.8619	0.00488	0.02091	0.2505
0.8600	0.00010	0.10000	0.0020	0.8565	0.00450	0.02283	0.2212

n-Butanol

Experimental				Calculated			
x'_1	x'_2	x''_1	x''_2	$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9601	0.0036	0.0003	0.9687	0.9573	0.0064	0.0011	0.8948
0.9490	0.0036	0.0004	0.9489	0.9461	0.0065	0.0016	0.8438
0.9416	0.0036	0.0005	0.9332	0.9386	0.0066	0.0021	0.8000
0.9289	0.0053	0.0032	0.8478	0.9276	0.0066	0.0033	0.7148
0.9235	0.0053	0.0086	0.7295	0.9222	0.0066	0.0044	0.6624
0.9181	0.0053	0.0135	0.6471	0.9169	0.0065	0.0058	0.6056
0.9092	0.0071	0.0183	0.5657	0.9099	0.0064	0.0083	0.5292
0.9038	0.0053	0.0237	0.5029	0.9029	0.0062	0.0112	0.4590
0.9004	0.0070	0.0281	0.4466	0.9013	0.0061	0.0120	0.4439
0.8968	0.0053	0.0330	0.3822	0.8961	0.0059	0.0144	0.3976
0.8933	0.0053	0.0385	0.3311	0.8928	0.0058	0.0160	0.3695
0.8880	0.0052	0.0440	0.2899	0.8877	0.0055	0.0185	0.3303
0.8846	0.0052	0.0485	0.2553	0.8845	0.0053	0.0202	0.3067
0.8782	0.0052	0.0747	0.1155	0.8784	0.0050	0.0233	0.2657
0.8741	0.0035	0.0913	0.0599	0.8730	0.0046	0.0262	0.3215
0.8670	0.0001	0.1100	0.0020	0.8641	0.0039	0.0312	0.1807

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*Reference Figures 39-44.

TABLE XVIII*

n-PARAFFINS (1) - $(SO_2)_8$ (2) - BENZENE (3)

Experimental					Calculated			
				n-Butane				
x'_1	x'_2	x''_1	x''_2		$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9496	0.0245	0.3084	0.5452		0.9394	0.0356	0.2905	0.5735
0.9332	0.0267	0.3089	0.5226		0.9246	0.0354	0.3021	0.5149
0.8958	0.0321	0.3400	0.4040		0.8928	0.0372	0.3370	0.4185
0.8571	0.0410	0.3719	0.3296		0.8590	0.0409	0.3809	0.3388
0.8267	0.0479	0.4178	0.2691		0.8294	0.0456	0.4227	0.2808
0.8011	0.0555	0.4642	0.2318		0.8046	0.0504	0.4595	0.2389
0.7415	0.0747	0.5893	0.1480		0.7587	0.0613	0.5306	0.1745
0.7071	0.0891	0.6248	0.1274		0.7234	0.0716	0.5873	0.1349
				n-Hexane				
x'_1	x'_2	x''_1	x''_2		$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9567	0.0203	0.1418	0.7540		0.9408	0.0362	0.1366	0.7701
0.9120	0.0260	0.1463	0.6009		0.8998	0.0382	0.1603	0.6211
0.8675	0.0323	0.1670	0.5068		0.8589	0.0408	0.1891	0.5025
0.8590	0.0329	0.1650	0.4712		0.8505	0.0414	0.1957	0.4811
0.7940	0.0433	0.1966	0.3731		0.7906	0.0467	0.2474	0.3537
0.7418	0.0520	0.2469	0.2907		0.7415	0.0523	0.2953	0.2755
0.7052	0.0600	0.2892	0.2458		0.7083	0.0569	0.3308	0.2324
0.6647	0.0715	0.3737	0.1931		0.6735	0.0627	0.3693	0.1951
0.6250	0.0840	0.4416	0.1580		0.6400	0.0690	0.4079	0.1645
0.5740	0.1014	0.5090	0.1261		0.5971	0.0783	0.4825	0.1214
				n-Heptane				
x'_1	x'_2	x''_1	x''_2		$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9150	0.0249	0.1062	0.6589		0.9069	0.0330	0.1149	0.6807
0.8314	0.0336	0.1262	0.4602		0.8274	0.0376	0.1561	0.4720
0.7741	0.0426	0.1604	0.3401		0.7754	0.0413	0.1888	0.3713
0.6040	0.0737	0.2880	0.1938		0.6193	0.0584	0.3104	0.1830
0.5176	0.0952	0.3775	0.1463		0.5397	0.0731	0.3837	0.1301
0.4659	0.1124	0.4173	0.1284		0.4880	0.0903	0.3825	0.1313
				n-Decane				
x'_1	x'_2	x''_1	x''_2		$\overset{*}{x}'_1$	$\overset{*}{x}'_2$	$\overset{*}{x}''_1$	$\overset{*}{x}''_2$
0.9144	0.0235	0.0267	0.6910		0.9249	0.0130	0.0159	0.7388
0.8378	0.0278	0.0296	0.5082		0.8513	0.0143	0.0358	0.5202
0.7859	0.0307	0.0386	0.3891		0.8012	0.0154	0.0554	0.4068
0.7230	0.0364	0.0639	0.2973		0.7425	0.0169	0.0852	0.3011
0.6454	0.0441	0.0904	0.2418		0.6701	0.0194	0.1320	0.2043
0.5581	0.0545	0.1298	0.1872		0.5892	0.0233	0.1969	0.1300
0.4455	0.0742	0.2287	0.1364		0.4888	0.0309	0.2984	0.0716

*Reference Figures 45-48.

TABLE XIX*

n-PARAFFINS (1) - H_2O (2) - METHANOL (3)

n-Hexane

Experimental** x_1'	x_2'	x_1''	x_2''	Calculated $\overset{*}{x}_1'$	$\overset{*}{x}_2'$	$\overset{*}{x}_1''$	$\overset{*}{x}_2''$
0.9998	0.00003	0.00003	0.9998	0.9996	0.000029	0.00003	0.9989
0.9813	(0.00014)	(0.00061)	0.4164	0.9815	0.000033	0.00009	0.8710
0.9683	(0.00014)	0.0032	0.3487	0.9684	0.000035	0.00020	0.7711
0.9530	(0.00009)	0.0080	0.2649	0.9531	0.000037	0.00053	0.6510
0.9480	(0.00007)	0.0278	0.1544	0.9480	0.000037	0.00072	0.6128
0.8189	0.00000	0.1840	0.0000	0.8189	0.000000	0.1837	0.0000
				0.8300	0.000020	0.08100	0.0600

n-Heptane

x_1'	x_2'	x_1''	x_2''	$\overset{*}{x}_1'$	$\overset{*}{x}_2'$	$\overset{*}{x}_1''$	$\overset{*}{x}_2''$
0.9999	0.000009	0.000009	0.9999	0.9991	0.000009	0.000009	0.9995
0.9664	(0.000027)	0.009640	0.1808	0.9663	0.000011	0.000073	0.7701
0.9661	(0.000049)	0.000137	0.3328	0.9661	0.000011	0.000074	0.7679
0.9400	(0.000016)	0.032200	0.0785	0.9400	0.000012	0.000442	0.5615
0.8189	0.000000	0.069000	0.0000	0.8189	0.000000	0.085230	0.0000
				0.8999	0.000010	0.017230	0.1399

n-Octane

1	x_2'	x_1''	x_2''	$\overset{*}{x}_1'$	$\overset{*}{x}_2'$	$\overset{*}{x}_1''$	$\overset{*}{x}_2''$
0.9999	0.000003	0.000003	0.9999	0.9997	0.000003	0.000003	0.9994
0.9824	(0.000016)	0.00217	0.3332	0.9816	0.000003	0.000008	0.8881
0.9789	(0.000015)	0.00276	0.2604	0.9789	0.000003	0.000011	0.8632
0.9859	(0.000013)	0.00203	0.2271	0.9850	0.000003	0.000006	0.9122
0.9859	(0.000012)	0.00792	0.1823	0.9851	0.000003	0.000006	0.9123
0.9754	(0.000009)	0.01142	0.1284	0.9755	0.000003	0.000014	0.8375
0.9069	(0.000006)	0.02755	0.0527	0.9069	0.000004	0.002130	0.3179
0.8422	0.000000	0.05800	0.0000	0.8422	0.000000	0.06647	0.0000
				0.8701	0.000003	0.01982	0.1012

n-Nonane

x_1'	x_2'	x_1''	x_2''	$\overset{*}{x}_1'$	$\overset{*}{x}_2'$	$\overset{*}{x}_1''$	$\overset{*}{x}_2''$
0.9999	0.0000009	0.0000009	0.9999	0.9979	0.0000009	0.0000008	0.9991
0.9842	(0.0000070)	0.000904	0.2265	0.9829	0.0000008	0.0000050	0.8310
0.9619	(0.0000055)	0.013790	0.0624	0.9619	0.0000009	0.000121	0.5409
0.9139	(0.0000013)	0.022010	0.0410	0.9139	0.0000002	0.025470	0.3786
0.8967	0.0000000	0.045000	0.0010	0.8967	0.0000000	0.054230	0.0000

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*Reference Figures 49-52.

**Parenthesised concentrations are estimated.

TABLE XX*

COMPARISON OF PREDICTED AND EXPERIMENTAL EQUILIBRIUM CURVES

$(H_2O)_8$ (1) - BENZENE (2) - t-BUTANOL (3)

x_1'	x_2'	x_1''	x_2''
0.9848	0.0052	0.00050	0.9984
0.9332	0.0058	0.00051	0.9905
0.8230	0.0080	0.00063	0.9527
0.7297	0.0113	0.00108	0.8796
0.6536	0.0154	0.00258	0.7638
0.5366	0.0244	0.01407	0.5128
0.4357	0.0353	0.03851	0.3426
0.3280	0.0530	0.08301	0.2142
0.2542	0.0728	0.1302	0.1479
0.1149	0.1821	0.1118	0.1850

n-HEPTANE (1) - $(SO_2)_8$ (2) - BENZENE (3)

x_1'	x_2'	x_1''	x_2''
0.9376	0.0274	0.0725	0.7883
0.8440	0.0310	0.1188	0.4968
0.7490	0.0360	0.1822	0.3082
0.6515	0.0435	0.2626	0.1889
0.5839	0.0511	0.3277	0.1345
0.5315	0.0585	0.4023	0.0960

*Reference Fingure 57 - calculated curves only.

BIBLIOGRAPHY

1. Alberty, R. A. and Washburn, E. R. *J. Phy. Chem.*, *49*, (1954), 4.

2. Beech, D. G. and Glasstone, S. *Journal of the Chem. Soc.*, (London), (1938), 70.

3. Berndt, R. J. and Lynch, C. C. *J.A.C.S.*, *66*, (1944), 282.

4. Black, Cline *Ind. Eng. Chem.*, *50*, (1958), 403.

5. Dodge, Barnett, F. *Chemical Engineering Thermodynamics*. New York: McGraw-Hill, 1st ed., (1944) 104-133.

6. Dornte, R. W. *J. Phys. Chem.*, *33*, (1929), 1309.

7. Findlay, Alexander *The Phase Rule*. New York: 9th ed. by Campbell, C. N. and Smith, N. O., Dover, N.Y., (1951), 282-295, 455-470.

8. Galler, B. A. Class Notes, Math. 173, The University of Michigan, 1959.

9. Gibbs, J. Willard *The Collected Works*. New York: Longmans, Green and Co., I, (1928), 129-134.

10. Graham, R., and Arden, B. *Generalized Algebraic Translator*. University of Michigan Computing Center, Ann Arbor, Mich., 1959.

11. Griswold, John, Chu, Pao L., and Winsauer, W. O. *Ind. Eng. Chem.* *41*, (1949), 2325.

12. Haase, Rolf *Thermodymanik der Mischphasen*. Springer-Verlay, Berlin: 1st. ed., (1956),66-70, 86-91, 135-183.

13. Hala, Edward, Pick, J., Fried, V., and Vilim, O. *Vapor-Liquid Equilibrium,* translated by G. Standart, 1st. ed., Pergamon Press, London, (1958), 3-105.

14. Hildebrand, J. H. *Solubility of Non-Electrolytes*. New York: Reinhold, 1936.

15. *I.B.M. Programmers' Primer for FORTRAN*, I.B.M. Corp., 1957.

16. *I.B.M. Reference Manual for FORTRAN*, I.B.M. Corp., 1958.

17. Izmailov, N. A. and Franke, A. K. Zhur. Fiz. Khim. 29, (1955), 120.

18. Kenny, J. W. Chem. Eng. Sci., 6, No. 3, (1957), 116-122.

19. Kogan, V. B., Deizenrot, I. V., Kuldyaeva, T. A., and Fridman, V. M. Zhur Priklad. Khim. 29, (1956), 1387.

20. Margules, M. S. B. Akad. Wiss. Wien, Math. Naturw. Kl. II, 104, (1895), 1243.

21. Marquardt, D. W. Chem. Eng. Prog. 55, No. 6, (June, 1959), 65.

22. Masing, G. Ternary Systems, translation by Rodgers, B. A., Reinhold Publishing Co., (1944), 100-121.

23. Matsumoto, K. and Sone, S. J. Pharm. Soc. Japan, 76, (1956), 475.

24. McCants, J. F., Jones, J. H., and Hopson, W. H. Ind. Eng. Chem. 45, (1953), 454.

25. Murti, P. S., Venkataratnam, A., and Rao, C. V. J. Sci. Ind. Research 13B, (1954), 77.

26. Olsen, A. L. and Washburn, E. R. J.A.C.S., 57, (1935), 303.

27. Purnell, J. H. and Bowden, S. T. J. Chem. Soc. 4, (1954), 539-46.

28. Rao, M. R., Ramamurty, M., and Rao, C. V. Chem. Eng. Sci., 8, (1958), 265-70.

29. Rao, M. R. and Rao, C. V. J. Scient. and Ind. Research, 14B, (1955), 444.

30. Rao, M. R. and Rao, C. V. J. Scient. and Ind. Research 14B, (1955), 204.

31. Rao, M. R. and Rao, C. V. J. Scient. Ind. Research, 16B, No. 3, (1957), 102.

32. Rao, M. R. and Rao, C. V. J. Appl. Chem. 7, (1957), 435.

33. Redlich, O. and Kister, A. T. Ind. Eng. Chem. 40, (1948), 341.

34. Redlich, O., Kister, A. T., and Turnquist, C. E. Chem. Eng. Progress Symp. Ser. 48, No. 2, (1952), 49.

35. Satterfield, C. N., Powell, J. H., Oster, E. A., and Noyes, J. P. Ind. Eng. Chem. 47, (1955), 1458-62.

36. Saunders, K. W. *Ind. Eng. Chem.* 43, (1951), 121.

37. Scarborough, J. B. *Numerical Mathematical Analysis.* The John Hopkins Press, Baltimore, (1950), 463-469.

38. Ibid., 382-391, 399-409.

39. Scatchard, G. and Hamer, W. J. *J.A.C.S.*, 57, (1935), 1805.

40. Scheibel, E. G. *Pet. Refiner.* 38, No. 9, (1959), 227.

41. Scheibel, E. G. and Friedland, D. *Ind. Eng. Chem.* 39, (1947), 1329.

42. Schweppe, J. L. and Lorah, J. R. *Ind. Eng. Chem.* 46, (1954), 2391.

43. Seidell, Atherton, *Solubilities of Organic Compounds.* New York: D. Van Nostrand Co. Inc., II, (1941), 368.

44. Simonsen, D. R. and Washburn, E. R. *J.A.C.S.* 68, (1946), 235.

45. Teague, P. C. and Felsing, W. A. *J.A.C.S.* 65, (1943), 485.

46. Treybal, Robert E. *Liquid Extraction.* New York: McGraw Hill, (1951), 22-37.

47. Van Laar, J. J. *Z. Phys. Chem.* 185, (1929), 35.

48. Varteressian, K. A. and Fenske, M. R. *Ind. Eng. Chem.* 28, (1956), 928.

49. Venkataratnam, A., Jagannadha Rao, R., and Venkata Rao, C. *Chem. Eng. Science.* 7, (1957), 102-10.

50. Vierk, A. L. *Z. Anorg Chem.* 261, (1950), 283.

51. Washburn, E. R., Hnizda, V. andVold, R. *J.A.C.S.* 53, (1931), 3237.

52. Washburn, E. R. and Strandsov, C. V. *J. Phys. Chem.* 48, (1944), 241.

53. White, Robert R. *Personal Communication*, The University of Michigan, Ann Arbor, 1958.

54. Wohl, K. *Trans. A.I.Ch.E.* 42, (1946), 215.

55. Woods, F. S. *Advanced Calculus.* Boston, Mass: Ginn and Company, (1934), 9-102.

56. Ibid. 15-16.

57. Wrewski, M. S. *J. Russ. Phys. Chem. Soc.* 42, (1910), 1.

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