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AZEOTROPIC RULE AND THREE-PHASE DISTILLATION

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

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degree of

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BY

SUN-FU YANG

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1974

AZEOTROPIC RULE AND THREE-PHASE DISTILLATION

APPROVED BY

Frank Canfield

James Wilkinson

K E Starling

Mike Devine

F M Townsend

DISSERTATION COMMITTEE

ABSTRACT

Recently, a number of semi-empirical molecular models, such as the Wilson equation and the NRTL equation have been developed. These models provide good simulations for multi-component mixtures based only on the data for constituents of binaries. Also with increasing popularity and availability of computers, models can be developed quickly and accurately.

Because of these facts, a few studies were stimulated to emphasize the proposed computer method in predicting fundamental phenomena of nonideal solutions, such as azeotropes, separations of two liquid phases. However, some simple rules have been neglected. They govern the behavior of nonideal solutions, and are as important as the computational method itself. This dissertation is to bridge the gap between these two points. Thus an azeotropic rule is introduced and modified. Also is a classic thermodynamic stability condition revived.

Usually, a conventional method of predicting the separation of two liquid phases is to solve a set of thermodynamic equilibrium equations. This kind of approach is unstable with the increased number of components of a mixture. Also, the calculation function burden is increased because of the introduction of a penalty function, which is supposed

to eliminate the occurence of a trivial solution. Therefore one of the aims of this dissertation is to introduce a new liquid-liquid calculation method based on Null's method. By introducing a simple guidance rule, the method has proved to be stable and reliable in predicting homogeneous liquid phases as well as heterogeneous phases. Classic thermodynamic stability conditions are found to be credible in predicting the phase separation for an overall composition of mixtures. Predictions have also proved to be consistent with the calculated results of the modified method.

It is a trend that the plate-to-plate method for a conventional distillation process has been gradually overridden by a successive method. The method developed previously by Tomich, to solve all system equations simultaneously with Broyden method, has been proved to be more stable and more efficient. But there is rarely a method proposed to improve the calculation of a nonideal solution separation process which is highly composition-dependent as well as temperature-dependent. Another aim of this dissertation is to develop a general algorithm for this purpose. The algorithm is proposed for a variety of equilibrium stage processes involving a nonideal solution by modifying the Tomich method. It is demonstrated very successfully for liquid-liquid equilibrium, three-phase flash and distillation, azeotropic distillation and countercurrent extraction problems.

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AZEOTROPIC RULE AND THREE-PHASE DISTILLATION

CHAPTER I

INTRODUCTION

With the development of distillation for azeotropic multicomponent mixtures, the phenomenon of azeotropy has drawn increasing attention. According to Swietoslaske's estimation(55), 47% of all the mixtures investigated were azeotropes.

From the knowledge on azeotropy, we can deduce that a pinch point occurs when the assumed reflux ratio is less than the minimum or when an azeotrope is present. We can also have a complete description on the behavior of the distillation lines around azeotropes with which we are able to deduce the optimum distillation policy. Thus, it is apparent that a technique is needed to predict the existence, composition, and temperature for a multicomponent azeotrope.

Probably the most common method of determining an azeotrope of a mixture is by experiment. This approach, however, is very expensive and sometimes leads to serious difficulties. A second approach is mathematically describing azeotropic condition, which leads to the composition of

an azeotrope and its temperature. Much work has been done in this area, and some literature can be found. For instance, Hasse (15) has a general discussion of ternary azeotropes and Malesinke (28) has a detailed method concerning the determination of azeotropic properties for a multicomponent mixture. However, the methods proposed for calculating azeotropic compositions do not always give satisfactory results. Graphic determination of the region of a ternary azeotrope is described by Horvath (21), and by Susarev and his colleague (52-53) in their series of publications. But these methods are not practical in applying to the computer-oriented design. Several methods have been proposed, some are completely empirical and others semi-empirical. The proposed methods are applicable only to a small class of problems. Recently, some suggestions with general applicability have appeared. Using the Wilson equation, Raju and Rao (10) proposed a method to determine azeotrpic properties of binary and ternary systems under isobaric conditions. Aristovich and Stepanova (1) dealt with the determinations of azeotropes with a regression method for isothermal systems.

The methods described above are based on either the assumption that an azeotrope is present prior to the calculation, or that results of the calculation can determine the existence of an azeotrope. If a convergence result cannot be obtained, or an unreasonable answer is found, then it will imply that no azeotrope is present. This approach is

too trivial and will introduce serious mistakes because of the occasional failure of a numerical method. Therefore, a rule of governing the existence of azeotropes is preferable before computing the composition and the temperature of an azeotrope.

In 1901, Schreinmaker (45) developed a rule concerning the loci of distillation lines near azeotropic points, and vertices of a concentration simplex. Later, Hasse (16) modified the rule and formation conditions for different types of singular points. Reider and H. de Minijer (43) also illustrated the course of distillation lines around azeotropes for different ternary systems. A rigorous mathematical relation describing the relation among azeotropes on a phase diagram was not derived until 1958. It is known that an azeotrope is a singular point of a set of differential equations representing processes of batch distillation. Azeotropes can be classified by different types of singular points according to the behavior of distillation lines in the vicinity of an azeotrope. Therefore, from the mathematical theory of differential equations and from the Poincare formula, Gurikov (12) successfully obtained a simple mathematical equation concerning the relation between azeotropes of a phase diagram for ternary nonideal solutions. From rigorous thermodynamic relations, Zharov (64-65) showed that the behavior around a singular point can be examined qualitatively with a set of first order differential equations. Consequently,

a singular point can be described by eigenvalues of a characteristic equation. He also formulated a generalized azeotropic rule from a topology principle (66) and demonstrated this general rule experimentally (59-60). Sarafimov (46-49) systematically introduced a classification of multicomponent azeotropies as well as the rule relating the type of singular points which correspond to different dimension azeotropes in a multicomponent mixture.

In the next two chapters, relations between mathematical singular points and azeotropes are introduced first. A modification on the definition to classify the type of singular points will be made. A relation of thermodynamic quantities with a singular point is presented section by section, to which the effort of reducing the calculation process is dedicated. Then the general azeotropic rules by Zharov and Sarafimov are introduced. From the detailed comparisons between both equations we can appreciate the flexibility of the modified definition in determining a set of singular points. Some extensive work will be shown to demonstrate the consistency between experimental data and the prediction. A misinterpreted example from Smith's book is readjusted based on the azeotropic rule. Further extensive work in this area is also mentioned in the last section.

I. Azeotropes and Singular Points

To relate the types of singular points, we may start

from a set of differential equations which describe the behavior of a simple batch distillation for an (n+1) component mixture. This equation is shown as:

$$\frac{dx_i}{dt} = y_i - x_i \qquad i = 1,...n \qquad (1\text{-}1)$$

where y_i, x_i is respectively, mole fraction of component i in the liquid and vapor, and dt = dlnS, S is the number of moles of solution in a still.

Obviously, the solution y = x, is a singular point for the above set of equations, since the right hand sides of the equations will be zero. This singular point corresponds to a pure component or an azeotrope of an (n+1) -component mixture.

To have a singular point at the origin, i.e., $v_i = 0$ instead of $x_i = \alpha_i$, we let,

$$v_i = x_i - \alpha_i$$

$$u_i = y_i - \alpha_i$$

so equation (1-1) becomes

$$\frac{dv_i}{d_t} = u_i - v_i \qquad (1\text{-}2)$$

where $(u_i - v_i)$ is a function of v_i. Thus we can express equation (1-2) as:

$$\frac{dv_i}{dt} = u_i - v_i = f(\underline{v}) \qquad (1\text{-}3)$$

To investigate the behavior of the solution in vicinity of a singular point, we can utilize a method of the qualitative theory of differential equations. This method involves choosing a set of equations which are simpler than the basic equations because they have the same qualitative properties, the behavior of solutions for the set of equations in the vicinity of a singular point can be studied.

An Equivalent Approximate Set of Equations

Taking Taylor series expansion about the origin of equation (1-3), we find

$$f_i = f_i(0) + \sum_{i=1}^{n} v_i f_i'(0) + 0$$

where

$f_i(0) = 0$, at azeotropic point

so we have the following set of first-order ordinary differential equations;

$$u_1 - v_1 = B_{11}v_1 + B_{12}v_2 + \ldots B_{1n}v_n$$

$$u_n - v_n = B_{n1}v_1 + B_{n2}v_2 + \ldots B_{nn}v_n \qquad (1\text{-}4)$$

where

$$B_{ij} = \left(\frac{\partial(u_i - v_i)}{\partial v_j}\right)_{\underline{v}=0} \qquad (1\text{-}5)$$

It has been shown that if solutions of the characteristic equations (1-4) are nonzero and real, the behavior of solutions for equation (1-4) and equation (1-3) will be equivalent in the qualitative sense (64).

This characteristic equation is;

$$\begin{vmatrix} B_{11}-\lambda & B_{12} & \cdots & B_{1n} \\ B_{21} & B_{22}-\lambda & & B_{2n} \\ \cdot & \cdot & & \cdot \\ B_{n1} & & & B_{nn}-\lambda \end{vmatrix} = 0 \qquad (1\text{-}6)$$

In general, solutions of the above equation (1-6), or eigenvalues, can reflect the behavior of solution loci about a singular point.

Description of Type of Singular Points

Let us suppose a singular point corresponds to a pure component and has coordinate $\alpha_1 = 0$, $\alpha_2 = 0$, and $\alpha_3 = 0$, and let it be the corner of a concentration tetrahedron. On this basis, we have;

$$v_1 = x_1,\ v_2 = x_2,\ \text{and}\ v_3 = x_3 \qquad (1\text{-}7)$$

and

$$B_{12} = B_{13} = B_{21} = B_{23} = B_{31} = B_{32} = 0 \qquad (1\text{-}8)$$

If $x = 0$, then $y = 0$, and at the singular point we have $B_{ik} = 0$ for all $i=k$. Variations in concentrations of components other than i do not affect the values of $y_i - x_i = 0$ where $i = 1$ to 3.

Under conditions (1-7, 8), the equation (1-4) can be greatly simplified as follows:

$$\frac{dx_1}{dt} = B_{11}t$$

$$\frac{dx_2}{dt} = B_{22}t \qquad (1\text{-}9)$$

$$\frac{dx_3}{dt} = B_{33}t$$

The general solutions will be:

$$x_1 = C_1e^{B_{11}t} \quad x_2 = C_2e^{B_{22}t}, \text{ and } x_3 = C_3e^{B_{33}t} \qquad (1\text{-}10)$$

Several conceivable cases for solutions (1-10) are:

Case 1) $B_{11}>0$, $B_{22}>0$, $B_{33}>0$

According to the above conditions, we shall have general solutions for each of the solution loci about the vertex, such as:

$$\lim_{t\to-\infty} x_1 = 0, \quad \lim_{t\to-\infty} x_2 = 0, \quad \lim_{t\to-\infty} x_3 = 0 \qquad (1\text{-}11)$$

These relations show that as $t \to -\infty$, all loci for a set of equations (1-4) will meet at the vertex of the tetrahedron. A singular point in the vicinity of which all loci meet as $t \to \infty$, or $t \to -\infty$ is termed as a node. At the present time, the singular point is a node. As $t \to -\infty$, $S \to 0$ for batch distillation processes, in the physical meaning of equation (1-11), all distillation lines will be converged at the corner of the tetrahedron. In other words, if the boiling point of the fourth component is the highest one at isobaric conditions, then the final product is the fourth component in a simple batch distillation.

Case 2) $\quad B_{11} < 0, \quad B_{22} < 0, \quad B_{33} < 0$

To conform with the above inequalities general solutions for each of solution loci around the vertex will be:

$$\lim_{t \to \infty} x_1 = 0, \quad \lim_{t \to \infty} x_2 = 0, \quad \lim_{t \to \infty} x_3 = 0 \qquad (1\text{-}12)$$

These relations show that as $t \to \infty$, all loci of solutions will move away from the singular point. In the physical sense, during batch distillation processes, distillation lines are moving away from the corner. It can be seen that the fourth component having the lowest boiling point will be evaporated first. We regard a node as a stable node if all distillation lines enter it, and as an unstable node if all distillation lines emerge from it.

Case 3) $B_{11}>0,\ B_{22}<0,\ B_{33}>0$

To discuss the matter conveniently, we let $C_2 = 0$ be in the general solutions. Then only the behavior of distillation lines on the 1-3-4 faces of the tetrahedron is considered. Since $C_2 = 0$,

at

$$\lim_{t\to-\infty} x_1 = 0, \quad \lim_{t\to-\infty} x_3 = 0$$

on 1-3-4 face, all loci adjoin the corner, hence every distillation line enters the corner.

If $C_1 = 0$, $C_3 = 0$, then only the behavior of distillation lines along the edge of 3-4 will be considered, since

$$\lim_{t\to\infty} x_2 = 0$$

So along the edge 3-4, distillation lines will emerge from the corner. Therefore, for the remaining lines defined by the general solutions, which are located on the 1-3-4 face or the 2-3-4 face or in the tetrahedron, the loci will move away from the singular point with either the increasing or the decreasing t. A singular point with these properties is called a saddle point. This indicates that the fourth component is an intermediate product during a simple batch distillation.

Case 4) $B_{11}<0,\ B_{22}>0,\ B_{33}<0$

In this case the signs of inequalities are just reversed compared with the case 3. The arrangement of the distillation line is the same, but the direction is reversed. The following figures show the cases we have just discussed.

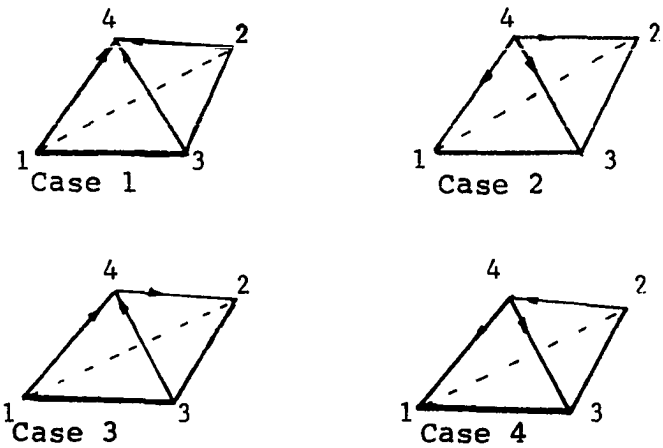

Figure 1. Descriptions of Types of Singular Points

Regarding the two above saddle points, we have a negative saddle point for case 3, and a positive saddle point for case 4.

From the above illustrations we may conclude the following:

1. Values of B_{11} , B_{22} and B_{33} are eigenvalues of equation (1-6) so we can say the sign of each eigenvalue determines the type of a singular point.

2. There are two main types of singular points, namely: node and saddle points. But for a system containing more than three components we have the node as a stable node and an unstable node and the saddle point as the negative and positive saddle points.

No attempt is made to give further descriptions for higher dimension singular points, such as binary azeotropes or ternary azeotropes. They can be found elsewhere (65, 47). However, they all have similar types of singular points described above.

Singular Points and Thermodynamic Quantities

Unless we can relate measurable quantities to B_{ij} of equation (1-6), they will have no practical values. From equation (1-5) we can have;

$$
\begin{aligned}
B_{ij} &= \left(\frac{\partial (u_i - v_i)}{\partial v_j}\right)_{\underline{v}=0} \\
&= \left(\frac{\partial (y_i - x_i)}{\partial x_j}\right)_{\underline{x}^{\circ}=\underline{\alpha}} \\
&= \left[\frac{\partial}{\partial x_j}\left(x_i (K_i - 1)\right)\right]_{x^{\circ}=\underline{\alpha}} \\
&= \left(x_i \frac{\partial K_i}{\partial x_j} + \delta_{ij}(K_i - 1)\right)_{\underline{x}^{\circ}=\underline{\alpha}}
\end{aligned}
\qquad (1\text{-}13)
$$

where K_i is the equilibrium constant for component i, and

$$\delta_{ij} = 1, \text{ if } i=j, \quad \delta_{ij} = 0, \text{ if } i \neq j$$

since x_i, x_j are independent variables.

In terms of thermodynamic quantities equation (1-6) can be rewritten in the following form:

$$\begin{vmatrix} (K_1-1) + x_1\frac{\partial K_1}{\partial x_1} - \lambda & x_1\frac{\partial K_1}{\partial x_2} & x_1\frac{\partial K_1}{\partial x_n} \\ x_2\frac{\partial K_2}{\partial x_1} & (K_2-1) + x_2\frac{\partial K_2}{\partial x_2} - \lambda & x_2\frac{\partial K_2}{\partial x_n} \\ x_n\frac{\partial K_n}{\partial x_1} & (K_n-1) + x_n\frac{\partial K_n}{\partial x_n} - \lambda & \underline{x}^\circ \end{vmatrix} = 0 \qquad (1\text{-}14)$$

A Practical Way of Defining Singular Points

As shown above, for quaternary systems there are four types of singular points, and it would be very difficult and impractical to determine the sign of each eigenvalue from the characteristic equation (1-6). So we would rather take the idea from Sarafimov (47) who divided singular points into positive and negative singular points. Our definition is slightly different from Sarafimov's. We define that the positive singular point is one which has a positive product of eigenvalues for equation (1-6). Stable nodes and positive saddle points are under this term. For a negative singular point we define one which has a negative product of eigenvalues for equation (1-6). Unstable nodes and negative saddle points are under this term. Although such a classification of singular points will not represent the real function of singular points, it can allow us to

determine the type of singular points in a more flexible and convenient fashion.

Under such definition to decide the type of singular points corresponding to the azeotrope of an (n+1)-component mixture, instead of obtaining n eigenvalues from equation (1-6), we only have to evaluate the determinant value of the equation (1-6).

The Explicit Equation for Determining the Type of Various Dimension Azeotropes for an (n+1)-Component Mixture.

The above section clearly classified two main types of singular points which correspond to azeotropes. Each type of singular point depends on the sign of the product of eigenvalues. The following shows the explicit equation which represent the form to decide the type of singular points for different dimension azeotropes in an nth simplex.

1) For a pure component

$$\underline{x}^{\circ} = (0,0,.....0)$$

The product form of eigenvalues is

$$(K_1-1).....(K_n-1)$$

2) For a binary azeotrope

$$\underline{x}^{\circ} = (0,.....0,\ x_n^{\circ})$$

and $K_n = 1$

The product form of eigenvalues is

$$(K_1-1).....(K_{n-1}-1)\ \frac{\partial K_n}{\partial x_n}$$

3) For a kth azeotrope $\underline{x}^\circ = x_1^\circ, x_2^\circ,....x_{k-1}^\circ, 0,...0)$

$K_1 = 1,.....K_{k-1} = 1$

equation (1-14) becomes

$$\begin{vmatrix} x_1^\circ\frac{\partial K_1}{\partial x_1} - \lambda & x_1^\circ\frac{\partial K_1}{\partial x_2} & x_1^\circ\frac{\partial K_1}{\partial x_{k-1}} & 0 & 0 & 0 \\ x_2^\circ\frac{\partial K_2}{\partial x_1} & x_2^\circ\frac{\partial K_2}{\partial x_2} - \lambda & & & & \\ x_{k-1}^\circ\frac{\partial K_{k-1}}{\partial x_1} & & x_{k-1}^\circ\frac{\partial K_{k-1}}{\partial x_{k-1}} - \lambda & 0 & 0 & 0 \\ 0 & 0 & & & & (K_{n-1}) - \lambda \end{vmatrix} = 0$$

Since the product of eigenvalues is the determinant of the related function itself, the product form of eigenvalues is

$$\begin{vmatrix} \frac{\partial K_1}{\partial x_1} & \frac{\partial K_1}{\partial x_{k-1}} \\ \frac{\partial K_{k-1}}{\partial x_1} & \frac{\partial K_{K-1}}{\partial x_{k-1}} \end{vmatrix} (K_{k+1}-1)....(K_n-1)$$

4) For the (n+1)th azeotrope, $\underline{x}^\circ = (x_1^\circ, x^\circ_2.....x_n^\circ)$,

The product form of eigenvalues is

$$\begin{vmatrix} \frac{\partial K_1}{\partial x_1} & \frac{\partial K_1}{\partial x_n} \\ \frac{\partial K_n}{\partial x_1} & \frac{\partial K_n}{\partial x_n} \end{vmatrix}$$

Coupling Process

We know that each vertex of a tetrahedron is formed from the intersection of three faces. Each edge is resulting from the intersection of two faces. Using the coupling process defined by Sarafimov (48), we can formulate the following algorithms:

$$N_o^{(2)} + N_o^{(2)} + N_o^{(2)} \rightarrow N_o^{(3)}$$

$$N_o^{(2)} + N_o^{(2)} + C_o^{(2)} \rightarrow CN_o^{(3)}$$

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$$N_1^{(2)} + C_1^{(2)} \rightarrow CN_1^{(3)}$$

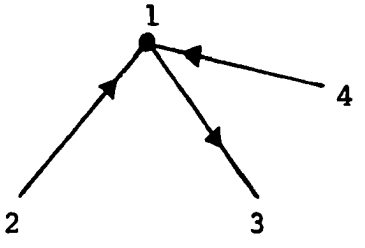
The subscripts is the dimension of a singular point, and the superscripts is the dimension of a simplex to which singular points belong. For instance, $N_1^{(2)}$ is a binary azeotrope in a ternary system. Obviously, the above process does not show what we desire the most, the negative singular point or positive singular point. Here we give a more rigorous approach and modify the above process. The modified process allows us a more accessible way to determine the type of singular points for a multicomponent azeotrope.

Taking a quaternary system as an example, we determine the type of a singular point corresponding to a pure component 1 from the following product:

$$(K_2-1)(K_3-1)(K_4-1).$$

The value of K_i, i = 2,3,4, is evaluated at the temperature and composition of the pure component 1, therefore it should not matter whether it is in a ternary system 1-2-3 or a quaternary system 1-2-3-4. After deciding the type of singular point of pure component 1 in 1-2-3 and 1-2-4 (or 1-3-4) we definitely have the type of singular point for pure component 1 in a quaternary 1-2-3-4.

Let us have a line drawn toward vertex 1, if K_2-1 is negative, and toward 2, if value of (K_2-1) is positive. So if $(K_2-1)>0$; $(K_3-1)<0$; and $(K_4-1)>0$, we can have:



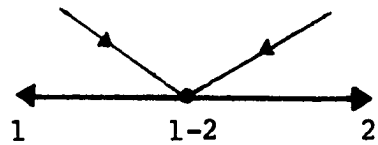
Then we may draw an important and practical conclusion: A point with odd number of outward lines is a negative singular point.

For a binary azeotrope, the type of singular points is decided from:

$$\frac{\partial K_1}{\partial x_1}(K_3-1)(K_4-1).$$

The values of K_3, K_4 are evaluated at the azeotropic temperature and composition. The sign of $\partial K_1/\partial x_1$ is dependent on the physical nature of the azeotrope. These values make no

difference whether the binary azeotrope is in a ternary or quaternary system. Similarly, we can have the following diagram for a minimum boiling binary azeotrope if $(K_3-1) > 0$ $(K_4-1) > 0$:



Accordingly, the binary azeotrope 1-2 is a negative singular point, since there is only one outward line which is toward 1 (or 2). Note that the line toward 1 or toward 2 is considered to be the same.

Thermodynamic Conditions of a Positive or a Negative Multicomponent Azeotrope

Azeotropes can be divided into positive and negative azeotropes. Positive azeotropes are characterized by a minimum boiling temperature under isobaric conditions, or a maximum vapor pressure at isothermal conditions. Negative azeotropes, on the other hand, have a maximum boiling temperature and a minimum vapor pressure. These two types of azeotropes of an (n+1)-mixture have the following relations (28):

For a positive azeotrope, the determinant of

$$\begin{vmatrix} \frac{\partial K_1}{\partial x_1} & \cdots & \frac{\partial K_1}{\partial x_n} \\ \vdots & & \vdots \\ \frac{\partial K_n}{\partial x_1} & \cdots & \frac{\partial K_n}{\partial x_1} \end{vmatrix} < 0 \qquad (1\text{-}15)$$

and for a negative azeotrope, the determinant of

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As for a binary system, we have the following conditions:

$\frac{\partial K_1}{\partial x_1} < 0$ for a minimum boiling azeotrope

$\frac{\partial K_1}{\partial x_1} > 0$ for a maximum boiling azeotrope

Obviously, by applying conditions shown in equations (1-15, 16) to evaluate the product of eigenvalues, a lot of calculations can be skipped. Consequently, we have a more convenient way to decide the type of a singular point.

Binary Azeotropic Formation Conditions

Many studies have concerned with formation conditions of a binary azeotrope. Some of them are restricted to special occasions and are not generalized. For example,

Jaques and Lee (26) gave a condition in terms of the Redlich-Kister empirical equation. Prigogine (39) showed a condition for a regular solution. Some (2, 37) offer a general demonstration for which point of view is described below.

For a large number of binary mixtures, which are characterized by either positive or negative deviation from ideal solution behavior, they can be described by the monotonically positive or monotonically negative activity coefficients. These two cases are shown in the following two figures:

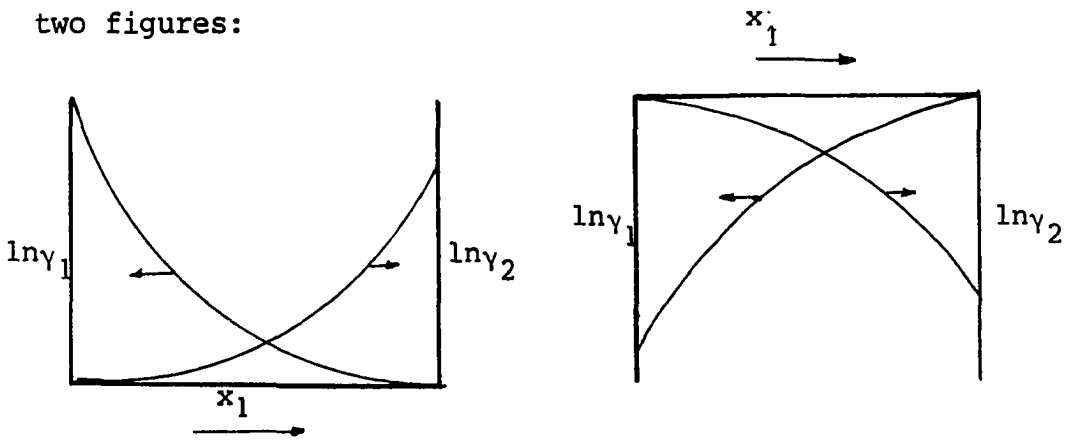

Figure 2. Description of Characteristics of Nonideal Solution

As for a binary system where the nonideality of the vapor phase is neglected, the total pressure is:

$$P = p_1 x_1 \gamma_1 + p_2 x_2 \gamma_2 \cdot$$

At azeotropic point, $\underline{x} = \underline{y}$, so $P = p_1 x_1 = p_2 \gamma_2$

i.e., $p_1\gamma_1 - p_2\gamma_2 = 0$

Then $\ln\gamma_1 - \ln\gamma_2 = (\ln p_1 - \ln p_2)_{az}$

TABLE 1. Confirmation of Binary Azeotropic Condition with Experimental Data*

Component				Azeotrope	
A	B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Observed	Predicted
ACETONE	Benzene	0.362	0.803	No	No
	Carbon tetra-chloride	0.763	0.682	Min	Min
	Chloroform	-0.638	0.170	Max	Max
	2,3 Dimethyl-butane	1.515	0.059	Min	Min
	Ethanol	0.658	0.948	No	No
	Methanol	0.647	0.359	Min	Min
	Methylacetate	0.134	0.041	Min	Min
	Methyl-isobutyl-ketone	0.089	2.110	No	No
	N-Heptane	1.755	0.739	Min	Min
	2-Propanol	0.618	1.200	No	No
	Water	1.585	1.809	No	No
ACETONITRILE	Water	2.035	0.688	Min	Min
BENZENE	1-Butanol	1.375	1.493	No	No
	Carbon tetra-chloride	0.083	0.104	No	No
	Chloroform	-0.190	0.617	No	No
	Cyclohexane	0.378	0.019	Min	Min
	Cyclopentane	0.378	1.052	No	No
	Ethanol	1.375	0.053	Min	Min

TABLE 1 (Continued)

Component				Azeotrope	
A	B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Observed	Predicted
BENZENE (Con't)	I-Octane	0.621	0.575	Min	Min
	N-Heptane	0.420	1.587	No	No
	N-Hexane	0.336	0.365	No	No
	Methanol	1.833	0.500	Min	Min
	Methylacetate	0.300	0.767	No	No
	Methylcyclo-hexane	0.434	0.627	No	No
	Methylcyclo-pentane	0.312	0.256	Min	Min
	1-Propanol	1.844	0.698	Min	Min
	2-Propanol	1.603	0.084	Min	Min
	Methanol	1.942	0.500	Min	Min
1-BUTANOL	Methylcyclo-hexane	1.568	0.608	Min	Min
	Toluene	1.269	0.254	Min	Min
CHLOROFORM	Methanol	1.992	0.145	Min	Min
	Methylacetate	-0.526	0.136	Max	Max
	Methyl-ethyl-ketone	-0.827	0.618	Max	Max
	Methyl-iso-butyl-ketone	-1.100	1.889	No	No

TABLE 1 (Continued)

Component				Azeotrope	
A	B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Observed	Predicted
CYCLOHEXANE	Ethanol	1.971	0.071	Min	Min
	Methyl-ethyl-ketone	1.282	0.034	Min	Min
	Methylacetate	1.365	0.770	Min	Min
	2-Propanol	2.481	0.057	Min	Min
	Toluene	0.510	0.933	No	No
2,3-DIMETHYL-BUTANE	Methanol	3.865	0.280	Min	Min
1,4-DIOXANE	Hexene-1	0.821	1.204	No	No
ETHANOL	Ethyl acetate	0.922	0.050	Min	Min
	N-Heptane	2.688	0.628	Min	Min
	N-Hexane	3.248	0.393	Min	Min
	Methanol	0.018	0.564	No	No
	Methylcyclo-pentane	3.166	0.255	Min	Min
	Water	0.981	0.826	Min	Min
ETHYL ACETATE	Methanol	1.038	0.413	Min	Min
	1-Propanol	0.665	0.831	No	No
	2-Propanol	0.452	0.212	Min	Min
	Water	2.780	0.881	Min	Min
ETHYLBENZENE	N-Octane	0.205	0.288	No	No

TABLE 1 (Continued)

Component A	Component B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Azeotrope Observed	Azeotrope Predicted
N-HEPTANE	Methanol	4.620	1.109	Min	Min
	Methyl-ethyl-ketone	1.273	0.588	Min	Min
	I-Octane	0.012	0.024	No	No
	Toluene	0.084	0.360	No	No
N-HEXANE	Hexene-1	0.076	0.087	No	No
	Methylcyclo-pentane	0.012	0.097	No	No
	1-Propanol	1.454	1.210	Min	Min
	1,2,3-trichloro-propane	1.728	3.001	No	No
	Toluene	0.411	1.364	No	No
HEXENE-1	1,2,3,-trichloro-propane	1.002	3.123	No	No
METHANOL	Methylacetate	1.019	0.317	Min	Min
	2-Propanol	-0.078	0.769	No	No
	Toluene	1.970	1.515	Min	Min
	Water	0.569	1.412	No	No
METHYLACETATE	2-Propanol	0.722	1.148	No	No
METHYLCYCLO-PENTANE	Toluene	0.525	1.242	No	No
METHYLCYCLO-HEXANE	1-Propanol	1.512	0.105	Min	Min

TABLE 1 (Continued)

Component				Azeotrope	
A	B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Observed	Predicted
METHYL-ETHYL-KETONE	Toluene	0.309	0.972	No	No
I-OCTANE	Toluene	0.163	0.333	No	No
2-PROPANOL	2,2,4-Tri-methyl-pentane	1.648	0.505	Min	Min

*Subscript indicates the component which has the lower B.P. between components of A and B.

No attempt is made to give further descriptions for higher dimension singular points, such as binary azeotropes or ternary azeotropes. They can be found elsewhere (65, 47). However, they all have similar types of singular points described above.

Singular Points and Thermodynamic Quantities

Unless we can relate measurable quantities to B_{ij} of equation (1-6), they will have no practical values. From equation (1-5) we can have;

$$
\begin{aligned}
B_{ij} &= \left(\frac{\partial (u_i - v_i)}{\partial v_j}\right)_{\underline{v}=0} \\
&= \left(\frac{\partial (y_i - x_i)}{\partial x_j}\right)_{\underline{x}^\circ=\underline{\alpha}} \\
&= \left[\frac{\partial}{\partial x_j}\left(x_i(K_i-1)\right)\right]_{x^\circ=\underline{\alpha}} \\
&= \left(x_i\frac{\partial K_i}{\partial x_j} + \delta_{ij}(K_i-1)\right)_{\underline{x}^\circ=\underline{\alpha}}
\end{aligned}
\qquad (1\text{-}13)
$$

where K_i is the equilibrium constant for component i, and

$$\delta_{ij} = 1, \text{ if } i=j, \quad \delta_{ij} = 0, \text{ if } i \neq j$$

since x_i, x_j are independent variables.

In terms of thermodynamic quantities equation (1-6) can be rewritten in the following form:

$$\begin{vmatrix} (K_1-1) + x_1\frac{\partial K_1}{\partial x_1} - \lambda & x_1\frac{\partial K_1}{\partial x_2} & x_1\frac{\partial K_1}{\partial x_n} \\ x_2\frac{\partial K_2}{\partial x_1} & (K_2-1) + x_2\frac{\partial K_2}{\partial x_2} - \lambda & x_2\frac{\partial K_2}{\partial x_n} \\ x_n\frac{\partial K_n}{\partial x_1} & (K_n-1) + x_n\frac{\partial K_n}{\partial x_n} - \lambda & \underline{x}^\circ \end{vmatrix} = 0$$

(1-14)

A Practical Way of Defining Singular Points

As shown above, for quaternary systems there are four types of singular points, and it would be very difficult and impractical to determine the sign of each eigenvalue from the characteristic equation (1-6). So we would rather take the idea from Sarafimov (47) who divided singular points into positive and negative singular points. Our definition is slightly different from Sarafimov's. We define that the positive singular point is one which has a positive product of eigenvalues for equation (1-6). Stable nodes and positive saddle points are under this term. For a negative singular point we define one which has a negative product of eigenvalues for equation (1-6). Unstable nodes and negative saddle points are under this term. Although such a classification of singular points will not represent the real function of singular points, it can allow us to

determine the type of singular points in a more flexible and convenient fashion.

Under such definition to decide the type of singular points corresponding to the azeotrope of an (n+1)-component mixture, instead of obtaining n eigenvalues from equation (1-6), we only have to evaluate the determinant value of the equation (1-6).

The Explicit Equation for Determining the Type of Various Dimension Azeotropes for an (n+1)-Component Mixture.

The above section clearly classified two main types of singular points which correspond to azeotropes. Each type of singular point depends on the sign of the product of eigenvalues. The following shows the explicit equation which represent the form to decide the type of singular points for different dimension azeotropes in an nth simplex.

1) For a pure component

$$\underline{x}^{\circ} = (0,0,.....0)$$

The product form of eigenvalues is

$$(K_1-1).....(K_n-1)$$

2) For a binary azeotrope

$$\underline{x}^{\circ} = (0,.....0,\ x_n^{\circ})$$

and $K_n = 1$

The product form of eigenvalues is

$$(K_1-1).....(K_{n-1}-1)\ \frac{\partial K_n}{\partial x_n}$$

3) For a kth azeotrope $\underline{x}^\circ = x_1^\circ, x_2^\circ, ...x_{k-1}^\circ, 0, ...0)$

$K_1 = 1, ...K_{k-1} = 1$

equation (1-14) becomes

$$\begin{vmatrix} x_1^\circ\frac{\partial K_1}{\partial x_1} - \lambda & x_1^\circ\frac{\partial K_1}{\partial x_2} & x_1^\circ\frac{\partial K_1}{\partial x_{k-1}} & 0 & 0 & 0 \\ x_2^\circ\frac{\partial K_2}{\partial x_1} & x_2^\circ\frac{\partial K_2}{\partial x_2} - \lambda & & & & \\ x_{k-1}^\circ\frac{\partial K_{k-1}}{\partial x_1} & & x_{k-1}^\circ\frac{\partial K_{k-1}}{\partial x_{k-1}} - \lambda & 0 & 0 & 0 \\ 0 & & 0 & & (K_{n-1}) - \lambda & \end{vmatrix} = 0$$

Since the product of eigenvalues is the determinant of the related function itself, the product form of eigenvalues is

$$\begin{vmatrix} \frac{\partial K_1}{\partial x_1} & \frac{\partial K_1}{\partial x_{k-1}} \\ \frac{\partial K_{k-1}}{\partial x_1} & \frac{\partial K_{K-1}}{\partial x_{k-1}} \end{vmatrix} (K_{k+1}-1)....(K_n-1)$$

4) For the (n+1)th azeotrope, $\underline{x}^\circ = (x_1^\circ, x^\circ_2.....x_n^\circ)$,

The product form of eigenvalues is

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We know that each vertex of a tetrahedron is formed from the intersection of three faces. Each edge is resulting from the intersection of two faces. Using the coupling process defined by Sarafimov (48), we can formulate the following algorithms:

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$$N_1^{(2)} + N_1^{(2)} \rightarrow N_1^{(3)}$$

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The subscripts is the dimension of a singular point, and the superscripts is the dimension of a simplex to which singular points belong. For instance, $N_1^{(2)}$ is a binary azeotrope in a ternary system. Obviously, the above process does not show what we desire the most, the negative singular point or positive singular point. Here we give a more rigorous approach and modify the above process. The modified process allows us a more accessible way to determine the type of singular points for a multicomponent azeotrope.

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The value of K_i, i = 2,3,4, is evaluated at the temperature and composition of the pure component 1, therefore it should not matter whether it is in a ternary system 1-2-3 or a quaternary system 1-2-3-4. After deciding the type of singular point of pure component 1 in 1-2-3 and 1-2-4 (or 1-3-4) we definitely have the type of singular point for pure component 1 in a quaternary 1-2-3-4.

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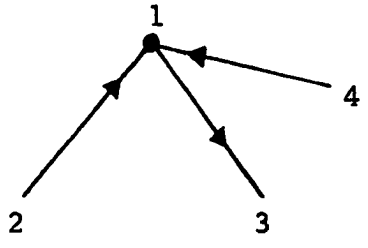

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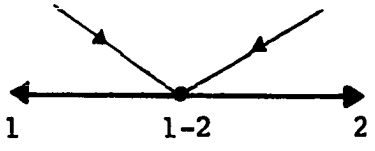

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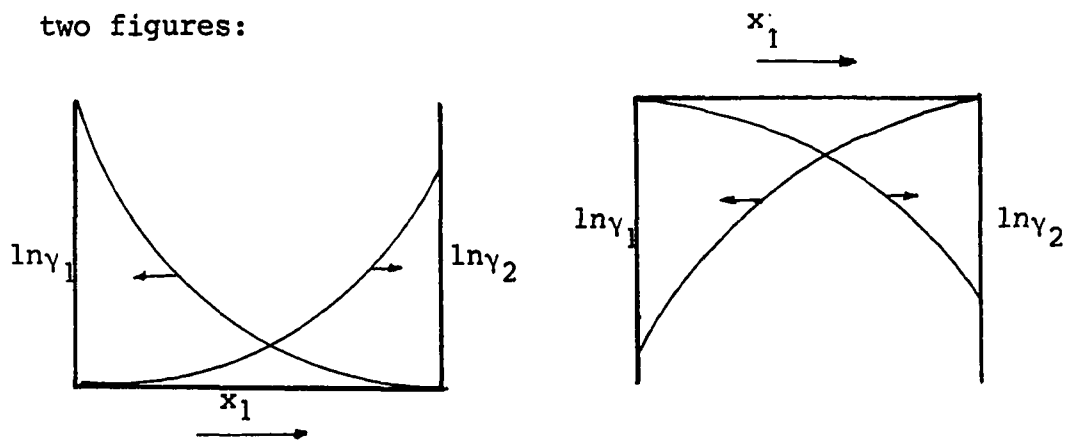

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	Water	1.585	1.809	No	No
ACETONITRILE	Water	2.035	0.688	Min	Min
BENZENE	1-Butanol	1.375	1.493	No	No
	Carbon tetra-chloride	0.083	0.104	No	No
	Chloroform	-0.190	0.617	No	No
	Cyclohexane	0.378	0.019	Min	Min
	Cyclopentane	0.378	1.052	No	No
	Ethanol	1.375	0.053	Min	Min

TABLE 1 (Continued)

Component				Azeotrope	
A	B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Observed	Predicted
BENZENE (Con't)	I-Octane	0.621	0.575	Min	Min
	N-Heptane	0.420	1.587	No	No
	N-Hexane	0.336	0.365	No	No
	Methanol	1.833	0.500	Min	Min
	Methylacetate	0.300	0.767	No	No
	Methylcyclo-hexane	0.434	0.627	No	No
	Methylcyclo-pentane	0.312	0.256	Min	Min
	1-Propanol	1.844	0.698	Min	Min
	2-Propanol	1.603	0.084	Min	Min
	Methanol	1.942	0.500	Min	Min
1-BUTANOL	Methylcyclo-hexane	1.568	0.608	Min	Min
	Toluene	1.269	0.254	Min	Min
CHLOROFORM	Methanol	1.992	0.145	Min	Min
	Methylacetate	-0.526	0.136	Max	Max
	Methyl-ethyl-ketone	-0.827	0.618	Max	Max
	Methyl-iso-butyl-ketone	-1.100	1.889	No	No

TABLE 1 (Continued)

Component				Azeotrope	
A	B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Observed	Predicted
CYCLOHEXANE	Ethanol	1.971	0.071	Min	Min
	Methyl-ethyl-ketone	1.282	0.034	Min	Min
	Methylacetate	1.365	0.770	Min	Min
	2-Propanol	2.481	0.057	Min	Min
	Toluene	0.510	0.933	No	No
2,3-DIMETHYL-BUTANE	Methanol	3.865	0.280	Min	Min
1,4-DIOXANE	Hexene-1	0.821	1.204	No	No
ETHANOL	Ethyl acetate	0.922	0.050	Min	Min
	N-Heptane	2.688	0.628	Min	Min
	N-Hexane	3.248	0.393	Min	Min
	Methanol	0.018	0.564	No	No
	Methylcyclo-pentane	3.166	0.255	Min	Min
	Water	0.981	0.826	Min	Min
ETHYL ACETATE	Methanol	1.038	0.413	Min	Min
	1-Propanol	0.665	0.831	No	No
	2-Propanol	0.452	0.212	Min	Min
	Water	2.780	0.881	Min	Min
ETHYLBENZENE	N-Octane	0.205	0.288	No	No

TABLE 1 (Continued)

Component A	Component B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Azeotrope Observed	Azeotrope Predicted
N-HEPTANE	Methanol	4.620	1.109	Min	Min
	Methyl-ethyl-ketone	1.273	0.588	Min	Min
	I-Octane	0.012	0.024	No	No
	Toluene	0.084	0.360	No	No
N-HEXANE	Hexene-1	0.076	0.087	No	No
	Methylcyclo-pentane	0.012	0.097	No	No
	1-Propanol	1.454	1.210	Min	Min
	1,2,3-trichloro-propane	1.728	3.001	No	No
	Toluene	0.411	1.364	No	No
HEXENE-1	1,2,3,-trichloro-propane	1.002	3.123	No	No
METHANOL	Methylacetate	1.019	0.317	Min	Min
	2-Propanol	-0.078	0.769	No	No
	Toluene	1.970	1.515	Min	Min
	Water	0.569	1.412	No	No
METHYLACETATE	2-Propanol	0.722	1.148	No	No
METHYLCYCLO-PENTANE	Toluene	0.525	1.242	No	No
METHYLCYCLO-HEXANE	1-Propanol	1.512	0.105	Min	Min

TABLE 1 (Continued)

Component				Azeotrope	
A	B	$\lim_{x_1=1} \gamma_2$	$\frac{p_1^o}{760}$	Observed	Predicted
METHYL-ETHYL-KETONE	Toluene	0.309	0.972	No	No
I-OCTANE	Toluene	0.163	0.333	No	No
2-PROPANOL	2,2,4-Tri-methyl-pentane	1.648	0.505	Min	Min

*Subscript indicates the component which has the lower B.P. between components of A and B.

So we can see that with a monotonic change in activity coefficients, the quantity $(\ln\gamma_1 - \ln\gamma_2)$ attains a maximum at points $x_1 = 0$, and $x_1 = 1$, and is equal to $\ln\gamma_1$ and $\ln\gamma_2$, respectively.

Thus an azeotrope is formed, if

$$|\ln\gamma_1|_{x_1=0} > |\ln(p_2/p_1)|_{az} \qquad (1\text{-}17)$$

$$|\ln\gamma_2|_{x_1=1} > |\ln(p_2/p_1)|_{az} \qquad (1\text{-}18)$$

In order to confirm validities of these two conditions, comparisons between predictions and the observed data are given in Table 1. Activity coefficients are evaluated from the Wilson equation. Pure component vapor pressure is obtained from the Antoine equation or Prausnitz equation. Constants of these equations are listed in the Appendix B, C, D.

Empirical Rules to Identify the Type of Singular Points for Pure Component

According to the previous discussion, the type of singular points corresponding to the pure component n has to be decided from the following product:

$$(K_1-1)(K_2-1).....(K_{n-1}-1)$$

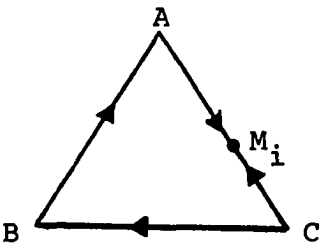
Under the above conditions (1-17, 18), we can show that the

type of singular points can be detected from the following simple rules. The rigorous demonstrations are given in Appendix A.

1. For a ternary system, if the boiling point of a vertex in Gibbs simplex is the lowest one (or the highest one), compared with that of the other two neighbor substances, then this vertex is a node.

2. For a ternary system, if the boiling point of a vertex in a Gibbs simplex is neither the highest one nor the lowest one compared with that of the other two neighbor side substances (azeotrope or pure component), then the vertex is a saddle point.

For example, a Gibbs simplex is shown below and the order of the boiling points are B>A,C>Mi



Since B>A,C so it is a node for component B, and B>A>Mi, so it is a saddle point for component A.

3. For a multicomponent system, if the boiling point of a vertex in an nth dimension simplex is the highest one compared with that of the other (n-1) neighbor substances, then it is a positive singular point for an odd-component system as well as for an even-component system. But if the boiling point of this vertex is the lowest one,

then for an even-component system, it is a negative singular point. For an odd-component system, it is a positive singular point.

4. For a multicomponent system, the vertex is a positive singular point if the number of neighbor substances whose boiling points are higher than that of the vertex is an even number. Similarly, if the number is an odd number, then the vertex is a negative singular point.

CHAPTER II

GENERAL AZEOTROPIC RULES

Now having recognized the type of singular points, we can introduce azeotropic rules. The first azeotropic rule for a ternary system was derived by Gurikov (12) in 1958. This rule was formulated from relations of singular points.

$$N_o + N_1 + 2N_2 = C_1 + 2C_2 + 2 \qquad (2\text{-}1)$$

where N_i, C_i are the numbers of node points and saddle points of (i+1)th dimension azeotrope. In other words, N_o, C_o are the numbers of nodes and saddle points of pure components, N_1, C_1 the numbers of nodes and saddle points of binary azeotropes.

With the relation of $N_o + C_o = 3$ the number of saddle points, C_o, can be added into the equation (2-1) as shown below:

$$(N_o - C_o) + 2(N_1 - C_1) + 4(N_2 - C_2) = 1 \qquad (2\text{-}2)$$

As mentioned previously, there are only two types of singular points for a ternary system, a node and a saddle. To suit the generalization which we use later, we will consider the node to be a positive singular point and the saddle

to be a negative singular point.

Generalization of azeotropic rules has recently derived by Zharov (67) and by Sarafimov (48) independently. Zharove's equation is as follows:

$$\sum_{k=1}^{n} 2^k (N_{k-1}^{+} + C_{k-1}^{+} - N_{k-1}^{-} - C_{k-1}^{-}) = (-1)^{n-1} + 1 \qquad (2\text{-}3)$$

for an (n+1)-component mixture.

Sarafimov obtained his rule as

$$2(G^{+}) + G_b^{+} = 2(G^{-}) + G_b^{-} + 1 + (-1)^{n-1} \qquad (2\text{-}4)$$

where N_{k-1}^{+}, N_{k-1}^{-} (or C_{k-1}^{+}, C_{k-1}^{-}) are numbers of positive and negative nodes (or saddle) representing a kth dimension azeotrope and G_b^{+}, G_b^{-} are the numbers of positive singular points and negative singular points representing azeotropes on the boundary of a concentration simplex, such as pure components, binary azeotropes, or ternary azeotropes of a tetrahedron simplex.

G^{+}, G^{-} are the numbers of positive and negative singular points within a concentration simplex, such as a quaternary azeotrope for a tetrahedron simplex.

Comparison Between Zharov's and Sarafimov's Generalized Azeotropic Rules

From a different point of view, Zharov and Sarafimov

developed their generalized azeotropic rules, which we have shown in equations (2-3) and (2-4). Both of the rules are proved by experimental data. The main difference between their equations is the definition of singular points corresponding to azeotropes in a multicomponent mixture. Zharov (64) classifies a singular point simply from the behavior of solution loci of a set of ordinary differential equations around a corresponding azeotrope. For this point, we have already given a detailed description in the first chapter. By coupling processes, a kth dimension azeotrope of an (n+1) component mixture, or an nth dimension simplex, can be resulted from (n-k) adjoining (n-1)th dimension simplexes. With this additional consideration, Sarafimov gives a more restrictive definition of classifing singular points. Therefore, in addition to saddle and node singular points, there is a complex-type singular point given by Sarafimov. This kind of singular points is a combination of different types of singular points of the adjoining simplexes. For example, a complex-type singular point can be resulted from a saddle-type and a node-type singular points of two adjoining Gibb's simplexes. It is not included in Sarafimov's equation. In order to make this point more clearly, we postulate a quaternary system, 1-2-3-4, characterized by four ternary systems and shown in Figure 3. For each ternary system, the relation between the singular points is held by the azeotropic rule as in equation (2-2). The

number of each type of singular points is shown in the following list

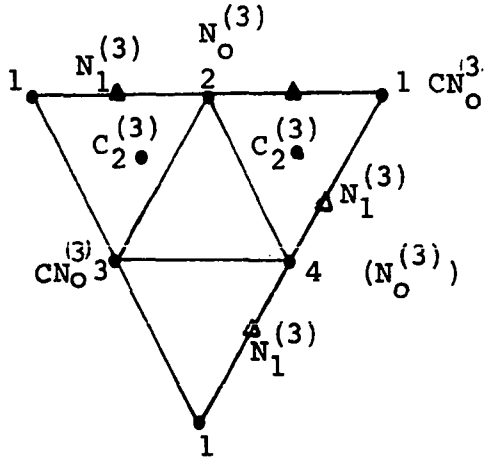


Figure 3. A Quaternary system

TERNARY MIXTURE	TYPE OF SINGULAR POINTS			
	$N_o^{(2)}$	$C_o^{(2)}$	$N_1^{(2)}$	$C_2^{(2)}$
1-2-3	3	0	1	1
1-2-4	2	1	1	1
1-3-4	1	2	1	0
2-3-4	2	1	0	0

Thus singular points of the tetrahedron simplex can be built from the adjoining ternary systems by coupling processes:

For pure components:

Point 1 $C_o^{(2)} + C_o^{(2)} + N_0^{(2)} \rightarrow CN_o^{(3)}$

Point 2 $N_o^{(2)} + N_o^{(2)} + N_o^{(2)} \rightarrow N_o^{(3)}$

Point 3 $N_o^{(2)} + C_o^{(2)} + C_o^{(2)} \rightarrow CN_o^{(3)}$

Point 4 $N_o^{(2)} + N_o^{(2)} + N_o^{(2)} \rightarrow N_o^{(3)}$

For binary azeotropes:

$$\text{Binary 1-2} \quad N_1^{(2)} + N_1^{(2)} \rightarrow N_1^{(3)}$$

$$\text{Binary 1-4} \quad N_1^{(2)} + N_1^{(2)} \rightarrow N_1^{(3)}$$

Thus, we can see that Point 1 is built from two saddle points and one node of three related ternary mixtures. This point is a complex-type singular point, since it is not a combination of the same type of singular points but, rather, is a hybrid. Consequently, it will not be considered in Sarafimov's equation. The Point 2 is from a combination of three nodes. Thus, it will be considered in the equation as a positive or a negative-type singular point, depending on the sign of the determinant.

If the saddle point of the ternary azeotrope 1-2-3 is a negative singular point and of ternary azeotrope 1-2-4 is a positive singular point, same conclusions can be obtained for the above example using either equation. For Sarafimov's equation we have

$$G_b^+ = 3 \text{ and } G_b^- = 3$$

Thus, in order to satisfy the equation, there is no quaternary azeotrope. For Zharov's equation points 1, 2 are considered as positive singular points and points 3, 4 as

negative singular points, according to rules given in the coupling processes section. Therefore, the azeotropic rule is satisfied as:

$$(1 + 1 - 1 - 1) + 2(1 - 1) + 4(1 - 1) = 0$$

and thus no quaternary azeotrope if found.

Generally, for a quaternary system total number of singular points corresponding to pure components which are considered in two equations should be:

For Zharov's equation $\quad G_o^+ + G_o^- = 4.$

For Sarafimov's equation $\quad G_o^+ + G_o^- = 4 - CN_o$,

where CN_o is the number of complex singular points.

For binary azeotropes, since they can be coupled from two neighbor ternary systems, some of them may become complex points, CN_1. Therefore, total number of singular points is:

For Zharov's equation $\quad G_1^+ + G_1^- = M_1.$

For Safarev's equation $\quad G_1^+ + G_1^- = M_1 - CN_1.$

where M_1 is number of binary azeotropes.

A Modified Azeotropic Rule

As we discussed before, if Zharov's equation is used, there are many lengthy and cumbersome calculations to perform in order to distinguish a singular point from four kinds of singular points. For the Sarafimov formula, not all azeotropes in a simplex are included. Some azeotropes, which are saddle-node type singular points, are excluded from his equation. Just like in equation (2-1) a saddle-type pure component, C_o, is not included in the equation. Consequently, applying this equation we have a lot of work to do in order to recognize which azeotrope is ineligible for the equation. To obtain a handy, convenient azeotropic rule, we have to make a slight modification such that it can be handled without involving many calculations and considerations.

What we are going to do is to combine advantages of two equations while keeping their original spirits. We take the Zharov's equation as the basis. Then make the modification on definitions of singular points, for which we have mentioned in the first chapter. So let G^+_{k-1}, G^-_{k-1}, respectively, be the number of $(k-1)$th dimension positive and negative singular points we can have the following modified azeotropic rule:

$$\sum_{k=1}^{n} 2^k (G^+_{k-1} - G^-_{k-1}) = (-1)^{n-1} + 1 \qquad (2\text{-}5)$$

Thus, a more specific expression for a ternary system is:

$$(G_o^+ - G_o^-) + 2(G_1^+ - G_1^-) + 4(G_2^+ - G_2^-) = 1 \qquad (2\text{-}6)$$

and for a quaternary system, it is

$$(G_o^+ - G_o^-) + 2(G_1^+ - G_1^-) + 4(G_2^+ - G_2^-) + 8(G_3^+ - G_3^-) = 0 \qquad (2\text{-}7)$$

Restriction to the Azeotropic Rule

The derivation of the azeotropic rule is based on the assumption that there is only an nth azeotrope for an n-component mixture. Fortunately, this assumption can be applied to the existing systems since there is rarely a case for a mixture to have two azeotropes. Recently, a case was reported for Perfluorobenzene and Benzene system (61).

With this restriction one can write the following inequalities for a ternary system:

$$\begin{aligned} G_o^+ + G_o^- &= 3 \\ G_1^+ + G_1^- &\leq 3 \\ G_2^+ + G_2^- &\leq 1 \end{aligned} \qquad (2\text{-}8)$$

For an (n+1)-component system, we have:

$$\begin{aligned} G_o^+ + G_o^- &= n \\ G_k^+ + G_k^- &\leq {}_nC_{k+1} \qquad k=1,\ldots n-1 \end{aligned}$$

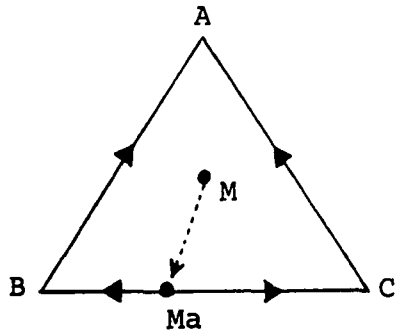
$$G_n^+ + G_n^- \leq 1 \qquad (2\text{-}9)$$

Compatable with Thermodynamic Relations

For all vapor-liquid phase diagrams, the azeotropic rule is satisfied, however, the converse of this statement is not true unless the thermodynamic relation is compatable.

For the phase diagram shown below, where the order of boiling points is

$M > Ma > B, C > A$



the azeotropic rule is satisfied, since

$$(1\text{-}2) + 2(-1) + 4(1) = 1$$

In order for a binary maximum boiling azeotrope to be a saddle point, it has to satisfy the following condition:

$$\left(\frac{\partial K_B}{\partial x_B}\right)_{Ma} (K_A - 1)_{Ma} < 0 \qquad (2\text{-}10)$$

As shown before, for a maximum boiling azeotrope we shall have:

$$\left(\frac{\partial K_B}{\partial x_B}\right)_{Ma} > 0,$$

so to satisfy the inequality of (1-28) it requires $K_A<1$. For an ideal vapor phase, equilibrium constant K_A is shown to be

$$K_A = \left(\frac{\gamma_A P_A}{P}\right)_{Ma}$$

since the boiling point of A is less than that of Ma, at the azeotropic temperature, the vapor pressure of A will be greater than the total pressure. The value of the activity coefficient, γ_A has to be greater than 1. Thus,

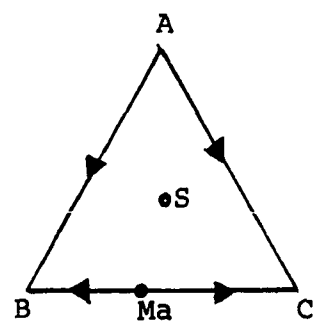
$$K_A = \left(\frac{\gamma_A P_A}{P}\right)_{Ma} > 1$$

This is contradicted by the equation of inequality of (2-11) and therefore we can prove that such a system cannot exist.

Application of the Azeotropic Rule

1) Decide upon a reasonable phase diagram.

With the azeotropic rule, we can judge a reasonable vapor-liquid phase diagram. An example of illustrating distillation lines given by C.H. de Minijer (43) is shown below: A maximum boiling azeotrope, Ma, is formed from component B and C. The order of the boiling points of A, B, C and Ma is B, C < A < Ma



Singular points corresponding to components and binary azeotrope are all positive-type. Consequently, the azeotropic rule cannot be satisfied and the phase diagram is nonexistent. Apparently, a saddle point has to be in the system such that the azeotropic rule can be satisfied as shown as follows:

$$(1 + 1 + 1) - 2(1) + 4(-1) = 1$$

2) To predict the existence of an azeotropy for a multicomponent mixture.

The azeotropic rule states that if the type of each singular point corresponding to an azeotrope on the boundary of an nth dimension simplex, is determined, the existence of an azeotrope of an (n+1)-component mixture can be induced by whether the rule is satisfied.

Therefore, for a ternary system, if the type of singular points corresponding to pure components or binary azeotropes, are declared, then the following results can be shown:

$(G_o^+ - G_o^-) + 2(G_1^+ - G_1^-)$	Type of Ternary Azeotrope
5	saddle point
-3	maximum or minimum
1	no

From the above criterion, we have the azeotropic rule against the experimental data. Results are shown in Table 3.

The type of a singular point corresponding to a pure component is evaluated from the empirical rules mentioned before. For binary azeotropies, the azeotropic temperature and composition are found from the available literatures (19, 20). Wilson constants are also from the published references and listed in Appendix C. Table 2 gives the numerical data to show that for an i-j minimum boiling azeotrope,

$$\frac{\partial K_i}{\partial x_i} < 0$$

and for an i-j maximum boiling binary azeotrope,

$$\frac{\partial K_i}{\partial x_i} > 0$$

By a coupling process we can also demonstrate that the experimental data is fitted for two quaternary systems and results are shown in Table 4.

3) To sketch distillation fields and products regions.

It has been known that the existence of azeotropes causes various distillation behavior for different types of ternary systems. Ewell and Welch (7) have presented experimental facts to show that the overproduct of a batch distillation process will be dependent on the feed location in a phase diagram. Recently, Petlyuk (36) gave a detailed description of the distillation product regions and fields for different types of ternary mixtures. We shall use the

TABLE 2. Maximum Azeotropes Have Positive $\partial K/\partial x$ and Minimum Azeotropes Have Negative $\partial K/\partial x$

Component A	Component B	$\frac{\partial K_A}{\partial x_A}$	$\frac{\partial K_A}{\partial x_B}$	Observed Azeotrope
ACETONE	Chloroform	0.874	0.492	Max
	Carbon tetra-chloride	-1.434	-0.495	Min
	Cyclohexane	-0.772	-2.269	Min
	Methanol	-0.262	-1.060	Min
	Methylacetate	-0.108	-0.134	Min
	N-Heptane	-2.568	-0.847	Min
	2,3-Dimethyl-butane	-1.314	-1.410	Min
BENZENE	1-Butanol	-1.102	-0.704	Min
	Chloroform	-1.954	-1.249	Min
	Carbon-tetra-chloride	-0.307	-0.355	Min
	Cyclohexane	-0.334	-0.386	Min
	Methanol	-0.027	-0.017	Min
	2-Propanol	-1.023	-1.577	Min
	Ethanol	-1.283	-1.578	Min
	Methanol	-1.917	-1.225	Min
	Methylcyclo-pentane	-0.493	-0.055	Min
	1-Propanol	-0.790	-2.987	Min
	Methylcyclo-hexane	-0.631	-2.387	Min
BUTANOL	Toluene	-1.406	-0.824	Min
CHLOROFORM	2,3-Dimethylbutane	-0.488	-0.312	Min
	Methanol	-0.976	-1.815	Min
	Methylacetate	0.479	0.967	Max
CYCLOHEXANE	Ethanol	-1.591	-1.981	Min
	Methanol	-2.57	-1.597	Min
	Methylacetate	-12.67	-0.71	Min
	2-Propanol	-1.248	-1.806	Min
	MEK	-0.281	-0.36	Min
ETHANOL	Ethylacetate	-0.891	-0.765	Min
	Hexane	-2.8	-1.392	Min
	Methylcyclopentane	-2.329	-1.418	Min
	Water	-1.31	-2.893	Min
ETHYLBENZENE	Methanol	-1.872	-0.487	Min
	2-Propanol	-0.601	-0.349	Min
	Water	-0.310	-2.893	Min

TABLE 2 (Continued)

Component A	Component B	$\frac{\partial K_A}{\partial x_A}$	$\frac{\partial K_A}{\partial x_B}$	Observed Azeotrope
ETHYLACETATE	Methanol	-1.663	-0.432	Min
	Water	-1.31	-2.897	Min
HEPTANE	Methanol	-2.749	-0.828	Min
	Toluene	-0.366	-0.097	Min
HEXANE	Methylayclopentane	-0.002	-0.007	Min
	1-Propanol	-0.15	-2.514	Min
METHANOL	Methylacetate	-1.267	-0.71	Min
	Toluene	-0.543	-3.478	Min
	Water	-0.666	-1.386	Min
	2,3-Dimethylbutane	-2.423	-1.628	Min
MEK	2-Propanol	-0.346	-0.612	Min
	Water	-1.252	-2.456	Min
2-PROPANOL	Water	-0.666	-1.386	Min

TABLE 3. Confirmation of Azeotropic Rule for Ternary Systems

System			Number of Singular Point N_o	C_o	N_1	C_1	Predicted Azeotrope	Observed Azeotrope	(Ref.)
Acetone	Benzene	Chloroform	3	0	0	1	No	No	(20)
Acetone	Benzene	Carbon tetra-chloride	1	2	1	0	No	No	(18-58)
Acetone	Benzene	Cyclohexane	2	1	1	1	No		
Acetone	Benzene	Ethanol	3	0	0	1	No		
Acetone	Benzene	Methanol	2	1	1	1	No		
Acetone	Benzene	Methylacetate	1	2	1	0	No		
Acetone	Benzene	N-Pentane	1	2	1	0	No		
Acetone	Benzene	2-Propanol	3	0	0	1	No		
Acetone	Carbon tetra-chloride	Methylacetate	2	1	1	1	No		
Acetone	Chloroform	MEK	3	0	0	1	No	No	(18)
Acetone	Chloroform	2,3 DMB	1	2	2	1	No	No	(56)
Acetone	Chloroform	Methanol	1	2	3	0	Saddle	Saddle	(20)
Acetone	Chloroform	MEK	2	1	1	1	No	No	(20)
Acetone	Cyclohexane	Ethanol	2	1	1	1	No		
Acetone	Cyclohexane	Methylactate	2	1	1	1	No		
Acetone	Cyclohexane	2-Propanol	2	1	1	1	No		
Acetone	2,3 DMB	Methanol	3	0	0	3	Min or max	Min	(56)
Acetone	Ethanol	Methanol	1	2	1	0	No	No	(20)

TABLE 3 (Continued)

System			Number of Singular Point N_o	C_o	N_1	C_1	Predicted Azeotrope	Observed Azeotrope	(Ref.)
Acetone	Ethanol	Water	3	0	0	1	No	No	(20)
Acetone	Methanol	Methylacetate	3	0	0	3	Min or max	Min	(20)
Acetone	Methanol	2-Propanol	1	2	1	0	No		
Acetone	Methanol	Water	1	2	1	0	No		
Acetone	Methylacetate	2-Propanol	1	2	1	0	No		
Acetone	MEK	2-Propanol	3	0	0	1	No		
Acetone	MEK	Water	3	0	0	1	No	No	(20)
Acetone	2-Propanol	Water	3	0	0	1	No	No	(20)
Benzene	1-Butanol	Toluene	2	1	0	1	No		
Benzene	Chloroform	Methylacetate	3	0	0	1	No	No	(18-37)
Benzene	Chloroform	Methanol	2	1	1	1	No		
Benzene	Carbon tetrachloride	Cyclohexane	3	0	0	1	No		(57)
Benzene	Cyclohexane	Methanol	3	0	1	2	No	No	(20)
Benzene	Cyclohexane	Methylacetate	3	0	0	1	No	No	(18-39)
Benzene	Cyclohexane	2-Propanol	3	0	0	3	Min or max	Min	(20)
Benzene	Cyclohexane	Ethanol	3	0	0	3	Min or max	Min	(20)
Benzene	Ethanol	n-Hexane	2	1	1	1	No	No	(20)
Benzene	Ethanol	n-Heptane	2	1	0	2	Min or max	Min	(20)
Benzene	Ethanol	Methanol	2	1	1	1	Min or max	Min	(20)
Benzene	Ethanol	Methylcyclopentane	2	1	1	1	No		

TABLE 3 (Continued)

System			Number of Singular Point N_o	C_o	N_1	C_1	Predicted Azeotrope	Observed Azeotrope	(Ref.)
Benzene	n-Hexane	Toluene	2	1	1	1	No		
Benzene	n-Hexane	1-Propanol	2	1	1	1	No		
Benzene	Methanol	2-Propanol	2	1	1	1	No		
Benzene	Methanol	Toluene	2	1	1	1	No		
Benzene	Methylacetate	2-Propanol	3	0	0	1	No		
Benzene	Methylcyclo-hexane	1-Propanol	2	1	1	1	No		
Benzene	n-Heptane	Methanol	2	1	2	0	Saddle		
Chloroform	2,3 DMB	Methanol	3	0	1	2	No		(56)
Chloroform	Methanol	Methylace-tate	1	2	3	0	Saddle	Saddle	(20)
Chloroform	Ethylacetate	Methanol	1	2	0	3	Min or Max	Min	(18)
Cyclohexane	Ethanol	n-Hexane	2	1	1	1	No		(18-38)
Cyclohexane	Ethanol	Methylcyclo-pentane	2	1	1	1	No		
Cyclohexane	Methanol	Methylace-tate	3	0	0	3	Min or max		
Cyclohexane	Methanol	2-Propanol	2	1	1	1	No		
Cyclohexane	Methanol	Toluene	2	1	1	1	No		
Cyclohexane	MEK	2-Propanol	3	0	1	1	No		
Cyclohexane	MEK	Toluene	1	2	1	0	No		

TABLE 3 (Continued)

System			Number of Singular Point N_o	C_o	N_1	C_1	Predicted Azeotrope	Observed Azeotrope	(Ref.)
Cyclohexane	Methylacetate	2-Propanol	3	0	1	2	No		
Ethylbenzene	Methanol	2-Propanol	2	1	1	1	No		
Ethylbenzene	Methanol	Water	2	1	1	1	No		
Ethanol	Ethylacetate	Methanol	2	1	1	1	No		
Ethanol	Ethylacetate	Water	3	0	0	3	Min or max	Min	(19)
Ethanol	Methanol	Water	3	0	0	1	No	No	(20)
Ethanol	n-Heptane	Methanol	2	1	1	1	No		
Ethanol	n-Hexane	Methylcyclo-pentane	3	0	1	2	No		
Methanol	2-Propanol	Water	3	0	0	1	No	No	(20)
Methanol	Methylacetate	2-Propanol	1	2	1	0	No		
MEK	2-Propanol	Water	3	0	0	3	Min or max	Min	(20)
n-Heptane	MEK	Toluene	3	0	0	1	No	No	(19)
n-Heptane	Methanol	Toluene	2	1	1	1	No		

TABLE 4. PREDICTION OF A QUATERNARY AZEOTROPE

1. Benzene(1)-Chloroform(2)-Methanol(3)-Methylacetate(4)

COMPONENT	TYPE OF SINGULAR POINT
Benzene	G_o^+
Chloroform	G_o^-
Methanol	G_o^+
Methylacetate	G_o^+
1-3 Azeotrope	G_o^-
1-4 Azeotrope	G_1^-
2-3 Azeotrope	G_1^-
2-4 Azeotrope	G_1^+
3-4 Azeotrope	G_1^+

Since by azeotropic rule, we have,

$$(1 - 1 + 1 + 1) + 2(-1 - 1 - 1 + 1 + 1) = 0$$

So there is no quaternary azeotrope.

TABLE 4. PREDICTION OF A QUATERNARY AZEOTROPE (CONTINUED)

2. Benzene(1)-Ethanol(2)-Hexane(3)-Methylcyclopentane(4)

COMPONENT	TYPE OF SINGULAR POINT
Benzene	G_o^+
Ethanol	G_o^+
hexane	G_o^-
Cl-cyclo-C5	G_o^+
1-2 Azeotrope	G_1^-
1-4 Azeotrope	G_1^-
2-3 Azeotrope	G_1^-
2-4 Azeotrope	G_1^+
3-4 Azeotrope	G_1^+

Since by azeotropic rule, we have,

$$(1 + 1 - 1 + 1) + 2(-1 - 1 - 1 + 1 + 1) = 0$$

So there is no quaternary azeotrope.

separation of a ternary mixture, which has two binary azeotropes and one ternary azeotrope, as an example. Figure 4 shows the diagram which contains four regions; A-C_2-N_3, C_2-N_3-B, A-C_2^1-N_3, and B-C-C_2^1-N_3. Because of restrictions of material balances, the prospect product corresponding to feed F in each region is shown in the shadow area. Adjusting a proper reflux ration, feed location, etc., we can obtain a specific distillation routine such that a ternary azeotrope, N_3, as the overproduct, and C_4 at the bottom product. We can also have B as the bottom product and C_3 as the overproduct. The same process can be applied to C_2^1 and C_5. Before designing the column for a nonideal solution separation, a sketch of product regions of a phase diagram is required. That is determined by the azeotropic rule.

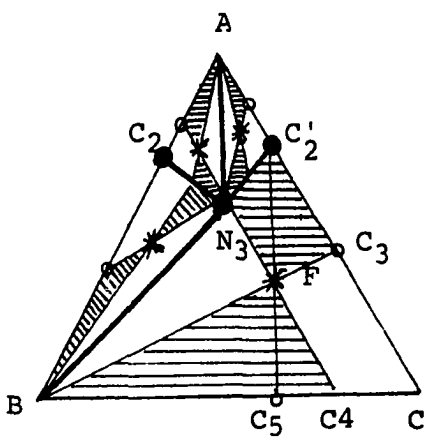


Figure 4. Diagram Showing Product Regions for an Azeotropic Separation Process.

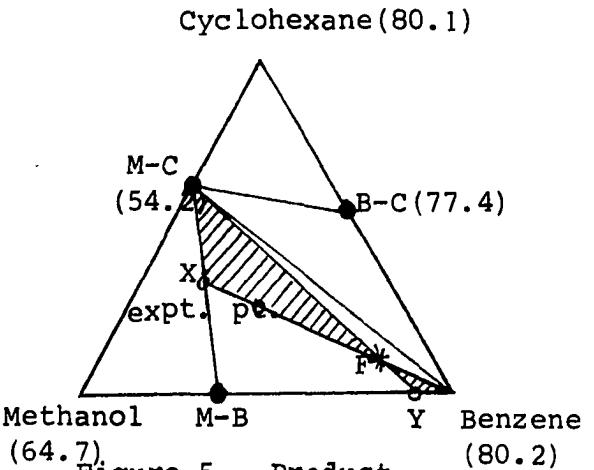


Figure 5. Product Region Diagram for Methanol-Cyclohexane-Benzene.

Methanol-Cyclohexane-Benzene Case

Let us take a look at a practical example which is from Figure 11-19 of Smith's book (58). A ternary system of methanol, cyclohexane and benzene consists of three binary azeotropes. Their boiling points are shown in the Figure 5. To satisfy the azeotropic rule, there are two possible cases; a. the existence of a saddle ternary azeotrope or b. no ternary azeotrope at all. Smith presumed that a saddle point existed in the system, then hypothesized a ridge be across the diagram from the methanol corner toward the opposite side. Under such an interpretation, an overhead product is predicted to be in the diagram, but not on the methanol-cyclohexane side. This supposition is supported by a report of Ratliff and Strogel (41).

Unfortunately, this is not the whole story. There is actually no such ridge. Calculations show that binary azeotropes of cyclohexane-benzene (C-B) and of methanol-benzene (M-B) are the negative-singular point-type azeotropes. Methanol-cyclohexane (M-C) belongs to the positive-singular-point type azeotrope. Therefore, from the azeotropic rule, there is no ternary azeotrope in this system. This result is supported by the Horsley's data (20).

Now, how can we explain Ratliff and Strogel's report? The fact is interpreted as the following by refering to Figure 5. There are four different distillation regions

separated by lines of (M-B) to (M-C), B to (M-C) and C-B) to (M-C). Because of the restriction of material balances, the possible products of feeds in the region of B-(M-C)-(M-C) will be located in the shadow area. Thus, with pure benzene as a bottom product, the overhead product has to be point X. This is what Smith predicted; the overhead product is somewhere in the diagram. Apparently, the cause for this result is not from a ridge of methanol to (C-B), but of (M-B) to (M-C). The figure also shows that stages in the Ratliff and Strogel column is not enough to have overproduct reach the point X. We may have another operation policy for this column; if the overhead product is desired to be (M-C), then the bottom product will be point Y, which is on the methanol-benzene side. From this example, we can be more sensitive about the importance of the azeotropic rule for judging distillation behaviors of a nonideal solution, and for having a good distillation policy to design a desired tower.

A General Scheme of Predicting a Multicomponent Azeotrope Based on Binary Data

Wilson Equation

The Wilson equation has been proved to be very accurate in predicting the behavior of nonideal behavior of a multicomponent system (33, 18, 22). Based on binary data, it can be applied to predict an azeotropic temperature and

composition, as well as to decide its type of singular point. This equation is shown below and constants of $(\lambda_{ij} - \lambda_{ii})$, $(\lambda_{ij} - \lambda_{jj})$ for several binary systems are summarized in Appendix C.

$$\ln\gamma_i = 1 - \ln \sum_{j=1}^{n} x_j G_{ji} - \sum_{j=1}^{n} \frac{x_j G_{ij}}{\sum_{k=1}^{n} G_{kj} x_k}$$

where

$$G_{ij} = \frac{v_j^L}{v_j^L} \exp\left[-(\lambda_{ij} - \lambda_{ii})/RT\right]$$

v^L = molar volume c.c./gmole

A General Scheme of Predicting a Multicomponent Azeotrope

A general scheme is summarized as follows:

1. For all binary systems, apply azeotropic formation conditions to predict the existence of a binary azeotrope. Then find the azeotropic temperature and composition by solving the following simultaneous equations:

$$\sum_{i=1}^{n} x_i = 1$$

$$P = \gamma_i x_i p_i \qquad i=1,\ldots n \qquad (2\text{-}12)$$

2. where p_i: the vapor pressure of component i

   γ_i: the activity coefficient of component i

   P : system pressure

3. Determine the type of singular points corresponding to binary azeotropes. Then we can predict the existence of a ternary azeotrope for all ternary mixtures involved in a multicomponent system.
4. Find the ternary azeotropic temperature and composition by solving equations (2-12). If the azeotrope is found to be at a maximum or minimum, we can decide the sign of determinant of $|\partial K/\partial x|$ by its natural property, otherwise by calculations.
5. For a quaternary system, by coupling processes, determine the type of singular point corresponding to binary azeotropes and pure components. With the calculation value of (K_i-1) and results of Step 3, decide the type of singular points corresponding to ternary azeotropes. Then the existence of a quaternary azeotrope can be induced from the azeotropic rule.
6. Repeat the same procedures as Step 3, and 4, but this time determine the type of singular points which correspond to pure components, binary azeotropes...to (k-2)th dimension azeotropes by coupling processes. With the calculation or the natural properties determine the singular points corresponding to the kth dimension azeotropes, then the existence of a (k+1)th azeotrope can be found from the azeotropic rule. For programming the above purpose, the following problems have to be considered:

1. How can we let the computer find out all binaries, ternaries, etc.?
2. How can it index the binary azeotropes for ${}_nC_2$ binaries, and the ternary azeotropes for ${}_nC_3$ ternaries?

For the first problem, we have shown a solution in a later section which deals with the liquid-liquid calculation. The approach is to index each component of a mixture as the number starting from 1 and the combination of these index numbers is always in the order of magnitude of the index number. That is, we can have 4-5 binary but no 5-4 binary.

With the result from the first problem, we can assign each azeotrope a number, Ix, from the following formula. This is believed to be the most reasonable approach to the second problem.

For a binary azeotrope I - J

$$Ix = \sum_{m=1}^{I-1} (n-m)\ C_1 + (J-I)$$

so for (4-5) binary azeotrope in a six-component system, it gives

$$Ix = 5 + 4 + 3 + (5-4) = 13$$

For a ternary azeotrope I - J - K

$$Ix = \sum_{m=1}^{I-1} (n-m)\ C_2 + \sum_{m=I+1}^{J-1} (n-m)\ C_1 + (K-J)$$

and for a nth azeotrope (I, J,.....K, L, M)

$$Ix = \sum_{m=1}^{I-1} (n-m)C_{n-1} + \sum_{m=I+1}^{J-1} (n-m)C_{n-2} + \ldots.$$
$$+ \sum_{m=K+1}^{L-1} (n-m)C_{1} + (M-L)$$

where

$$NC_i = \frac{N!}{(N-i)!i!}$$

The Possible Extension of Azeotropic Rule to the Heterogeneous Phase

The azeotropic rule is given for homogeneous vapor-liquid phase systems. However, there is the possibility of extending it to the heterogeneous phase. Solokov (54) has shown that if the overall liquid composition of the heterogeneous phase is considered as the liquid phase in the homogeneous region, the behavior of distillation loci around the heterogeneous binary or the ternary azeotrope, is quite similar to that of the homogeneous phase. Zharov (67) presents a general azeotropic rule for a solid-liquid-vapor three phase system. Its form is similar to that which we introduced before for a two phase system. Therefore, it is not very difficult to extend the azeotropic rule to the heterogeneous phase. The question, for most of the heterogeneous phases is: Is there a unique azeotrope for a mixture? Probably the answer is negative, since C.H. de Minijer (42)

has shown that there are two azeotropes in the heterogeneous phase of water-chloroform-acetone system. Anyway, for the further investigation of the aspects of the heterogeneous phase, it is still worthwhile for us to pay attention to these references.

Predicting the temperature and compositions for a heterogeneous phase becomes more complicated than for the homogeneous azeotrope. A generalization of the Gibbs-Konovalow theorems (39) has to be used to describe the azeotropic state, in addition to the standard equilibrium relation between phases and stoichiometry relations for each phase. So, for an n-component mixture, there are

$$\sum_{i=1}^{n} x_i^I = 1$$

$$\sum_{i=1}^{n} x_i^{II} = 1$$

$$\sum_{i=1}^{n} y_i = 1$$

$$\gamma_i^I x_i^I = \gamma_i^{II} x_i^I \qquad i=1,\ldots n$$

$$y_i = K_i^I x_i^I \qquad i=1,\ldots n$$

and n-2 indifferent conditions.
to 3n composition variables and one temperature variable.

Conclusions

Since the general azeotropic rule has been developed, it was ignored in the U.S.A. No papers have appeared on the related topics, yet its application to nonideal solution

separation has been increased by the U.S.S.R. scientists. A recent paper on the general review of separation processes design (29) clearly indicates that the azeotropic rule plays one of the most essential roles to the nonideal solution separation. Upon its great merit for building a reasonable nonideal solutions phase diagram, we are able to profile the distillation fields and product regions, from whence a desired operation policy can be made. Thus, we have the intention of introducing this general rule and its related background. Meantimes, to allow its application to a general computer-oriented design basis, we made modifications such that the type of singular points for each azeotrope can be done in a more accessible fashion and computational efforts can be reduced to a minimum. These modifications are on both an empirical and a rigorous thermodynamic basis. These include the following items:

1. Revise the classification of singular points, such that Zharov's general azeotropic rule can be used straightforwardly without any consideration.
2. Modify the coupling processes, so for predicting the existence of a $(k+1)$th dimension azeotrope, determinations of singular points corresponding to pure components, to $(k-1)$th dimension azeotropes can be decided without further calculation.
3. Formation conditions of binary azeotropes are introduced, such that empirical simple rules are set up

and the type of a singular point corresponding to a pure component can be decided from the relation of its boiling point with that of its neighbor components without any numerical efforts.

4. Relations between the type of singular points and thermodynamic quantities have been shown plainly. Conditions of forming minimum or maximum boiling azeotropes are introduced. Thus sign of its determinant of $|\partial K/\partial x|$ can be observed.

Further work to compare the observed data with predictions from the binary azeotropic conditions and from the azeotropic rule for ternary and quaternary azeotropes lead us to a more firm recognition of these rules. In a later section, a general scheme to program the azeotropic rule for a multicomponent azeotrope is sketched. The possibility of a heterogeneous azeotropic rule is also mentioned.

CHAPTER III

LIQUID-LIQUID EQUILIBRIUM CALCULATION

Introduction

Liquid-liquid calculation is a difficult problem in process designs. It involves a rather complicated activity coefficient equation which is highly composition-dependent like the Renon equation. Many articles have appeared on this topic, most of them are based on the thermodynamic criterion of equilibrium, which states each component activity of an n-component mixture is the same in all of the present phases, and on the stoichiometry relations in each phase. That is, for two phases;

$$(x_i\gamma_i)^I = (x_i\gamma_i)^{II} \qquad i=1,\ldots,n \tag{3-1}$$

$$\sum_{i=1}^{n} x_i^I = 1 \tag{3-2}$$

$$\sum_{i=1}^{n} x_i^{II} = 1 \tag{3-3}$$

To solve the above equations, (n-2) composition values have to be arbitrarily set, and the rest (n+2) composition values in two phases are solved through various mathematical programming methods. This type of algorithm is exhibited in

recent works, such as the LSQ2 method by J. M. Marina and D. P. Tassios (30), Powell's method by C. G. Guffey and A. H. Wehe (14), and the Newtonian-Rapheson method by G. Cohen and H. Renon (5). These methods are mainly used to compare experimental data with predictions based on binary data. Therefore, we cannot argue that these methods are not applicable to realistic design problems, even though some of the above authors (14) claim that their method is very efficient. In a realistic problem, we always have overall liquid compositions instead of liquid compositions in one phase. To apply one of the above methods, we have to guess (n-2) compositions prior to calculation. Undoubtedly, such guesses are not feasible. Therefore, a different approach was formulated to eliminate these inconvenient guesses. A variable, ϕ, was introduced to account for the split fraction of the total feed into liquid phase I. Thus a material balance gives:

$$z_i^F = \phi x_i^I + (1-\phi)x_i^{II} \qquad i=1,\ldots,n \qquad (3\text{-}4)$$

where z_i^F is the overall liquid composition of component i. Yang (63) has derived a method based on this similar concept for a ternary system. By using ϕ, x_1^I, x_2^I, as the unknown variables, x_1^{II}, x_2^{II} can be found from material equation (4). From equations (2) and (3), x_3^I, x_3^{II} can be found. A mathematical programming method, called the Broyden method (3),

is then used to solve equation (1). This method is not always reliable because the activity coefficients γ_i^I and γ_i^{II} are exponential functions of the mole fractions and x_i^I, x_i^{II} respectively. Function values of equation (3-1) will be very sensitive to the minor changes of x_i^I. Introducing x_i^I to be unknown variables to solve the equations, we will find adjustments of x_i^I are unstable and uncontrollable according to residue of equation (3-1). Thus a calculation is always interrupted, as x_i^I is out of feasible values.

Realizing that convergence might become more difficult and much computation effort would be spent if the above proposed method is applied to a quaternary or highly component system, we become interested in a method which can avoid introducing compositions as main iterative variables. Such an approach will lead to a promising, reliable, and stable liquid-liquid equilibrium calculation algorithm for multicomponent systems. By such a method, the dimension of a problem will not be increased with the increased number of components in mixtures and the system calculation will not be interrupted because of infeasibility of composition values. This method was introduced by Null (34) in his book. The main scheme of the method is to combine equation (1) with equation (4), then we have

$$x_i^{II} = \frac{x_i^F}{1+(\beta_i-1)\phi} \qquad (3\text{-}5)$$

where the distribution factor, $\beta_i = \gamma_i^{II}/\gamma_i^{I}$.

Thus, if two liquid phases exist, we must find a solution to the equation for which

$$\sum_{i=1}^{n} x_i^{II} = 1$$

Null's method can be outlined as following:

1) Assumed values of x_i^I, and $\phi = 0.5$.
2) Obtain x_i^{II} from equation (4).
3) Evaluate values of activity coefficients γ_i^I, γ_i^{II}.
4) Find x_i^I from equilibrium relations; i.e. $x_i^I = \beta_i\, x_i^{II}$.
5) Normalize x_i^I, and recalculate γ_i^I.
6) Obtain x_i^{II} from equation (5).
7) Repeat step (4) to step (6) until the x_i^{II} value before step (6) agrees with the values obtained in step (6).
8) Adjust value ϕ and repeat steps (4) to (7) until the sum of the x_i^{II} values becomes unity.

The value of ϕ is adjusted according to the Newton-Rapheson method by letting

$$f = \sum_{i=1}^{n} x_i^{II} - 1$$

and neglecting dependence of β_i on composition, i.e.,

$$\frac{\partial f}{\partial \phi} = \sum_{i=1}^{n} \frac{dx_i^{II}}{d\phi} = - \sum_{i=1}^{n} \frac{(x_i-1)x_i^{I}}{[1+(\beta_i-1)\phi]^2}$$

so the successive estimate of ϕ is

$$\phi_{new} = \phi_{old} - \frac{\phi f}{df/d\phi} \qquad (3\text{-}6)$$

Obviously, Null's method is very stable for multicomponent systems, since there is only one explicit adjusted variable, ϕ, to satisfy equation (3-3), and the composition is only evaluated by a direct substitution method during the inner loop. Also, in the mathematical sense, a one-dimensional problem is much easier to trace to its solution than a multidimensional problem.

The disadvantage of Null's method is its inefficient convergence. There are two facts accounting for this discrepancy; a) before composition becomes consistent during the inner loop, too much computation time is spent on activity coefficients evaluation for each component of both liquid phases, and b) each successive value of the fraction variable, ϕ, is estimated by the approximate first derivatives where the distribution factor is assumed to be independent of composition. Table 5 and Figure 6 show the inefficient way to adjust the variable following the typical Null's method.

In this chapter we establish an efficient, reliable,

and economic liquid-liquid calculation method based on Null's main concept. The efficiency of the method compares well with that of the methods mentioned previously. The method is reliable even with the ill-conditioned initial values. Amounts of the computer memory of this method can be reduced to n^2 times order, where n is number of components in a mixture.

Fifteen ternary type II mixtures, two ternary type I mixtures, five quaternary mixtures, three five-component mixtures, and one six component mixtures, where the Renon constants can be found in the literature, are used to test the validity of the proposed method. At least ten calculations are performed for each mixture; thus, about two hundred calculations are executed using this method without any difficulty or computer system trouble. The thermodynamic stability conditions are used to check calculation results. It is found that predictions from these conditions are consistent with the calculation results. Therefore these classic thermodynamic stability conditions are highly recommended for liquid-liquid calculations. The unnecessary calculations can be skipped in case one liquid phase condition is identified. On the other hand, it can help us to assure whether a solution is trivial. To coincide with the general scheme of nonideal solution process calculations, for which we will mention later, the algorithm is totally changed from the Null's method.

TABLE 5. A Comparison of Efficiency Between Null's Method and the Modified Method
T = 289.16°K

Null's Method		The Modified Method	
ϕ	$1-\Sigma x_i^{II}$	ϕ	$1-\Sigma x_i^{II}$
0.5	-0.1272	0.5	-0.1272
0.6707	-0.9808 E-1	0.6707	-0.9898 E-1
0.7368	-0.7662 E-1	0.8732	0.4902 E-1
0.7769	-0.6197 E-1	0.8058	-0.4963 E-1
0.8033	-0.4921 E-1	0.8397	-0.1956 E-1
0.8208	-0.3770 E-1	0.8618	0.176 E-1
0.8325	-0.2733 E-1	0.8513	-0.4601 E-2
0.8400	-0.1897 E-1	0.8535	+0.6933 E-3
0.8449	-0.1271 E-1	0.8532	-0.9405 E-3
0.8479	-0.8325 E-2	0.8534	<0.1 E-3
0.8499	-0.5367 E-2		

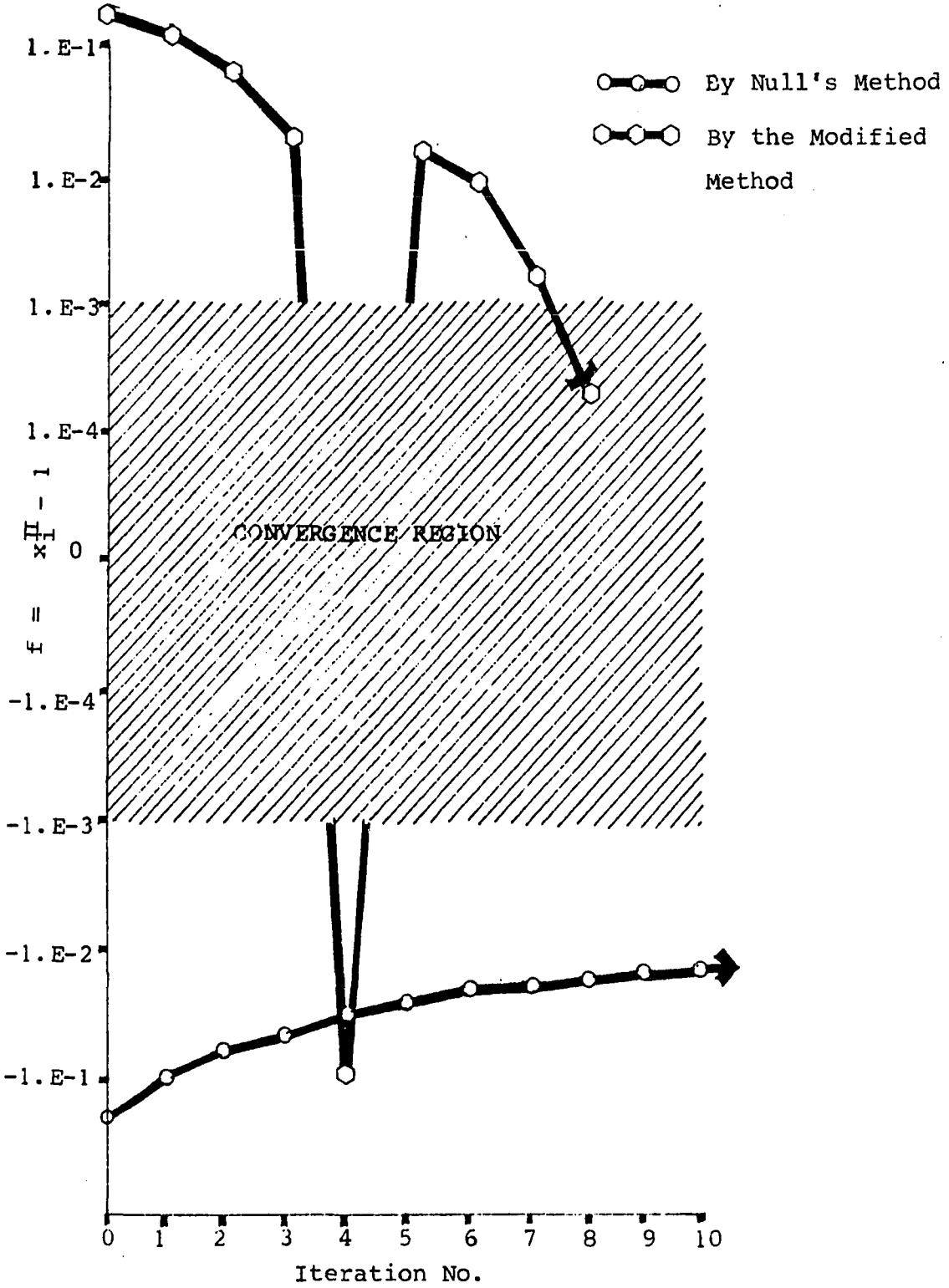


Figure 6 Comparisons of Null's Method and the Modified Method

Description of Calculation Method

The configuration of our method is the Figure 7.

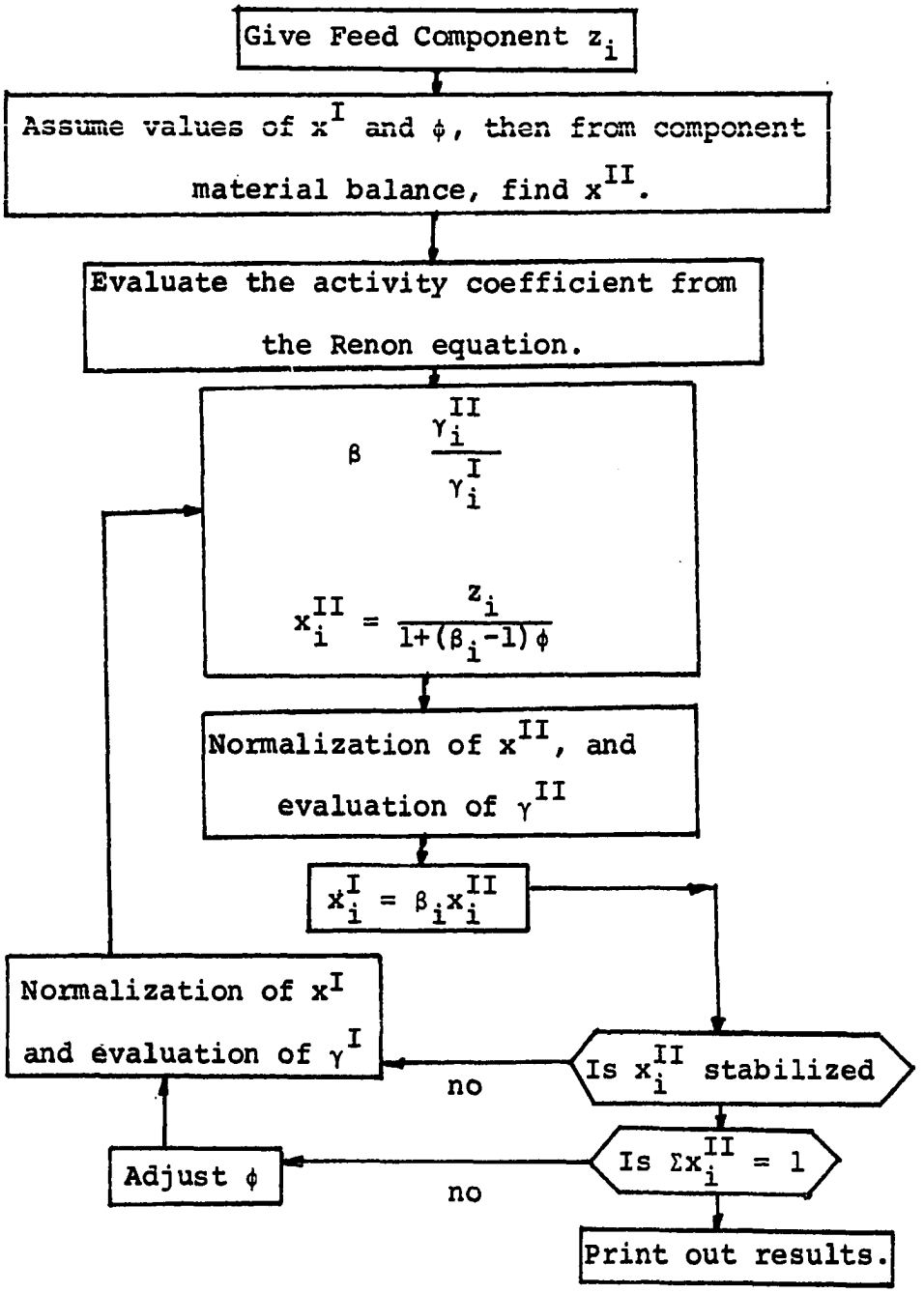


Figure 7 General Scheme for a proposed Liquid-Liquid Equilibrium Calculation Algorithm.

Obviously, the key points for an efficient method rely on the following arguments: 1) how to make x_i^{II} become stabilized efficiently during an inner loop, and 2) how to adjust the main variable ϕ of the outer loop.

a) Inner Loop Stabilization Algorithm

Because the activity coefficient value is too sensitive to a minor change of composition values, the direct substitution method is found to be the most stable method to make composition x_i^{II} become constant during the inner loop. The method, however, is not very efficient in terms of the required number of activity coefficient evaluations. It always takes more than ten activity coefficient evaluations before composition values approach constants.

Nevertheless, we still have to find other althernatives to overcome this basic discrepancy. There are two schemes in our method; a) When the variable ϕ is far from the real solution, we found a strict convergence criterion for the inner loop calculation is unnecessary, since it does not affect final results to any great extent. Therefore, we divide the calculation into two parts, a rough and a finer inner loop calculation. The rough inner loop calculation is used at the first several iterations when the variable is not close to the real solution. At this calculation, either activity coefficient evaluations is limited, regardless whether composition values are constants, or a rough criterion is given.

When the variable ϕ is found to be close to the solution, a finer inner loop calculation is taken, assuring that the composition difference before and after step (6) is not off more than 0.1%. b) We found that a better initial estimate of composition values can greatly reduce the number of activity coefficient evaluations needed for the composition values to approach constants. A linear interpolation is used to find the estimate of the current composition value from that of the previous two iterations. For each component this linear relation between compositions of two different split fraction variables is very accurate, especially when the variable is close to the solution. Figure 9 demonstrates this fact. The composition of a component i at the $(k+1)^{th}$ iteration is shown as:

$$x_i^{II(k+1)} = x_i^{II(k-1)} - \frac{(\phi_i^{k-1} - \phi^{k+1})(x_i^{II(k-1)} - x_i^{II(k)})}{(\phi^{(k-1)} - \phi^{k})}$$

where

$x_i^{(k)}$ = composition at k^{th} iteration

ϕ^k = split fraction at k^{th} iteration

To give a definite idea of how much improvement in computation time and function evaluations can be made from the above schemes; we have the following demonstration: For six overall liquid compositions which are within the two phase regions of the water-acetone-heptane system, we limit

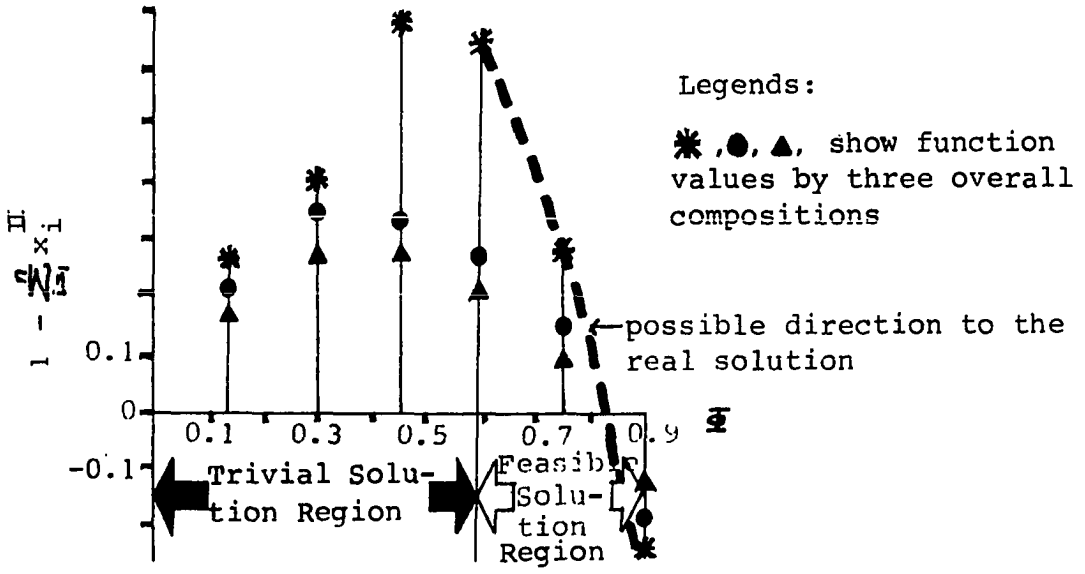


Figure 8 Examples showing Function Values in the Interval of $0 \leq \Phi \leq 1$

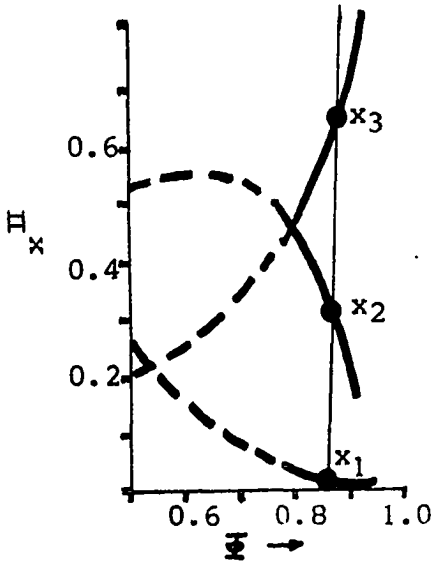


Figure 9 Illustration showing a Linear Relation for Liquid Compositions with Split Fraction around the Feasible Region

one minute of total computer time and start each liquid-liquid calculation with the same initial values and same calculation procedure by various inner loop schemes, which are:

1) Direct substitution method with strict criterion for composition stabilization at each iteration.
2) Direct substitution method with scheme a.
3) Direct substitution method with scheme a and b.

Results and comparisons are shown in Tables 6, 7 and Figures 10.

b) Outer Loop to Adjust the Main Variable

For our method, there is only one explicit adjustable variable, i.e., split fraction ϕ, from which the following function value will be minimized.

$$f = \sum_{i=1}^{n} x_i^I - 1$$

Therefore, any one dimensional search method, such as the Fibonacci search, Golden cut, quadratic interpolation, etc. will be the prospective methods to adjust the variable ϕ. We understand all of these methods to have a common implication that a unimodal form will be built between the value of the variable and that of its related function. This unimodal

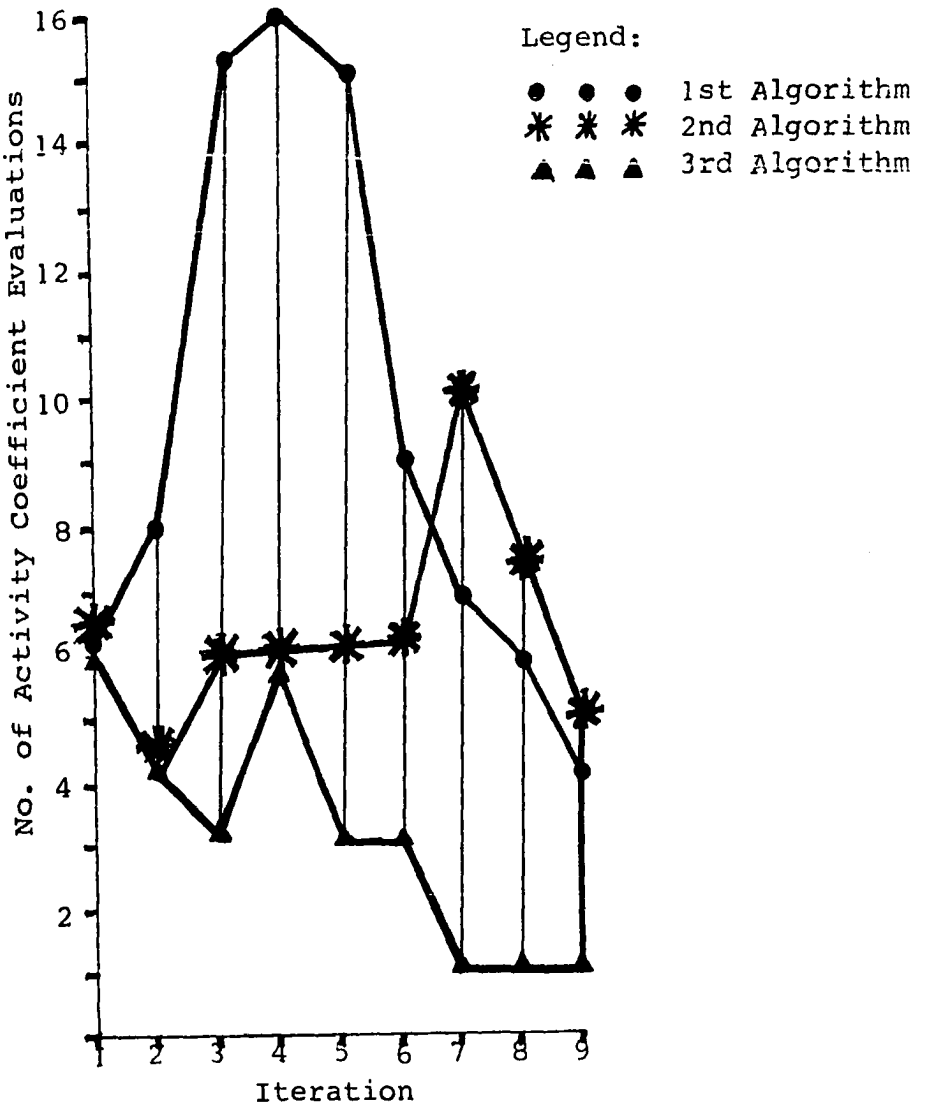


Figure 10 Comparisons of Number of Activity Coefficient Evaluations Required by Three Algorithms

TABLE 6. Comparison of Total Computation Time of Six Studied Problems by Three Algorithms

Algorithm	Time (sec)
I	more than 60 sec
II	44.14
III	29.92

TABLE 7. Comparison of the Required Number of Activity Coefficient Evaluations of Each Studied Problem by Three Algorithms

		Iteration Number									
Problem	Algorithm	1	2	3	4	5	6	7	8	9	Total
	I	9	8	15	16	15	9	7	6	4	89
1	II	6	4	6	6	6	6	10	8	5	57
	III	6	4	3	6	3	3	1	1	1	28
	I	10	12	15	17	12	11	10	8	7	102
2	II	6	4	6	6	6	6	11	10	7	62
	III	6	4	1	4	1					28
	I	11	8	11	15	12	12	12	12	11	
									10	9	123
3	II	6	5	6	6	6	6	5	11	9	60
	III	6	5	6	5	4	3	2	2	1	33
	I	12	9	19	16	13	8	3			80
4	II	6	5	6	12	9	7				44
	III	6	5	5	3	3	4	1			27

TABLE 7 (Continued)

Problem	Algorithm	Iteration Number 1	2	3	4	5	6	7	8	9	Total
	I										
5	II	6	6	6	6	5	7	14	12	4	66
	III	6	6	6	4	3	1				26
	I										
6	II	6	6	6	5	5	5	3	1		37
	III	6	6	6	3	3	1	1	3	1	30

form is like the sketch shown below.

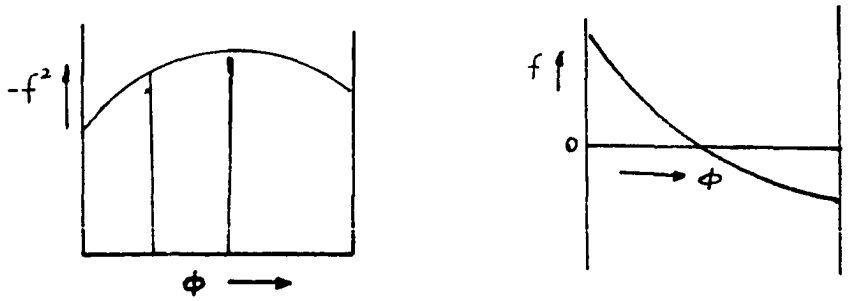


Figure 11. A Description of a Unimodal Form

For our problem this unimodal form is extended only over a local region around the real solution, rather than over the entire feasible region of the variable, i.e., $0 \leq \phi \leq 1$. Figure 8 interprets this statement. The region $0 \leq \phi \leq 1$ is divided into two parts, one is for the real solution, (we call it the feasible solution region), and the other is for the trivial solution region, where $x_i^I = x_i^{II}$ might be found, or no solution can be obtained.

According to this physical nature of problems, the feasible solution region has to be identified before any one dimensional method can be applied. As we mentioned before, a rough inner loop calculation is performed to omit the unnecessary computations, but this step tends to distort the unimodel shape within the feasible solution region. This is another concern for when a one dimensional method is used.

The one-dimensional method is the False-Position

method because it can be easily handled concerning the above two facts. For this method the next successive value of variable ϕ can be obtained using the previous two values of ϕ_1, ϕ_2 and their function values f_1, f_2, in the following formula:

$$\phi = \phi_1 - \frac{(\phi_2-\phi_1)}{(f_2-f_1)} f_2 ,$$

Two points have to be set up before we can use the above formula. Since the feasible solution region is only located in a limited region, we cannot arbitrarily set up the second point. In Figure 12 below, we have the first point at ϕ_1 with function value f_1, and the second point at ϕ_2, which is on the left side of ϕ_1. Using formula (6), we will find that the successive variable value is always in the trivial solution region. Therefore, before we move to the second step, we have to find something as a direction guide.

A) Guidance Rule

We found that the sign of the function value of the current iteration can be used as an indicator for the next movement. For

$$f = \sum_{i=1}^{n} x_i^I - 1 = \sum_{1}^{n} \frac{(\beta_i-1)x_i^F}{[1+(\beta_i-1)\phi]} - 1$$

Without considering the composition dependence of distribution factor β_i, we have the first derivative of f with respect to variable ϕ.

$$\frac{df}{d\phi} = \sum_{i=1}^{n} \frac{dx_i^I}{d\phi} = - \sum_{i=1}^{n} \frac{\beta_i(\beta_i-1)x_i^F}{[1+(\beta_i-1)\phi]^2}$$

since $\beta_i > 0$

so for $\beta_i < 1$, $\quad -1 < \beta_i(\beta_i-1) < 0$

and for $\beta_i > 1$, $\quad \beta_i(\beta_i-1) > 1$.

Thus, $df/d\phi$ has, always, a negative value. By the Newton-Rapheson formula, the successive value of variable ϕ is

$$\phi_{new} = \phi_{old} - f/\left(\frac{df}{d\phi}\right)$$

This relation provides the best guidance for our method. That is, if the current function value is negative, the successive value of the variable, ϕ, has to be decreased, or vice versa. This relation is the first priority before we have any movement to the next step. Any of the results from one-dimensional method, such as the False-Position method, is contradicted by this guidance rule will be of no further consideration. We might have the situation, shown in Figure 12, where the feasible solution region is found to be very narrow, so that when the second point is set up, its

function value f_2 is larger than that of the previous one, f_1. At this point, if the False Position Method were to be used to estimate the successive value of a variable, then, by the sense of False Position Method, the third value would be found where the previous two function values declined. This would be contradicted by the highest rule of our method, which indicates that the next stop should be a forward, instead of a backward movement.

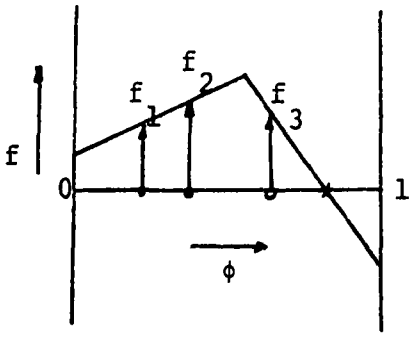


Figure 12. Illustrative Case 1 of Using Guidance Rule

Due to the side effect of the rough inner loop stabilization process, the following cases will occur in which the false position relation cannot be applied directly. 1) A distorted unimodel form may occur. As shown in Figure 13, we have f_1 at ϕ_1, f_2 at ϕ_2, and at ϕ_3 function value f_3 is expected, which is larger than the previous value, f_2. Evidently, the next step, by False Position, will be contradicted by the highest rule; thus, the conventional False Position Method has to be modified to keep two points recorded instead of only one. In such a case, we can decide the next

variable, ϕ_4, from ϕ_1 and ϕ_3 without contradicting the guidance rule.

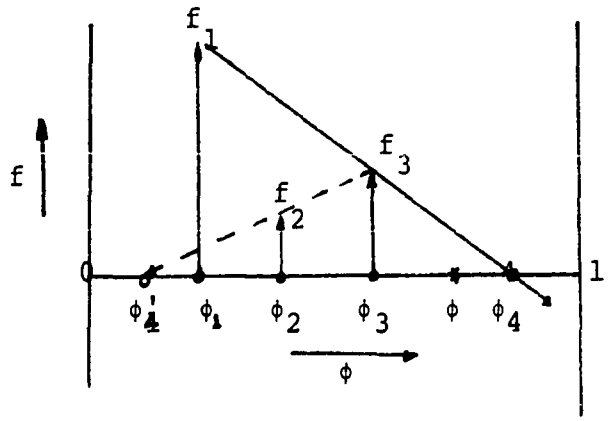


Figure 13. Illustrative Case 2 of Using Guidance Rule

A false convergence may occur. By the sense of False Position, the solution is always located between a negative value and a positive function value, but the sign of one of these two values might not be right, because of the side effect of rough inner loop calculation. Therefore, we have to get the variable out of this trap when function values of two variables are close, but don't show any convergence evidence with the finer inner calculation. Once again the False Position Method can be applied at this time. This case is shown in Figure 14.

Trivial Solution Region

One merit of our proposed method is that the region where the problem will not be convergent or where a trivial

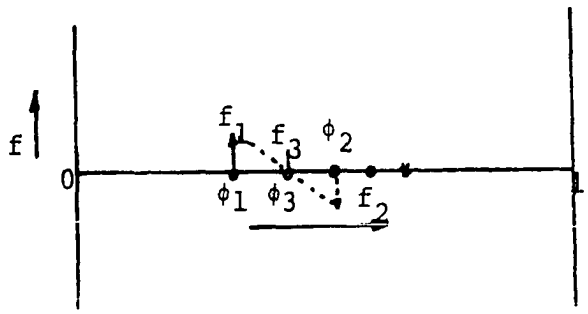


Figure 14. A Distorted Unimodel Due to a Rough Inner Loop Procedure

solution is found, can be avoided without any additional effort. For most mathematical programming methods (14,30), a trivial solution is the most serious problem. For these methods, in order to keep away from trivial solutions, which may result from the particular path followed in attempting to solve the equations, a penalty function has to be added to the objective function; for example, as x_i^I approaches x_i^{II}, the objective function value will become infinite. Obviously, in this way the number of function evaluations, as well as the amount of computation time, will be increased. Accordingly, the problem with an over-all composition, which is in the homogeneous phase, will become insolvable. For our method, however, these are not problems at all. Governed by the guidance rule, a solution will become a trivial solution, if an overall composition is within homogeneous phase,

TABLE 8. Demonstration of A Trivial Solution Region

Overall Composition mole %	Results From Rule	Results From Anti-Rule
1. System: i-Octane-Cyclohexane-Benzene-Furfural		
0.2,0.04,0.08,0.68	0.8043	trivial
0.1974,0.1453,0.745,0.5828	0.6802	divergent
2. System: Heptane-DMFA-Water-Benzene		
0.118,0.297,0.074,0.511	0.5816	divergent
0.2,0.1064,0.075,0.6187	0.7268	divergent
0.15,0.2,0.05,0.6	0.7318	divergent

and the solution will be two different values, if the overall composition is in the heterogeneous region. To demonstrate the existence of a trivial solution region, we force the programming to search for the solution around the trivial solution region. The results are shown in Table 8.

Thermodynamic Stability Criteria

Thermodynamic conditions for stability with respect to diffusion in a mixture containing N components were given by Gibbs (1873). A more recent and accessible analysis is given by Prigogine and Defay (1939) which will be followed here. The general criterion which is necessary and sufficient for stability is

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \mu_{ij} \delta\xi_i \delta\xi_j > 0 \qquad (3\text{-}8)$$

where the ξ_i are arbitrary and where μ_{ij} is the partial derivative of the chemical potential of component i with respect to the number of moles of component j. Necessary and sufficient conditions for equation (3-8) to be satisfied are that μ_{ii}, and all other minors of both odd and even order constructed on the principal diagonal of the determinant of the μ_{ij}, be positive or zero. Applications of these criteria along with the Gibbs-Duhm equation to a binary system shows that the condition for stability is

$$\mu_{11} \geq 0 \ .$$

If this condition is violated by the mixture at the given conditions, two liquid phases will be present in practice. For ternary system mixtures, the working equations for thermodynamic stability are

$$\mu_{11} \geq 0; \quad \mu_{22} \geq 0; \quad \mu_{11}\mu_{22}^{2}-\mu_{12}^{2} \geq 0$$

If one or more of these conditions are violated, two liquid phases will form. For systems with more than three components the number of working equations for thermodynamic stability will increase, e.g., for n component system, there are

$^{n}C_{1}$ 1st order determinant conditions,

$^{n}C_{2}$ 2nd order determinant conditions,

1 n^{th} order determinant conditions.

With the Gibbs-Duhm equation, the nth order determinant condition is zero. With this relation, any order determinant condition which consists of a term related with the nth component can be skipped, since these conditions can be substituted by conditions which contain the other (n-1) components. Therefore, the number of thermodynamic stability conditions can be reduced as follows:

$_nC_1 - 1$ 1st order determinant conditions

$_nC_2 - {}_{n-1}C_1$ 2nd order determinant conditions

$_nC_3 - {}_{n-1}C_2$ 3rd order determinant conditions

So for an n-component mixture, there are

$$\sum_{j=1}^{n-1} \frac{(n-1)!}{(n-j)!(j-1)!}$$

total number of conditions to be evaluated. A neat and simple computer program is written to find every determinant for the different order conditions. Following is a flow chart and an example illustrating how the program works to set up all of the thermodynamic stability conditions.

In this work, the partial derivative of the chemical potential of component i, with respect to the number of moles of component j, were evaluated using the NRTL equation as the molecular model for excess free energy. The detailed derivation is shown below:

$$\mu_{ik} = \frac{RT}{n}\left[\frac{\delta_{ik}}{x_i} - 1 + \frac{\tau_{ki}G_{ki}}{Q} - \frac{WG_{ki}}{Q^2}\right.$$

$$+ \sum_{j=1}^{m}\left[\delta_{jk}G_{ij}\left(\frac{\tau_{ij}}{U} - \frac{V^2}{U^2}\right) - \frac{x_jG_{ij}G_{kj}(\tau_{ij}+\tau_{ij})}{U^2}\right.$$

$$\left.\left. + 2\frac{\mathfrak{g}G_{ki}}{U^3}\right]\right]$$

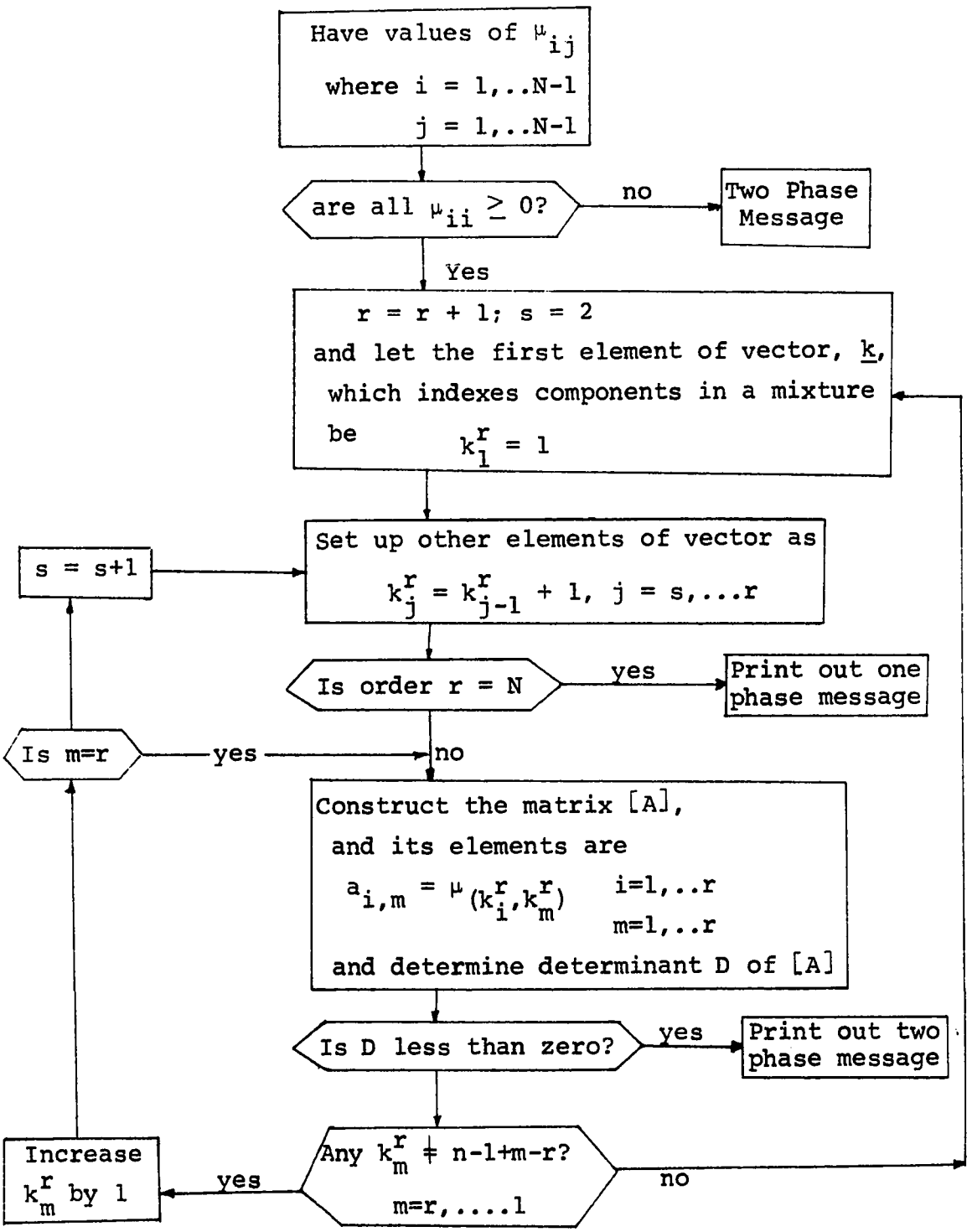
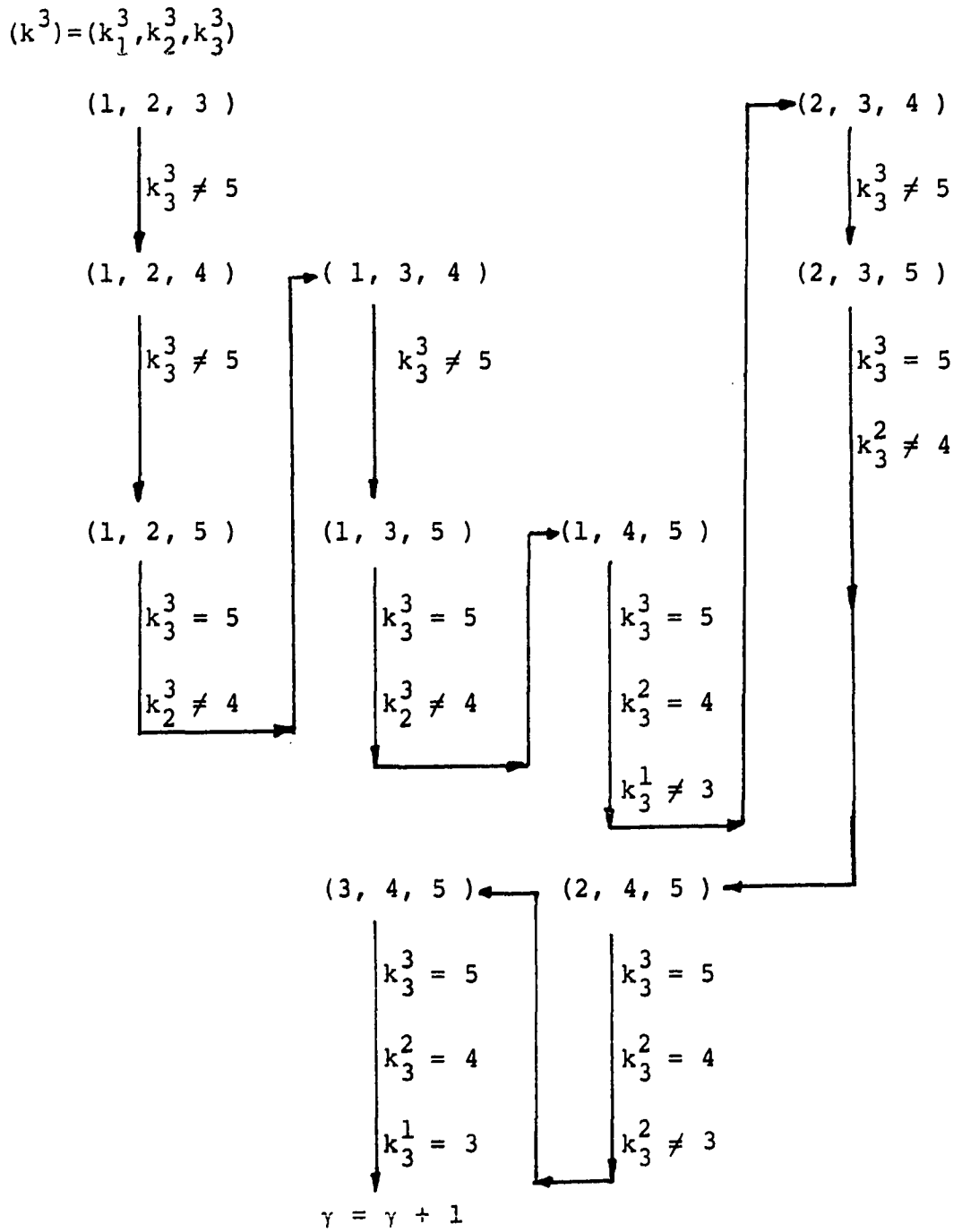


Figure 15. A scheme to predict liquid phase separation for an n-component mixture.

Example to illustrate how the program generates all ternary pairs in a 6-component mixture. For this case, N = 6, $\gamma = 3$



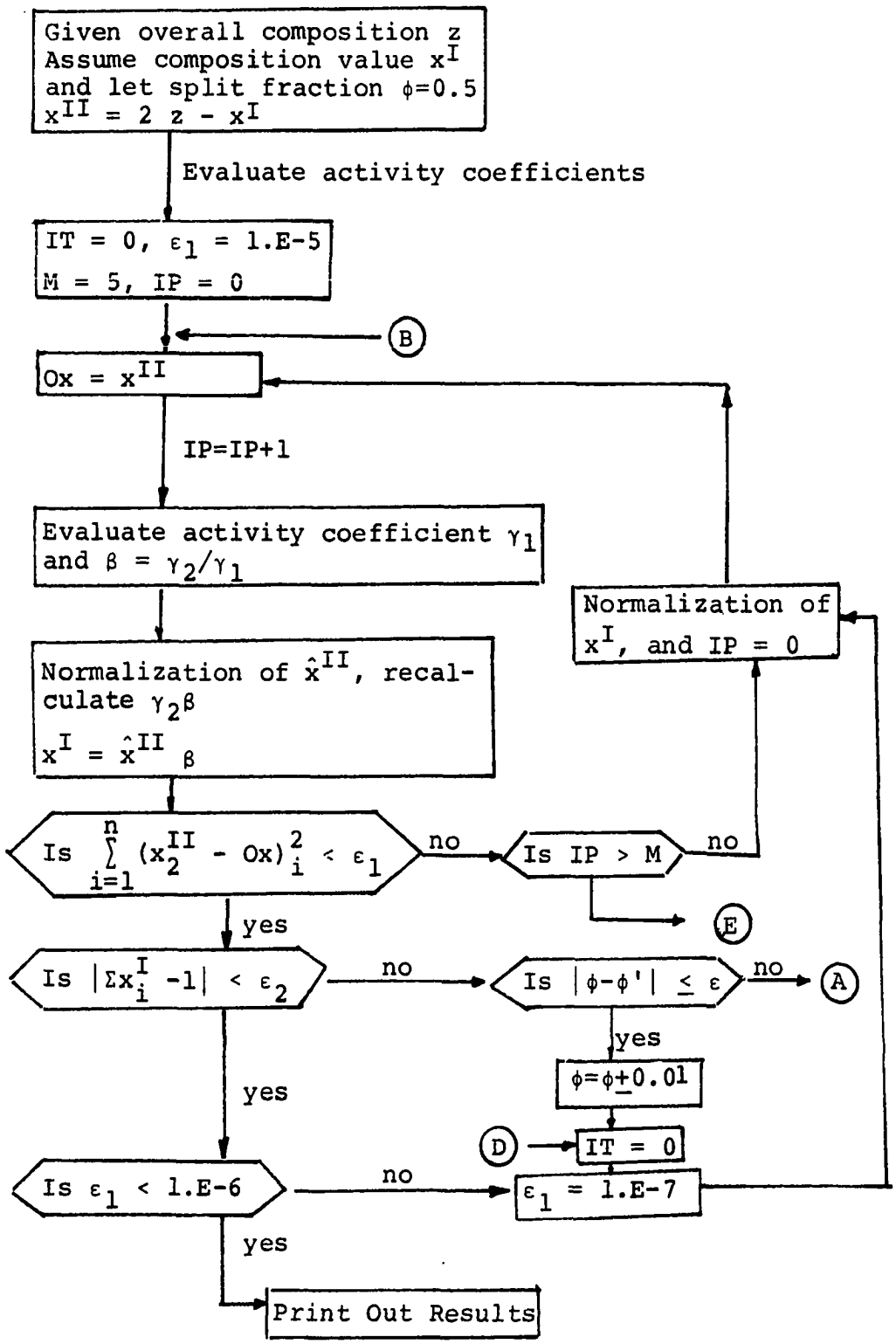


Figure 16. Detail Flow Chart of Liquid-Liquid Calculation Algorithm (continued)

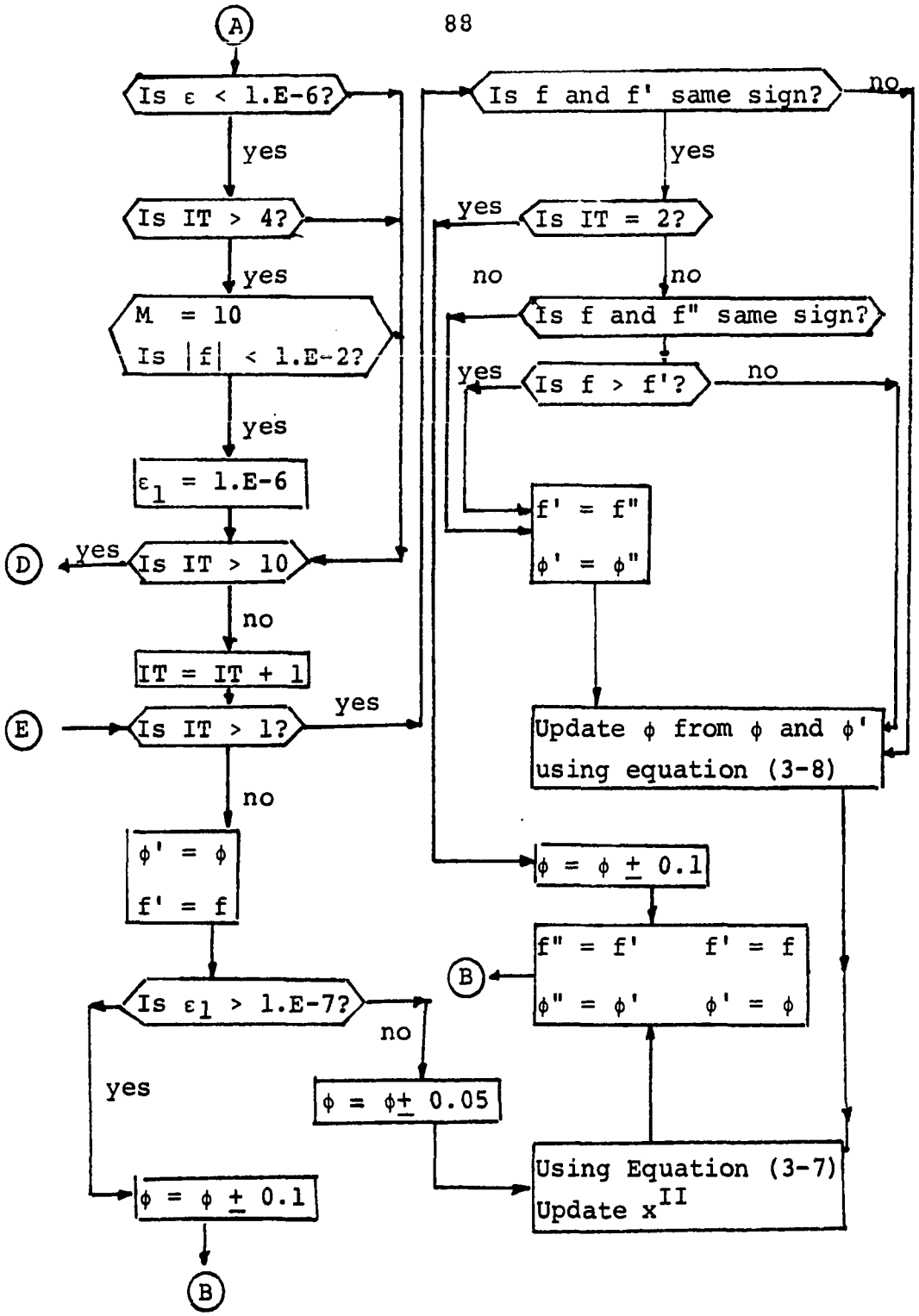


Figure 16. Detail Flow Chart of Liquid-Liquid Calculation Algorithm

where

$$\delta_{ij} = \begin{cases} 1 & i = j \\ 0 & i \neq j \end{cases} \qquad U = \sum_{\ell=1}^{n} G_{\ell j} x_{\ell}$$

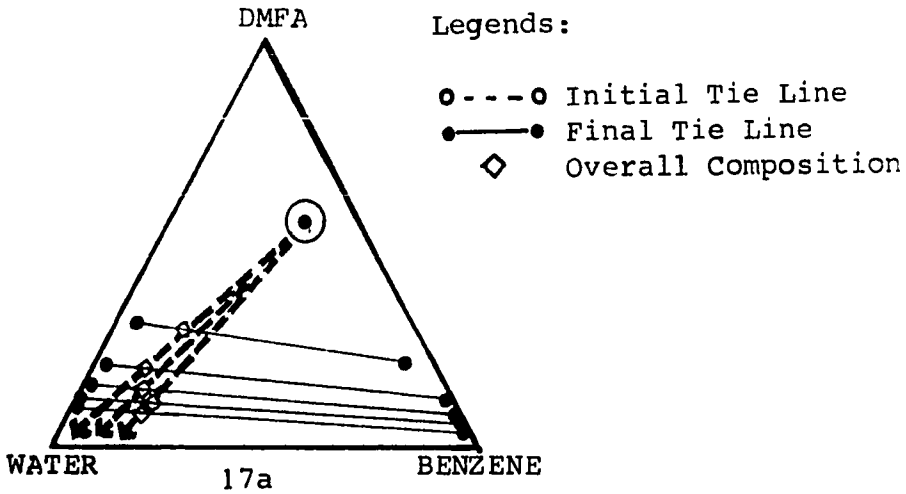
$$Q = \sum_{\ell=1}^{n} G_{\ell i} x_{\ell} \qquad V = \sum_{r=1}^{n} x_r \tau_{rj} G_{rj}$$

$$W = \sum_{j=1}^{n} \tau_{ji} G_{ji} x_j \qquad S = x_j G_{ij} V$$

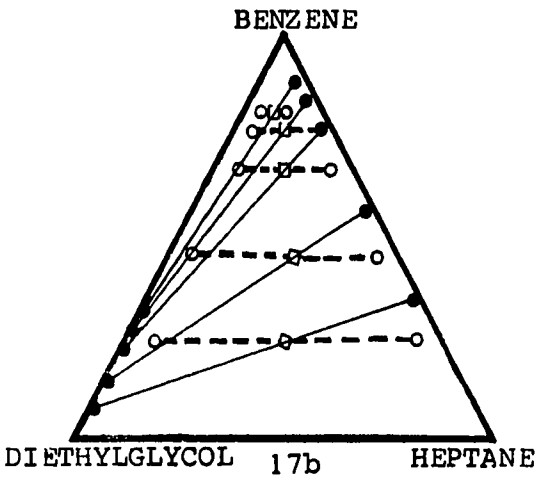
Discussion and Results

The method for liquid-liquid calculation has been used to predict the separation between two liquid phases for twenty-five systems which are listed in Table 9, and values of Renon constants and their sources are given in Appendix E. Of these twenty-five systems, there are sixteen ternary systems, five quaternary systems, three five-component systems and one six-component system. Some detailed results for tested systems are given in Appendix F. These detailed results show the feed compositions, initial values, and final results, phase prediction, and the number of activity coefficient evaluations.

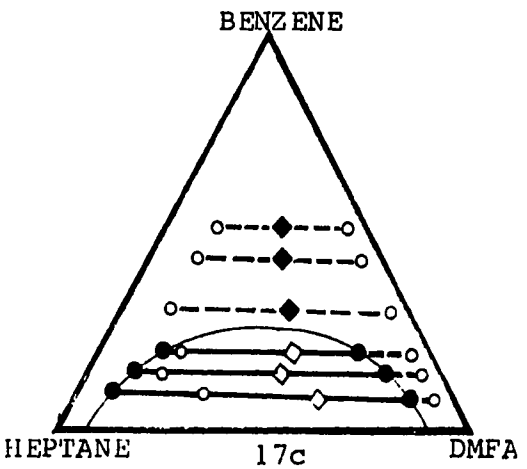
We can recognize the good behavior of the proposed method to solve the liquid-liquid calculation problem, and we can have a more practical understanding of how tremendous



Water-DMFA-Benzene System

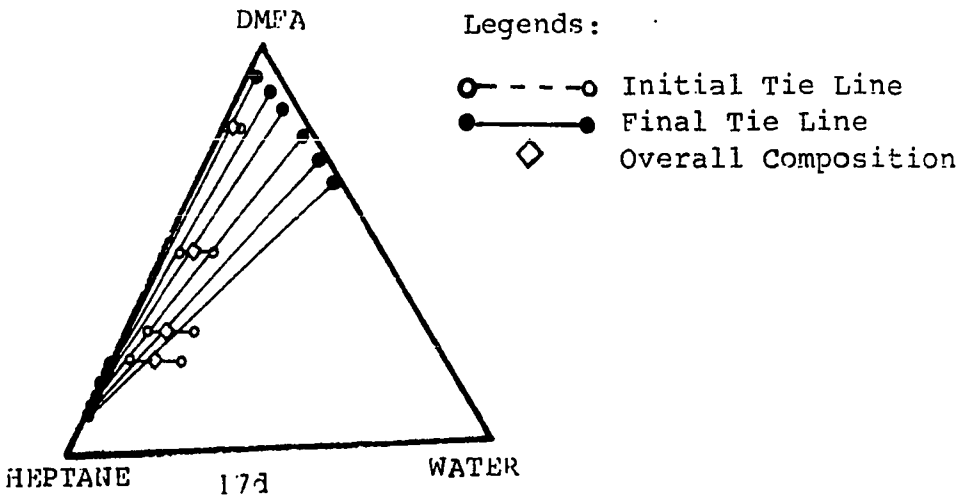


Diethylglycol-Benzene-Heptane System

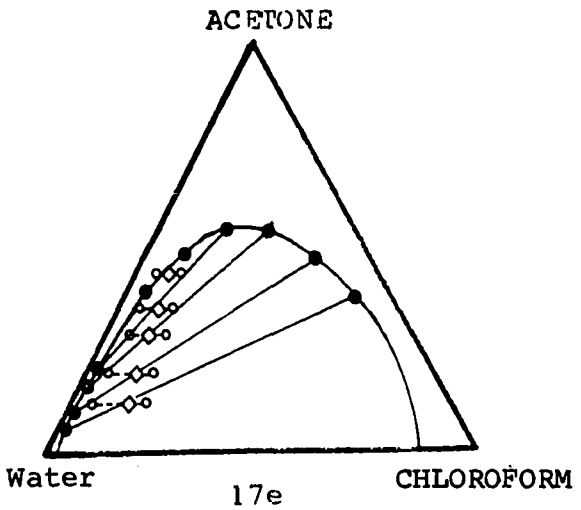


Heptane-Benzene-DMFA System

Figure 17 Exhibition of Convergence Performance of the Proposed Liquid-Liquid Calculation Method



Heptane-DMFA-Water system



Water-Acetone-Chloroform System

Figural 17 Exhibitions of Convergence Performance of the Proposed Liquid-Liquid Calculation Method

TABLE 9. List of Systems for Testing the Modified Liquid-Liquid Calculation Method

No.	System Tested	Reference
1	N-Hexane-5-Nonane-DMSO (25°C)	44
2	N-Hexane-5-Nonane-DMSO (60°C)	44
3	Hexene-5-Nonane-DMSO (25°C)	44
4	Hexene-5-Nonane-DMSO (60°C)	44
5	Water-Acetone-Heptane (25°C)	5
6	Water-Dimethylformamide-Benzene (20°C)	5
7	Water-Dimethylformamide-Heptane (20°C)	5
8	Heptane-Benzene-Dimethyl-Formamide (20°C)	5
9	Iso-Octane-Benzene-Furfural (25°C)	5
10	Cyclohexane-Benzene-Furfural (25°C)	5
11	Water-Methanol-Butanol (25°C)	13
12	Chloroform-Acetone-Water (25°C)	13
13	Diethylglycol-Benzene-Heptane (25°C)	13
14	Phenol-N-Butylacetate-Water (44°C)	13
15	Ethylacetate-Ethanol-Water (B.P.)	58
16	Ethylacetate-Methanol-Water (B.P.)	58
17	Iso-Octane-Cyclohexane-Benzene-Furfural (20°C)	5
18	Heptane-Dimethylformamide-Water-Benzene (20°C)	5
19	Methanol-Water-Aniline-Benzene (25)	58
20	Water-Ethanol-Butanol-Methanol (25)	58
21	Water-Ethanol-Butanol-Acetone (25)	58
22	Water-Ethanol-Butanol-Acetone-Benzene (25°C)	58
23	Water-Ethanol-Butanol-Methanol-Benzene (25°C)	58
24	Water-Ethanol-Butanol-Methanol-Acetone (25°C)	58
25	Water-Ethanol-Butanol-Methanol-Acetone-Benzene (25°C)	

consistency between stability conditions and calculation results.

We have plotted results of five systems on the triangle diagrams as shown in Figure 17. On each diagram, x---------x represents the given initial tie line, and o----------o represents the final tie line. This shows how reliable the proposed method is (In Figure 17-a). With negative initial values we still can obtain a convergence solution. For some initial tie lines which are given very close together, such as Figure 17-e, the separation between two phases is obtained. Let us look again at Figure 17-c. Even though there is a wide separation assumed between the two liquid phases, a trivial solution results as the feed composition is within the homogeneous region. The proposed method has proved to be reliable for the heterogeneous region as well as the homogeneous region.

One of the special features of our proposed method is that it can handle an overall point within the heterogeneous phase as well as that of the homogeneous phase. With this special property of method, we can compare predictions from stability conditions with the calculated results. Classic thermodynamic stability conditions were derived many years ago, and they are employed largely to demonstrate the equilibrium state in theory, but this is the first time for it to be used in practice for liquid-liquid calculations.

It has been shown that the stability conditions are

completely consistent with our predicted solution. These stability conditions are reliable for a large heterogeneous phase region, such as in DMFA-Heptane-Water system (Figure 17-d), as well as a small heterogeneous phase region, such as in the Heptane-Benzene-DMFA system (Figure 17-c). They are proved for six-component systems with thirty-one conditions as well as for ternary systems with three conditions. It is difficult for an overall composition of a six-component mixture to pass through thirty-one conditions, fourteen conditions for a five-component mixture and seven for a quaternary mixture, but have shown that stability conditions are endurable to this crucial challenge.

Conclusion

The proposed method has been proved to have the following special features;

1. Reliable. A real solution is always obtained even with the unreasonable initial composition values.
2. Economic. With only 20K bytes storages the program can work for up to a six-component system. Compared with the other matrix method, at least n^2 order computer storage can be saved, because no Jacobian matrix is required.

3. Efficient. Convergence rate is within a reasonable measure.
4. General. Will work for overall liquid compositions within the heterogeneous phase as well as the homogeneous phase.
5. Dependable. Trivial solutions can be easily avoided without any concern for the overall composition within the heterogeneous phase, which constitutes the most serious problem in the current proposed mathematical programming method.
6. Saves. Unnecessary steps can be avoided if the one phase is observed from the stability condition.

CHAPTER IV

NONIDEAL SOLUTION SEPARATION PROCESSES CALCULATION METHODS

MOLECULAR MODELS

To complete the description of a general simulation model, molecular models are selected to relate thermodynamic quantities in the equations to process variables. The complexity and realism of the resulting process model depends greatly on the molecular models selected. At the expense of considerable complexity, molecular models were chosen that provide realistic properties for the highly non-ideal solutions which occur in three-phase distillation, extraction, etc.

Vapor Phase

The Redlich-Kwong equation of state was selected for relating vapor phase properties to observables. For this equation of state, component fugacity is related to the observables, temperature, pressure, density, and composition, by

$$\ell n(f_i^V/y_i P) = (z-1)b_i/b - \ell n(z-bP)$$

$$- \frac{a^2}{b} (2a_i/a - b_i/b) \cdot \ell n(1+bP/z)$$

where $z = \rho RT/P$. Density is related to the process variables, temperature, pressure, and composition by the largest root of,

$$z^3 - z^2 + bP(a^2/b - bP - 1)z - a^2bP^2 = 0$$

Composition dependence, included implicitly in a and b, is given by,

$$a = \sum_{i=1}^{n} y_i a_i \qquad b = \sum_{i=1}^{n} y_i b_i$$

Vapor phase enthalpy deviation for the Redlich-Kwong equation of state is given by

$$H = H^* = 1.5\ RT(a^2/b)\ell n\left(\frac{1}{1+c}\right) + \frac{c}{1-c} - (a^2/b)\left(\frac{c}{1+c}\right)$$

$$c = bP/z$$

and ideal gas enthalpy was calculated by

$$H^* = a(T-T_R) + b(T^2-T_R^2) + c(T^3-T_R^3) + d(T^4-T_R^4)$$

where T_R was taken to be 298.15K which implies an enthalpy

reference of the ideal gas at that temperature.

Liquid Phase

Component fugacity in the liquid phase was calculated from

$$f_i^L = \gamma_i x_i f_i^{oL}$$

Activity coefficients were calculated from the NRTL equation (44).

$$\ell n\gamma_i = \frac{\sum_{j=1}^{n} \tau_{ji} G_{ji} x_j}{\sum_{k=1}^{n} G_{ki} x_k} + \sum_{j=1}^{n} \frac{x_j G_{ij}}{\Sigma G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_{r=1}^{n} x_r \tau_{rj} G_{rj}}{\sum_{k=1}^{n} G_{kj} x_k}\right)$$

where

$$\tau_{ji} = (g_{ji} - g_{ii})/RT$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji})$$

$(g_{ji} - g_{ii})$ is an empirically determined energy term which is closely related to the difference in cohesive energy between i-j pair and an i-i pair. α_{ij} is given empirically by the authors (44) based on the chemical nature of the components or from correlation of ternary liquid-liquid data.

Standard state fugacities, f_i^{oL}, were calculated from pure component vapor pressure in the manner suggested by

Prausnitz, et al. (38). Liquid enthalpy is calculated, with respect to the ideal gas state at 298.15 K, from pure component heat of vaporization data with enthalpy of mixing in the liquid state calculated from

$$h^M = RT \sum_i^n x_i \frac{\sum_j^n x_j G_{ji} \tau_{ji} (1+\tau_{ji}\alpha_{ji})}{(\sum_{k=1} G_{ki} x_k}$$

$$- \sum_{j=1}^n (\gamma_{ji} G_{ji} x_j) \sum_{k=1}^n (x_k G_{ki} \alpha_{ki} \tau_{ki}) / (\sum_{k=1}^n G_{ki} x_k)^2$$

which is derived from the NRTL equation.

NUMERICAL METHODS

Once a complete problem description has been made for a multicomponent multistage separation, the problem becomes one of solving a particular set of simultaneous equations. In general form, it is desirous to solve a set of m nonlinear equations

$$f_i(x_1, x_2, \ldots, x_m) = 0 \qquad i=1,\ldots,m$$

Since these equations are nonlinear and strongly interacting, it is not feasible to derive analytical derivatives of f_i with respect to x_j, i.e., the Jacobian matrix. In such cases, the Jacobian matrix often is evaluated numerically by perturbation. A different procedure, though purely numerical, is

followed here. Rather than calculating the Jacobian by perturbation, the method of Yang and Christensen (68) is used to calculate an initial approximation of the inverse of the Jacobian matrix. Then Broyden's method (3) is used to update the inverse of the approximate Jacobian matrix by applying function residuals calculated during the preceding iteration. Quadratic interpolation, concisely described by Yang and Christensen (68), is used to find the optimal step size in $\underline{x}$. The detailed procedures are shown as follows:

Initialization Step: Give a set of guessed values $\underline{x}^0$, and set up the corresponding initial Jacobian inverse matrix $[B^{-1}]$, using the method of Yang and Christensen. Let $[H]^0 = [B^{-1}]$ and $k = 0$.

Step 1. Evaluate function residues $\underline{f}(\underline{x}^k) = \underline{f}^k$.

Step 2. Evaluate $\underline{p}^k = [H]^k \underline{f}^k$.

Step 3. Find the value t^k by using a quadratic interpolation, such that

$$(\underline{f}^{k+1})' \underline{f}^{k+1} < (\underline{f}^k)' \underline{f}^k$$

where

$$\underline{f}^{k+1} = \underline{f}(\underline{x}^k + t^k \underline{p}^k)$$

Step 4. If $\underline{f}'(\underline{x}^{k+1}) \underline{f}(\underline{x}^{k+1}) \leq \epsilon$

Stop; otherwise, let

$$\underline{y}^k = \underline{f}(\underline{x}^{k+1}) - \underline{f}(\underline{x}^k)$$

Step 5. Calculate

$$[H^{k+1}] = [H^k] - ([H^k]\underline{y}^k + t^k\underline{p}^k)\underline{p}'^k[H^k]/$$

$$(p'^k[H^k]\underline{y}^k)$$

Let k = k = 1; return to step 1.

A General Scheme of Formulating Nonideal Solution Calculation Methods

The design of equipment for separation of a multicomponent mixture is often based on a steady state solution of equations describing an equilibrium stage column model. These equations are nonlinear so that a numerical method must be employed for their solutions. Many methods (10, 11, 31) have been proposed in the past, and exhibited good convergence characteristics for a wide range of problems. They became particularly unwieldy when composition-dependent equilibrium relations were to be involved.

Recently several calculations methods (24, 25, 8) appeared to deal with processes having composition-dependent relations like the Chao-Seader correlation (4), or the Margulas equation. These relations depend weakly on phase compositions. Therefore function values on which adjustment of variables depend, are not very sensitive to a minor change of composition values. For a system which has to be described by the Renon equation, these methods may become unreliable

and improper. Same as temperature and vapor rate, composition is also considered as the unknown variables by Ishii (24). Consequently; the dimension of a problem will increase to $(n-1)^2$ th order for an n-component system. Calculations become especially unstable and unreliable, when compositions are taken as unknown variables in liquid-liquid equilibrium problems. Having such an experience, we may hesitate to accept Ishii's idea to formulate an algorithm involving a strongly composition-dependent relation.

Erbar (8) proposed a method for three-phase flash problems. The logical diagram of his method is to adjust the liquid rates of two phases sequentially to satisfy working equations before compositions reach a nearly constant state. This kind of algorithm will work for problems where variations of function values are not rapidly changed with different composition values under the same temperature and vapor rates. Therefore it can be applied to problems with the Caho-Seader correlation, but not to problems with the Renon equation.

Therefore we attempt to propose a general scheme of formulating convergence methods for problems where a strongly composition dependent relation has to be considered. To account for the effect of compositions, an inner loop to converge equilibrium compositions is put as the first step of the scheme. A similar idea of converging equilibrium constants has also been mentioned in King's book (27). Taken

the effect of composition apart from the problem, to devise a nonideal solution convergence method is the same as the conventional two-phase distillation method. To solve a multivariable problem, there are two broad categories of convergence methods; stage-to-stage method, and successive convergence method. With the widespread availability of digital computers, stage-to-stage convergence method has been overridden by the more efficient successive method. For successive methods, these are also divided into two types; sequential method and simultaneous method. Based on the idea of simultaneous method, Tomich (55) has successfully developed a convergence method and has demonstrated its great capability and feasibility to handle different process problems which are always restricted by using sequential methods, such as the SR or BP method (9). By employing a modified Newton-Raphson method, Broyden Method, to update the Jacobian matrix for correcting new values of unknown variables at each iteration, the Tomich method is more efficient and stable. Therefore we adopt the Tomich method as the part to adjust the temperature and vapor rate profile in our scheme. This general scheme is shown as follows:

Step 1. Assume a rate, and temperature profile for a m-stage column problem (for flash calculation, m=1).

Step 2. Assume vapor, and liquid compositions. Then

find equilibrium constants. Or give equilibrium constant profiles directly. Skip to step 4.

Step 3. Normalize compositions of X, and evaluate the corresponding equilibrium constants of each stage.

Step 4. Solve for compositions of Y from the simultaneous equations, which are derived from component material equations and equilibrium relations.

Step 5. Normalize compositions of Y, and calculate X from equilibrium relation 6.

Step 6. Repeat steps 3 to 5, until Y converges.

Step 7. Adjust the vapor, temperature profile by the Broyden method, according to the working equations, which are summation equations,

$$f_j = \sum_{i=1}^{n} X_{ij} - 1 = 0 \qquad j=1,\ldots,m$$

and energy balances

$$f_{j+m} = \frac{(H_j)^{IN} - (H_j)^{OUT}}{(H_j)^{IN}} \qquad j=1,\ldots,m$$

where H^{IN}, H^{OUT} are the total input enthalpy and output enthalpy, and evaluated at normalized X and Y.

Step 8. Repeat steps 3 to 7 until all residues of working equations are within the tolerance criterion.

According to this general scheme we have successfully developed the more efficient methods in the following process calculations; three-phase flash, distillation, azeotropic distillation and counter-current extraction. The detailed procedures for these calculations will be introduced in the next two chapters. The scheme can also be applied to the method of liquid-liquid equilibrium, for which we have described in the previous chapter. Recently, a successful crude tower design program has also been developed according to this scheme (69).

Apparently, the most defects of this algorithm is that an inefficient but stable direct substitution method is used to converge composition in the inner loop. Several available methods have been tried unsuccessfully. In devising a convergence method, we should consider the desirable characteristics like convergence speed, stability, reliability, minimum computer storage, etc. When these quantities can not be put together, then the stability and the reliability have to be considered to be the first priorities. This is the principle to develop our convergence methods.

CHAPTER V

THREE-PHASE FLASH CALCULATIONS

For a highly nonideal solution separation, two phases of liquid region are always encountered. Even for a hydrocarbon-water system, where the mutual solubility is insignificantly small, when small amounts of impurities, like aromatics , olefins are added, the mutual solubility will be increased to some significant extent. Traditional calculations, assuming immiscible behavior of systems or ignoring the possibility of two liquid layer formations, are no longer sound engineering practices. Some works have been done in this area, such as convergence methods for three-phase equilibrium flash calculations, presented earlier by Osborne (35), Deam and Maddox (6). However; effects of compositions on the equilibrium are not expressed by these authors. Erbar (8) has considered the liquid separation by using a regular solution model and presented a more detailed algorithm for a three-phase flash model. The regular solution theory of Hildebrand and Scott (17) is somewhat more useful, but is valid only for systems having relatively low polarity. Few of these systems can form immiscible mixtures. Now matter what Erbar's "expedient

thermodynamic method" has been successfully applied, more or less, to high pressure water-hydrocarbon systems, the method is not generally applicable because it lacks a sound thermodynamic basis. Besides, as we described in the previous chapter, Erbar's algorithm is not proper to be applied to systems where strongly composition-dependent relations are involved.

Earlier, in reducing initial values to a minimum, we developed a sound algorithm for a three-phase equilibrium calculation (63). The algorithm is applied to the bubble point, isothermal as well as adiabatic flash calculations. Its main logical diagram is centered on a liquid-liquid calculation. That is, starting from the assumed vapor rate, and composition, we can obtain liquid compositions and rates from a liquid-liquid calculation. Find vapor compositions from equilibrium with liquid compositions of any one phase. Repeat the liquid-liquid calculation, until the assumed vapor compositions are agreed with the calculated one. Adjust the temperature, T, from the summation equation for bubble point calculations; the vapor rate, V, from the summation equation for isothermal flash calculations, and the temperature, T, from the summation equation, vapor rate, V, from energy equation for adiabatic flash calculations. Return to the liquid-liquid calculation step, until residues of all working equations are within a convergence criterion. Evidently, by this method, a lot of computation time has to

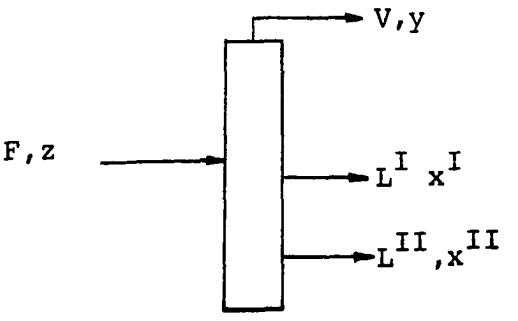
be consumed in the convergence of every liquid-liquid calculation. It can not consider to be a very efficient method. Because of its merits, of reliability and stability, we will keep on working on this method by improving its efficiency to some extent.

A main purpose of this chapter is to introduce a simultaneous convergence method for three-phase flash calculations. The algorithm is formulated according to the principle we devised in the previous chapter. Working equations, which are used to give new values of all unknown variables, play a significant role in affecting the convergence speed of a problem. Therefore, the efficiency from different combinations of working equations has been compared.

Based on a pseudo-bubble point calculation concept, the method can also be applied to liquid-liquid equilibrium calculations. The simultaneous convergence method will prove its efficiency as well as stability in three phase flash calculations.

A System Model

A general model of a three-phase equilibrium system is shown below. Phases are assumed to be in thermodynamic equilibrium with each other and any component can appear in all three phases. These assumptions give the following conventional relationships.



Three-phase equilibrium model

1. Material Balance

$$F = L^I + L^{II} + V \tag{5-1}$$

$$Fz_i = L^I x_i^I + L^{II} x_i^{II} + Vy \tag{5-2}$$

2. Equilibrium Relationships

$$y_i = K_i^I x_i^I \tag{5-3}$$

$$y_i = K_i^{II} x_i^{II} \tag{5-4}$$

$$(\gamma x)_i^I = (\gamma x)_i^{II} \tag{5-5}$$

3. Summation Equations

$$\sum_{i=1}^{n} x_i^I = 1 \tag{5-6}$$

$$\sum_{i=1}^{n} x_i^{II} = 1 \tag{5-7}$$

$$\sum_{i=1}^{n} y_i = 1 \qquad (5\text{-}8)$$

4. Energy Equation (for adiabatic process)

$$H_f = L^I h^I + L^{II} h^{II} + H V \qquad (5\text{-}9)$$

where F_j = amount of feed — moles/hr

L = liquid rate for phase j — moles/hr

V = vapor rate — moles/hr

x_i^j = liquid composition of component i in phase j — mole fraction

y_i = vapor composition of component i — mole fraction

z_i = feed composition of component i — mole fraction

h = liquid enthalpy — cal/mole

H = vapor enthalpy — cal/mole

H_f = feed enthalpy — cal/hr

By substiting equations (5-1, 3,4) into equation (5-2), we have the equation shown below;

$$y_i = \frac{F z_i (K^I K^{II})_i}{L^I K_i^{II} + L^{II} K_i^I + V(K^I K^{II})_i} \qquad (5\text{-}10)$$

Process Calculation Algorithm

Calculation methods based on the above system equations for various process calculations are presented here. There are two different methods for each process calculation

- bubble point calculation, isothermal flash calculation, and adiabatic flash calculation. For method A, most steps follow what we did previously, but some are changed in order to increase the efficiency. For method B, contrary to the conservative fashion in method A, all required measurable variables are solved simultaneously. This method turns out to be a more efficient method than we had expected. Below we introduce the detailed procedures for each process calculation.

I) Bubble point calculation

The composition of a feed and the total pressure are specified. It is desired to calculate the bubble temperature, vapor compositions, and liquid compositions of two phases. At the bubble point only an infinitesimal amount of vapor exists; hence, the overall composition of the liquid is equal to the feed composition.

i) Method A: In this method, the whole procedure is divided into two parts. The first part involves solving equations (5-1,2,5,6,7) by following the liquid-liquid method which we described in the previous chapter; then, from equation (5-3), find vapor composition. Repeat this part until vapor composition becomes stable. Thereafter, we proceed to the second part to adjust variable T, according

to the following formula and then back to the first part.

$$T^2 = T^1 + \Delta T$$

$$T^{K+1} = T^K - \frac{T^K - T^{K-1}}{f(T^K) - f(T^{K+1})} f(T^K) \qquad (5\text{-}11)$$

where $f(T_i^K) = 1 - \sum_{i=1}^{n} (y_i)^K$ at K^{th} iteration.

Repeat the above calculations until the function value of $f(T_i^K)$ has reached the described tolerance.

ii) Method B:

1) Initialize temperature T. Set the vapor rate V = 0, and assume the vapor composition and rate values from solving equations (5-1,2,5,6,7), or give any reasonable initial values for variables L^I, L^{II}, x^I, x^{II}.
2) Evaluate equilibrium constants K^I and K^{II}.
3) Calculate the vapor composition from equation (5-10).
4) Normalize the vapor composition, and henceforth obtain two phase liuqid compositions x^I and x^{II} from equation (5-3,4).
5) Use the Broyden method to adjust variable

T and liquid rate L^I according to the following equations:

$$f_1 = \sum_{i-1}^{n} x_i^I - 1$$

$$f_2 = \sum_{i=1}^{n} x^{II} - 1 \qquad (5\text{-}12)$$

6) Repeat steps (2) to (5) until norm of functions has reached the convergent criterion.

II) Isothermal Flash Calculations

In addition to specifications of the bubble calculation, the column temperature has also to be specified for the current study. Vapor rate and compositions, liquid rate and compositions of two phases are the desired objects. Therefore the basic procedure of both methods are the same as the bubble point calculation, except the unknown variable is the vapor rate V instead of the temperature T for both methods.

III) Adiabatic Flash Calculation

An energy balance has to be considered in this case. Therefore, it is desired to calculate vapor rate and compo-

sitions and rates as well as temperature of the flash column under the specified feed composition, rate, and pressure.

i) Method A: The algorithm for an adiabatic flash calculator is as follows:

1) Set feed rate, composition, temperature, and pressure. Perform isothermal flash, if required, to obtain feed phase distribution so that feed enthalpy can be calculated. Set the equilibrium pressure.
2) Assume values of vapor compositions, vapor rate, and the temperature.
3) Calculate the overall liquid compositions for current values of y and V from the equation:

$$z_i = Fz_i - Vy_i = x_i^I L^I + L^{II} x_i^{II}$$

which is derived from equation (5-2). From the resulting overall liquid composition, calculate composition of liquid phases at the current temperature by solving equations (5-5,6,7,12) as we did in liquid-liquid calculation.
4) Calculate y from equation (5-10). Repeat step 3 until y becomes stable. Then

adjust the temperature, T, and vapor rate, V, by using the Broyden method according to equations:

$$f_1 = \sum_{i=1}^{n} y_i - 1$$

$$f_2 = (H_F - VH_V - L^I h^I - L^{II} h^{II})/H_F \qquad (5\text{-}13)$$

5) Repeat stesp 3, 4, until the norm of function residues

$$F = f_1^2 + f_2^2 \qquad (5\text{-}14)$$

reaches the prescribed tolerance.

ii) Method B:

1) Same as step 1 in Method (A).
2) Same as step 2,3 of Method (A) to obtain initial values of L^I, L^{II}, V, y, x^I, and x^I, or to give any guessed values for these variables.
3) Obtain values of variables L^I, L^{II}, and T by solving the following equations:

$$f_1 = \Sigma x_i^I - 1$$

$$f_2 = \Sigma x_i^{II} - 1 \qquad (5\text{-}15)$$

$$f_3 = \frac{H_F - VH_V - L^I h^I - L^{II} h^{II}}{H_F}$$

where function values, f_1, f_2, and f_3, are obtained as the vapor compositions become constant.

Comparisons With a Conventional Method

As shown in equations (5-6,7,8), there are three equations to describe equilibrium relations among three phases. Any two of these three equations with other relations are enough to simulate a three-phase flash system. All of the previous works (6,8,35) use equations (5-7,8) as the main equations to obtain their solutions. They claim these equations may be a more efficient combination for a three-phase flash calculation. However; at the current study, equations (5-6,7) are considered to be the key equations. In order to understand which one is a more efficient combination for solving equations which involve a very strongly composition-dependent relation like Renon equation. Comparisons are made and shown in Tables 12, 13. Apparently, it reveals the current proposed method is the more efficient one for three phase flash calculations.

Alternative Method to Liquid-Liquid Calculation

As we have described in Chapter III, the function value is very sensitive to the change of the liquid composition, so, it is difficult to speed up the liquid

composition stabilization step except other alternatives are taken. From Method B, we can see vapor composition does not affect the function value as liquid composition; so, a different method for liquid-liquid calculation can be modified from Method B. The detailed steps are almost the same as in the bubble point calculation, except in step 5 instead of temperature, a liquid rate is adjusted according to the equation shown below:

$$f_1 = 1 - \Sigma x_i^{II}$$

where

$$x_i^{II} = \gamma_i^I \left(\frac{x_i^I}{\sum_{i=1}^{n} x_i^I} \right) / \gamma_i^{II}$$

Uniform Approach to the Equilibrium Process Calculations

Actually, of the above various processes the differences are the working equations and unknown variables. We can summarize them in the table on the following page. A general flow chart to these calculations is shown in Figure 18.

Arm-Level Rules

In order to have a better understanding of three-

Process Calculation	Number of Variables	Unknown Variables	Working Functions
Liquid-liquid	1	L^I	f_1
Isothermal flash	2	L^I, L^{II}	f_1, f_2
Bubble Point	2	L^I, T	f_1, f_2
Adiabatic flash	3	L^I, L^{II}, T	f_1, f_2, f_3

phase flash calculation, a conventional arm-level rule is introduced here. For a ternary system shown below, segment $\overline{vv'}$ represents the equilibrium vapor compositions line which are corresponding to liquid compositions on the binodal line, and segment $\overline{s_1's_2}$ represents the tie line of two equilibrium liquid phases. Let V be a point located on the segment $\overline{vv'}$, L will be the intercept of $\overline{VF}$ and $\overline{s^I s^{II}}$ lines. $\overline{VFL}$ line represents the material balances in the system. That is,

$$F = L + V \quad \text{and} \quad Fz = Lx + Vy$$

where L, x are the overall liquid rate and composition

$$Lx = L^I x^I + L^{II} x^{II}$$

Since points of V,L and F are represented by their composition we have the following arm-level rule;

TABLE 11. Verification of Verhoeye's Data with Susarev's Rule

1. For Ethylacetate-Methanol-Water System

$x_{methanol}$	$y_{ethylacetate}$	y_{water}	y_E/y_W
0.028	0.65	0.294	2.21
0.058	0.589	0.31	1.899
0.038	0.628	0.31	2.026
0.064	0.589	0.31	1.899
0.085	0.567	0.283	2.003
0.123	0.544	0.255	2.133

2. For Ethylacetate-Ethanol-Water System

$x_{ethanol}$	$y_{ethylacetate}$	y_{water}	y_E/y_W
0.043	0.652	0.278	2.345
0.074	0.627	0.266	2.357
0.107	0.60	0.290	2.069

TABLES 12-13. Comparisons of Number of Activity Coefficients Between Two Three-Phase Flash Calculation Algorithms

TABLE 12. For Ethylacetate-Methol-Water System

Feed Composition			Iteration		No. of Function Evaluations*	
			Ours	Theirs**	Ours	Theirs
0.45	0.04	0.51	9	11	90	273
0.45	0.06	0.49	6	7	71	135
0.45	0.08	0.47	6	7	69	96
0.45	0.1	0.45	6	6	61	79
0.45	0.12	0.43	7	6	75	74
0.45	0.15	0.40	7	6	80	126
0.45	0.2	0.35	6	6	49	88
0.45	0.3	0.25	6	6	32	37
0.45	0.4	0.15	7	6	22	31
Total			59	61	559	939

TABLE 13. For Ethylacetate-Ethanol-Water Systems

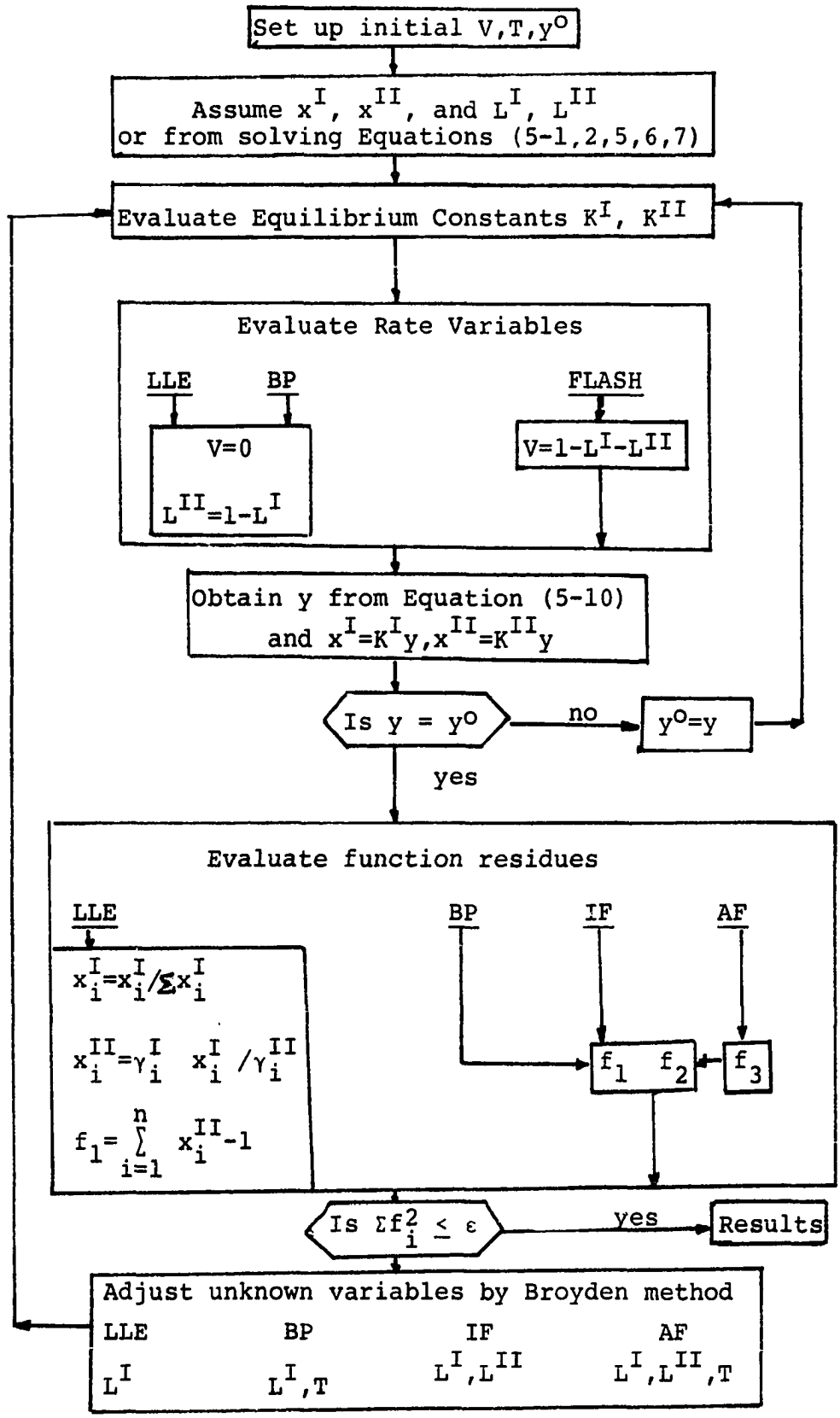
Feed Composition			Iteration		No. of Function Evaluations*	
			Ours	Theirs**	Ours	Theirs
0.45	0.04	0.51	7	14	86	516
0.45	0.06	0.49	6	7	69	96
0.45	0.08	0.47	6	6	49	78
0.15	0.10	0.45	7	7	76	79
0.45	0.12	0.43	7	6	107	184
0.45	0.15	0.40	6	10	58	119
0.45	0.20	0.35	6	6	43	51
0.45	0.3	0.25	10	6	69	32
0.45	0.4	0.15	7	6	24	23
Total			62	68	581	1188

*Total number of activity coefficient evaluations of two liquid phases for which

$$\sum_{i=1}^{3} (x_i^k - x_i^{k+1})^2 \leq 1.E\text{-}8.$$

**Equations (5-7,8) as the working equations.

Figure 18. A Uniform Approach of Using a Three-Phase Flash Calculation Method



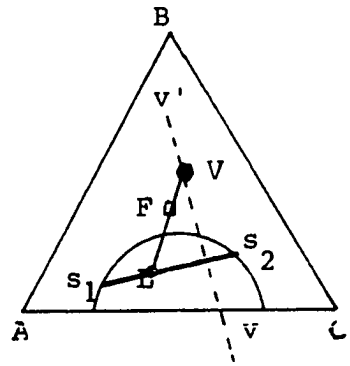


Fig. 19. Illustration of Using Arm-level Rule

For liquid-vapor equilibrium

$$\frac{\overline{FL}}{\overline{VL}} = \frac{z-x}{y-x} = \frac{\overline{V}}{F}$$

For liquid-liquid equilibrium

$$\frac{\overline{s_2L}}{\overline{s_1s_2}} = \frac{x-x^{II}}{x^{I}-x^{II}} = \frac{L^{I}}{L}$$

The above relations show, that the ratio of length of $\overline{FL}$ to the length of $\overline{VL}$ is the ratio of vapor rate to feed rate, and ratio of length of $\overline{s_2L}$ to the length of $\overline{s_1s_2}$ is the ratio of liquid rate of phase 1 to the total liquid rate. Several results confirmed by these rules are shown in Figure 21.

Susarev's Rule

In 1963, Susarev (51) derived a rule which dealt with

relations of vapor-liquid equilibrium of a ternary heterogeneous system based on thermodynamic stability conditions. With reference to Figure 19, this rule states that, "In the range of compositions where the liquid-liquid-tie lines slope toward the corner A, the addition of the third component B will increase the ratio of vapro composition of A to the vapor composition of C," i.e., $x_B \propto y_A/y_C$.

This is a very important conclusion in the area of liquid-liquid-vapor equilibrium. With this rule, we are able to judge whether a set of experimental data of heterogeneous equilibrium is reasonable. The data reported by C. H. de Minijer (42) and by Verhoeye (58) are examined by this rule. It is found that Minijer's data is quite fitted to the rule, but not Verhoeye's. In Table 11, we give detailed calculations from Veroeye's data, which will show the inconsistency between Susarev's rule and Verhoeye's data. In diagram 23, it also shows Verhoeye's data are not very smooth.

Special Properties for Vapor-liquid-liquid Equilibrium

The vapor-liquid equilibrium of a heterogeneous system involves determining the boiling point, the composition of both liquid phases, and the composition of the vapor phase in equilibrium. This explains the scarcity of experimental data on liquid-liquid-vapor in literature. Limited

sources, however, show some special features of three phase equilibrium, which is different from the conventional two phase equilibrium for tertiary systems.

Any overall liquid mixture on the same tie line within heterogeneous phases, has the following common properties:

1. They have the same compositions in both liquid phases, the only difference being their volume ratio.
2. They have the same boiling points.
3. They have the same corresponding equilibrium vapor compositions.

When the ends of these tie lines are connected, the constitute the boundary line between the homogeneous and heterogeneous areas. Therefore, the triangle diagram will be similar to the conventional isothermal triangle diagram, except that each tie line corresponds to a different boiling point temperature. Usually the differences among these boiling points are slight. The composition of vapor phases in equilibrium with the heterogeneous liquid composition can be correlated by one curve.

Because of the very narrow range of boiling point temperatures within heterogeneous phases, one has to be quite careful to set the temperature for isothermal flash calculations.

Results

From the special properties, described for a ternary three phase system, we have the following conclusions. If the equilibrium vapor line is close to the right side of the triangle, as shown in Figure 24, then: a) The feed composition is located on the left side but far away from the vapor equilibrium line. Therefore, in order to satisfy the conditions for which point V, L and F must be on the same line, and the length of $\overline{FL}$ to the length $\overline{VL}$ has to be the ratio of the vapor rate to the feed rate. So, point L has to be moved outside of the heterogeneous region or on the left side of the binodal line. Meanwhile, the results will be one phase liquid instead of two phases. However, as the feed composition is moved toward the vapor line, the distance of $\overline{FV}$ becomes shorter, and point L is then located within the heterogeneous region, and a solution of two liquid phases results. When feed composition is moved to the right side of the vapor line, the liquid becomes one phase again, and the liquid composition is rich in that of the component which represents the right corner of the triangle diagram. b) The effect of feed enthalpy will be significant to the results of a flash calculation. Although the point is far away from the vapor line, the enthalpy is kept low to allow a small amount of feed to be vaporized. The ratio of $\overline{FL}/\overline{VL}$ is then small, so point L

can keep within the heterogeneous region, and two liquid phase results are reasonable. If the enthalpy is very high, point L cannot be located within the feasible region, so no solution will reslut. That is why in Table 14, we can see the L^{II} becomes negative when feed enthalpy is increased to ten kcal/hr.

Analysis of Initial Values to the Convergence of Solutions

From a series of calculations, it can be found that composition values play a less significant role than the unknown variables, such as temperature, and rate variables, L and V, in affecting the convergence rate. Variations of function residues by giving different vapor rates for an isothermal flash calculation and an adiabatic flash calculation is shown in Table 15. It is not surprising that as a initial value is far away from the solution, the number of iterations reaching convergence is increased.

In order to find out how a convergence solution will be seriously affected by an estimated vapor rate, several adiabatic flash calculations are made for which the same initial value, say V = 1 /3, is given to problems with different feed enthalpy. As the feed enthalpy increased, the vapor rate becomes larger, and the convergence situation indicates more difficult. When feed enthalpy increased

TABLE 14. Results for Three-Phase Adiabatic Flash Calculation at Different Feed Enthalpy for Water-Acetone-Heptane System

Feed Compsoition = 0.3, 0.42, 0.28

H_F (cal/hr)	T °K	V (g-mole/hr)	L^I (g-mole/hr)	L^{II} (g-mole/hr)
5000	366.769	0.3662	0.3254	0.3084
6000	367.037	0.4868	0.2707	0.2425
6200	367.109	0.5108	0.2598	0.2294
6600	367.275	0.5588	0.2374	0.2038
7000	367.490	0.6069	0.2159	0.1772
7500	367.788	0.6659	0.1878	0.1464
8000	368.184	0.7247	0.1602	0.1150
8500	368.653	0.7831	0.1326	0.0843
9000	369.172	0.8423	0.1048	0.0529
9500	369.740	0.9006	0.0769	0.0225
10000	370.34	0.9588	0.0490	-0.0078

TABLE 15. Effects of Initial Vapor Rate to the Convergence of a Three-Phase Flash Problem

1. For an Isothermal Flash Problem

Iteration	Sum of Norm of Function Values x 10^3					
	Initial Vapor Rate					
	0.15	0.30	0.45	0.60	0.75	0.9
1	0.34	0.16	0.157	0.396	7.626	27.
2	0.0488	0.0239	0.35E-3	0.52E-1	0.436	1.867
3	0.874E-3	0.146E-3		0.004	0.0554	0.31
4				0.646E-4	0.0025	0.0374
5					0.355E-4	0.0045
6						0.0014
7						0.54E-3

2. For an Adiabatic Flash Problem
Fianl Solution: V = 0.4868

1	213.	65.5	2.57	26.57	143.5	363.7
2	0.3457	0.09	0.00134	0.109	2.32	17.15
3	0.08	0.68E-2	0.31E-3	0.299E-1	0.579	4.22
4	0.038	0.42E-2		0.747E-3	0.087	0.0178
5	0.0015	0.33E-4			0.222E-2	0.00144
6	0.27E-3				0.56E-3	0.714E-3

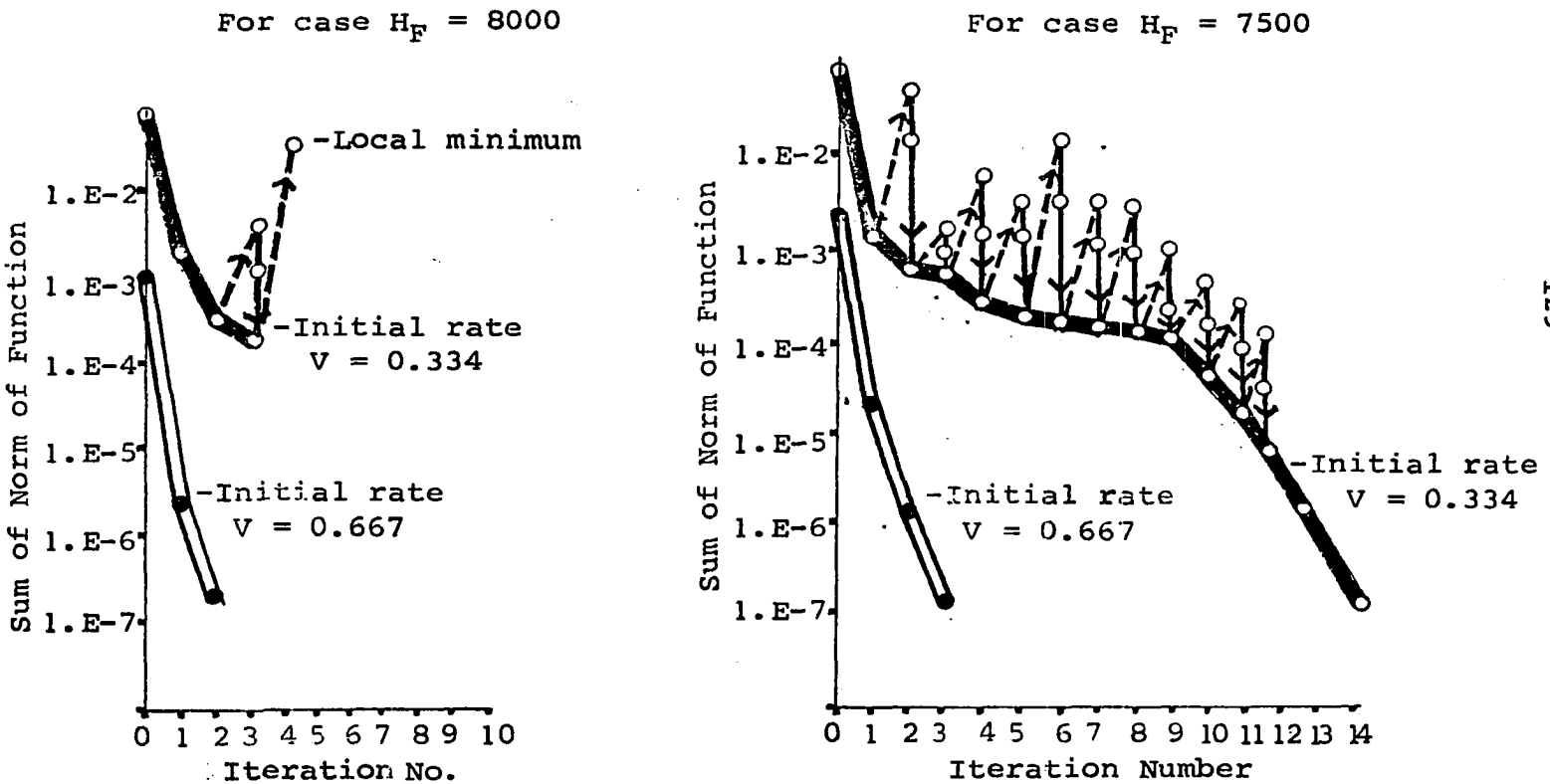


Figure 20 Effect of The Initial Vapor Rate on the Convergence of Three-phase Flash Problems

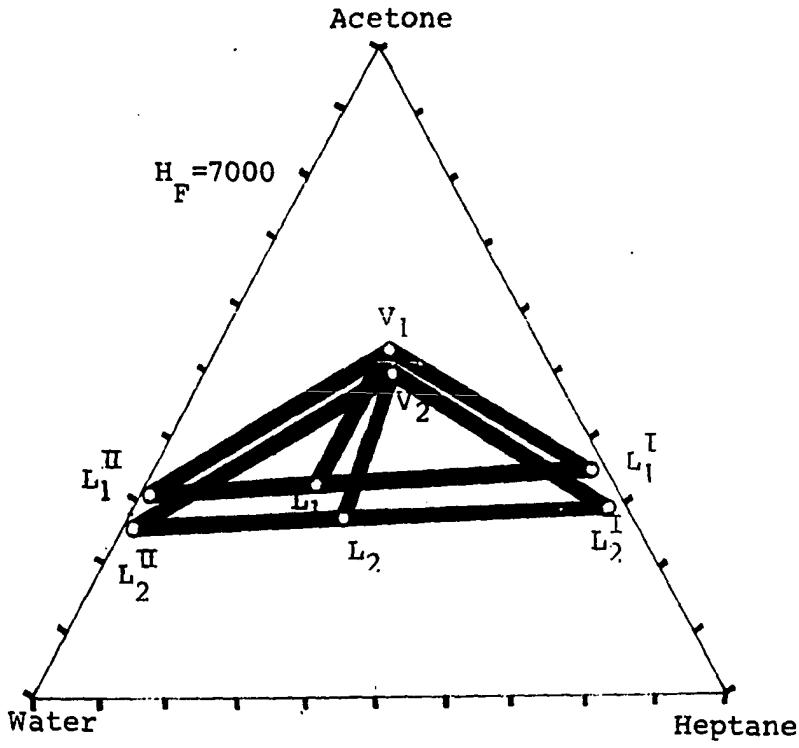


Figure 21 Verifications of two Adiabatic Flash Calculations by Diagram Method

1. z = 0.25, 0.5, 0.25

Calculation	Diagram
$L_1 = 0.137$	$\overline{FV_1}/\overline{L_1V_1} = 0.133$
$L_1^I/L_1 = 0.605$	$\overline{L_1L_1^{II}}/\overline{L_1^IL_1^{II}} = 0.6$

2. z = 0.3, 0.42, 0.28

Calculation	Diagram
$L_2 = 0.39$	$\overline{F_2V_2}/\overline{V_2L_2} = 0.4$
$L_2^I/L_2 = 0.55$	$\overline{L_2L_2^{II}}/\overline{L_2^IL_2^{II}} = 0.54$

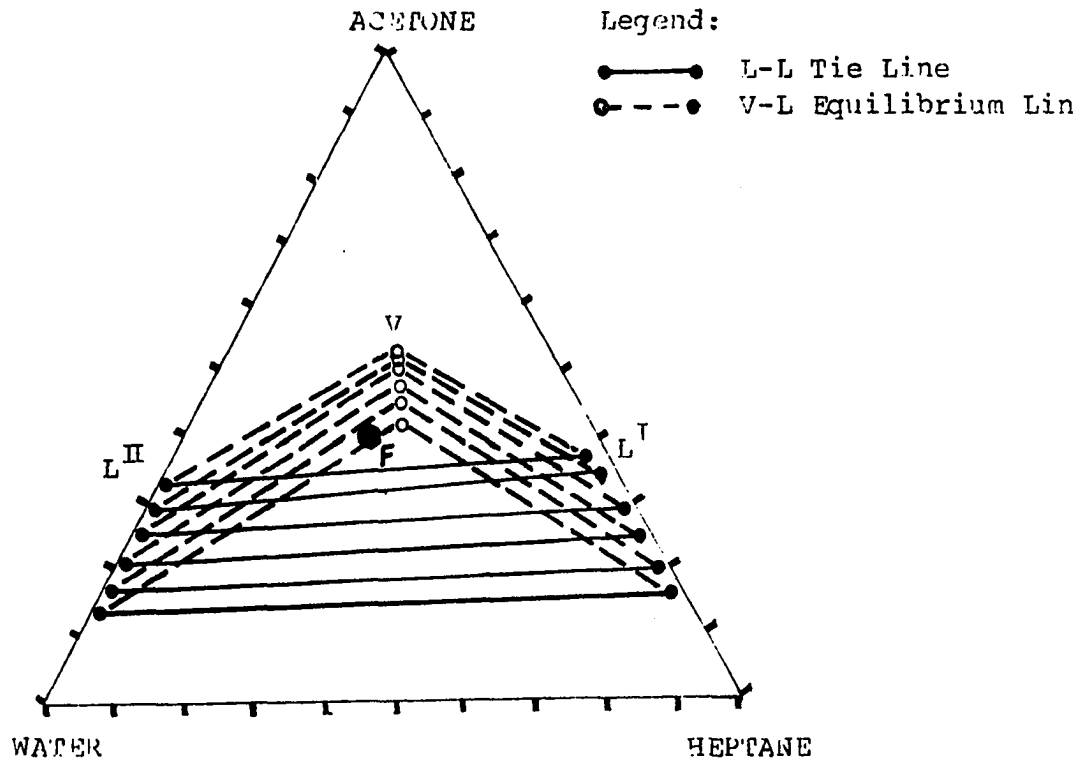


Figure 22 Results of Three-phase Adiabatic Flash Calculations at Different Given Feed Enthalpies

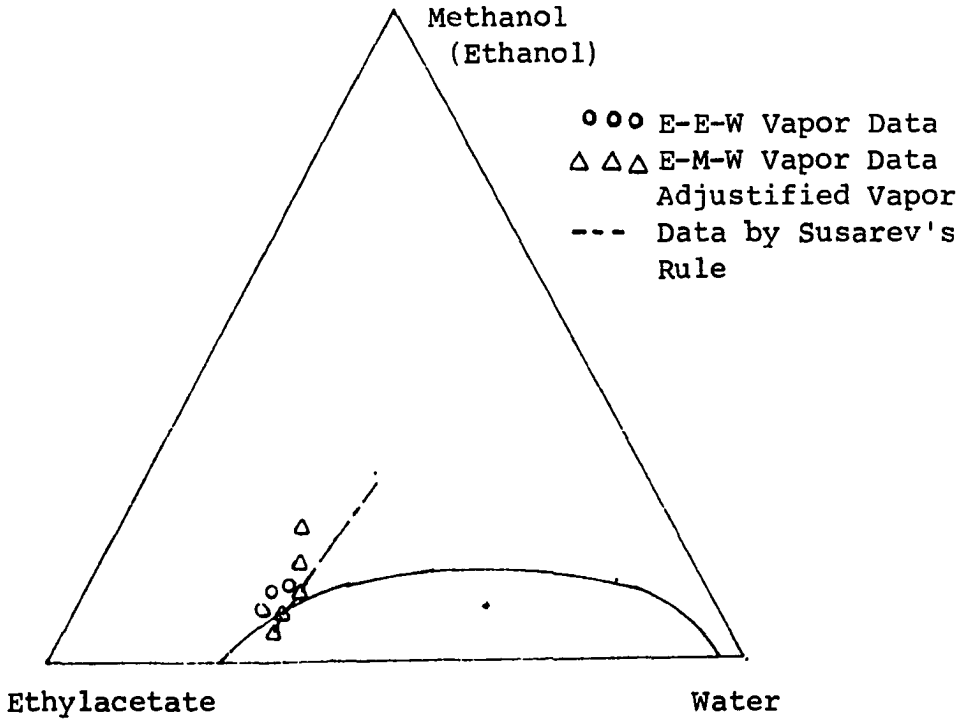


Figure 23 Verifications of Verhoeye's Data with Susarev's Rule

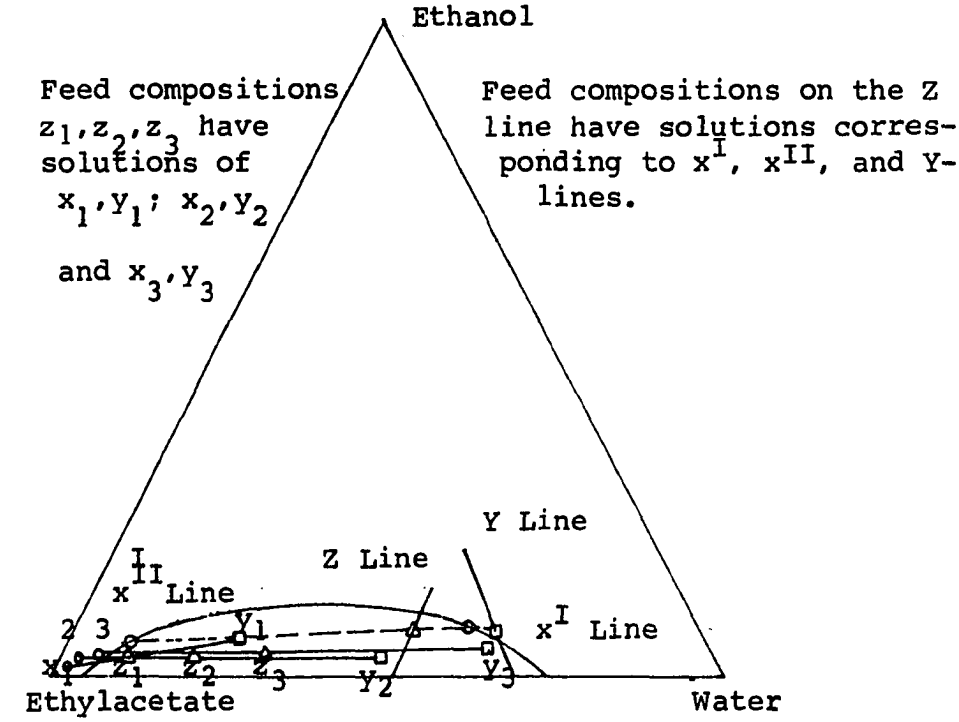


Figure 24 Examples of Three-phase Adiabatic Flash Calculations which will result one or two liquid phases solutions

to 7500, the problem cannot converge. The initial vapor rate is then changed to 0.6, the convergence speed improves greatly. In Figure 20, it shows how an initial value affects a convergence solution.

Conclusion

1. The method is reliable for homogeneous as well as heterogeneous solutions.
2. From practical comparison, the current method is better than the previous flash calculation methods.
3. The initial rate variable will affect the convergence of the solution. This does not constitute a serious shortcoming in our proposed method, since the choice of initial vapor rate can be limited to .25 - .75, based on one mole feed.

CHAPTER VI

THREE-PHASE DISTILLATION CALCULATION

For a three-phase distillation, two liquid phases are involved in a liquid stream of some stages in a distillation tower. The common cases we can encounter are heterogeneous azeotropic distillations. For example, separations of ethanol and water by benzene, separations of butanol and butylacetate by water, some of these column stages will be occupied by two liquid phases.

From a pure mathematical point of view to look at a three-phase distillation calculation there is only one additional design variable and phase equilibrium involved in every stage, which makes it different from a conventional two-phase distillation problem. However, because of the formation of two liquid phases, the molecular models and interactions among design variables are so intricate that a three-phase distillation calculation becomes more than a pure mathematical problem.

Previously, we have suggested a sequential method for this special purpose (63). The entire calculation is divided into two loop calculations. First, adjust temperature by bubble point calculation which is described in the previous

chapter. Then adjust vapor rates from energy equations by a direct substitution method. The method is deficient in its slow speed convergence. The instability of calculations will be observed with increased stage number. An advantage of this method is the capability to identify the formation of two liquid phases at each stage.

In this chapter, we propose a simultaneous convergence method for which the main scheme follows what we described in Chapter IV.

The method has demonstrated its efficiency and stability for the problems where the whole column is described by two liquid phases, however, at the expense of the capability to predict liquid phase separation. It is shown that the same scheme is able to be applied to the related processes calculations, for example, homogeneous azeotropic distillations and countercurrent extractions.

Simulation Model

The proposed model for a three-phase multicomponent distillation calculation is shown in Figure 25. The stages in this distillation column are numbered from top to bottom with a partial condenser as the first stage and the reboiler as the last stage. Each stage is assumed to be an equilibrium stage, therefore, the vapor stream leaving each stage will be in equilibrium with the liquid stream leaving the same stage. The liquid stream contains two liquid phases, L^I and

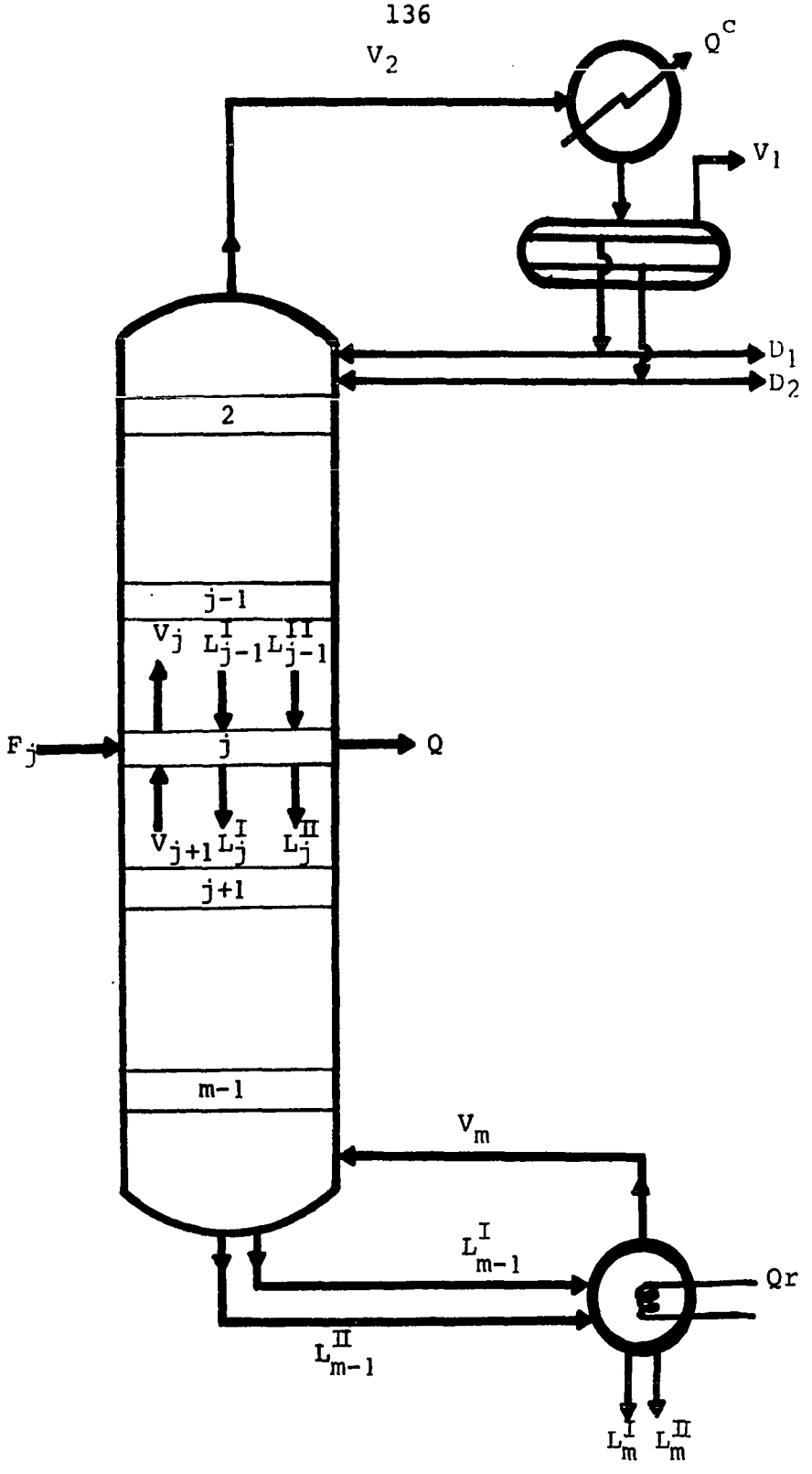


Figure 25 A Three-phase Distillation System Model

L^{II}, which are also in equilibrium with each other. There is one feed stream F_j and one heat addition or removal Q_j at each stage. Of course, minor changes can be made to account for vapor and liquid side draws and for various units at the top and bottom of the column, but they are not included here in order to simplify discussion.

Analysis of number of independent variables is determined easily by the method of Smith (50). Many different sets can be selected, and the following is merely representative of one of the more useful sets of independent variables for three-phase distillation with partial condenser:

1. Feed stream temperature, pressure and composition.
2. Pressure at each stage.
3. Heat leak in each stage, including reboiler and partial condenser.
4. Total number of stages.
5. Reflux ratios for each liquid phase returned to the first tray.
6. There is no sub-cooling of the reflux liquids.

Reflux ratio for each phase is defined in the usual way as the ratio of the liquid returned to the column divided by the top product for that phase. Implicit definitions of the reflux ratios are shown as a part of Figure 25.

System Equations

Mass and energy balances and equilibrium relationships for a m-stage and n-component three-phase ideal stage

operation are the same as a conventional two-phase distillation design.

Material Balance Equations

$$M_i^j = (L^I x_i^I + L^{II} x_i^{II})^{j-1} - (Vy_i)^j - (L^I x_i^I)^j$$

$$- (L^{II} x_i^{II})^j + (Vy_i)^{j+1} + (Fz_i)^j = 0$$

$$i=1,\ldots n$$

$$j=1,\ldots m \qquad (6\text{-}1)$$

Vapor-Liquid-Liquid Equilibrium

$$E_i^{1j} = f_i^{v,j} - f_i^{LI,j} = 0$$

$$E_i^{2j} = f_i^{LI,j} - f_i^{LII,j} = 0$$

$$E_i^{3j} = f_i^{v,j} - f_i^{II,j} = 0$$

$$i=1,\ldots n \qquad (6\text{-}2)$$

$$j=1,\ldots m \qquad (6\text{-}3)$$

where $f_i^{v,j}$, $f_i^{LI,j}$, $L_i^{LII,j}$ represent fugacity of vapor phase, liquid phase I and II.

Summation Equations

$$S^{v,j} = \sum_{i=1}^{n} y_i^j - 1 = 0 \qquad (6\text{-}4)$$

$$S^{LI,j} = \sum_{i=1}^{n} x_i^{I,j} - 1 = 0 \qquad i=1,\ldots n \quad j=1,\ldots m \qquad (6\text{-}5)$$

$$S^{LII,j} = \sum_{i=1}^{n} x_i^{II,j} - 1 = 0 \qquad (6\text{-}6)$$

Energy Balance Equations

$$E^j = (L^I h^I + L^{II} h^{II})^{j-1} - (VH + L^I h^I + L^{II} h^{II} + Q - Fh^F)^j$$

$$j=1,\ldots m \qquad (6\text{-}7)$$

Solution of Material Balance Equations

Vapor Rate Profile

While the liquid rates L_j^I, L_j^{II} have been assumed, the value of vapor rate can be obtained from total material balance of each stage.

$$V_j = V_{j+1} + (L^I + L^{II})_{j-1} - (L^I + L^{II})_m$$

$$j=2,\ldots n-1 \qquad (6\text{-}13)$$

$$V_j = V_j + F_f \qquad j \leq f$$

For $j=1$ $\qquad V_1 = V_2 - [(L^I + L^{II})_j + D]$

For $j=m$ $\qquad V_j = (L^I + L^{II})_{j-1} - (L^I + L^{II})_j$

Tridiagonal Matrix Method

Once the T_j and L_j^I, L_j^{II} have been assumed, material balances for every component become a family of equations of the form:

$$B_i X_{i1} + C_1 X_{i,2} = D_1$$

$$A_j X_{i,j-1} + B_j X_{i,j} + C_j X_{i,j+1} = D_j \qquad (6\text{-}8)$$

$$A_n X_{i,n-1} + B_n X_{i,n} = D_n$$

Where stage 1 represents the partial condenser, and stage n represents the reboiler, and if composition X is considered to be composition y, then

$$A_j = L^I_{j-1}/K^I_{i,j-1} + L^{II}_{j-1}/K^{II}_{i,j-1}$$

$$B_j = V_j - L^I_j - L^I_j/K^I_{i,j} - L^{II}_j/K^{II}_{i,j}$$

$$C_j = V_{j+1} \; ; \; D_j = -F_j z_{i,j} \qquad (6\text{-}9)$$

if composition X is considered to be liquid composition x^I_i, then

$$A_j = L^I_{j-1} + L^{II}_{j-1}\beta_{j-1}$$

$$B_j = -K_j V_j - L^I_j - L^{II}_j \beta_j$$

$$C_j = V_{j+1} K_{j+1}'$$

$$D_j = -F_j z_{ij} \qquad (6\text{-}10)$$

Written in matrix form, equation (6-8) becomes

$$\begin{bmatrix} B_1 & C_1 & & & & X_{i,1} \\ A_2 & B_2 & C_2 & & & X_{i,2} \\ & A_j & B_j & C_j & & X_{i,j} \\ & & A_{m-1} & B_{m-1} & C_{m-1} & X_{i,m-1} \\ & & & A_m & B_m & X_{i,m} \end{bmatrix} = \begin{bmatrix} D_1 \\ D_2 \\ D_j \\ D_{m-1} \\ D_m \end{bmatrix} \qquad (6\text{-}11)$$

A matrix, such as the ABC matrix in equation (6-10), which has entries only on the main diagonal B and two adjacent diagonals A and C is called a tridiagonal matrix. Highly efficient methods exist for solving sets of linear equations represented by a tridiagonal matrix. Perhaps the most suitable of these is the method which has been presented by Wang and Henke (62).

This method involves the calculation of two auxiliary quantities p_j and q_j, for each row, advancing forward through the matrix:

$$p_1 = C_1/B_1 \; ; \; q_1 = D_1/B_1$$

$$p_j = C_j/(B_j - A_j p_{j-1}) \qquad 2 \leq j \leq m-1 \qquad (6\text{-}12)$$

$$q_j = (D_j - A_j q_{j-1})/(B_j - A_j p_{j-1}) \qquad 2 \leq j \leq m$$

Values of $X_{i,j}$ then can be obtained by working back up the rows of the matrix:

$$X_{i,m} = q_m$$

$$X_{i,j} = q_j - p_j X_{i,j+1} \qquad 1 \leq j \leq m-1 \qquad (6\text{-}13)$$

Once each matrix solution is required for each component. This method is rapid, and does not require much computer memory. Besides, the method does not lead to any buildup of computer truncation errors caused, for example, by the subtraction of nearly equal quantities from one another.

Optimal Computation

In the previous chapter, we have mentioned that the most efficient method for three-phase flash calculations is to solve equations (5-6, 7) rather than equations (5-7, 8). Attempting to apply a similar conclusion to devise a method for multistage distillation problems, we find a convergence solution from solving equations (6-5, 6) and energy equation (6-7) are too critical to step sizes.

In generating an approximate Jacobian matrix inversion, the perturbation method is used for which each variable, X, is updated with a step size ratio, ϵ, by the relation shown below:

$$\hat{X} = X(1 + \epsilon)$$

In most cases, the method will fail to obtain a convergence solution if the right step size ratio of each unknown variable is not given. Several results are listed below:

	STEP SIZE RATIO	RESULTS
1.	0.025 for L^I, L^{II}, and 0.05 for T	Divergent
2.	0.025 for L^I, L^{II}, T	Divergent
3.	0.05 for L^I, L^{II} 0.025 for T	Convergent

Another option is then to set up by solving equations (6-4, 5) instead of equations (6-5, 6) with energy equation (6-7). With such a consideration, it is proved the method can be not only released from constraints of step sizes, but dependable for obtaining a convergence solution. So the optimal method for a m-stage three-phase distillation calculations to solve 3m equations as following:

$$f_j = \sum_{i=1}^{n} y_{i,j} - 1 = 0$$

$$f_{j+m} = \sum_{i=1}^{n} x_{i,j} - 1 = 0 \qquad j=1,\ldots m \tag{6-14}$$

$$f_{j+2m} = \frac{H^{IN} - H^{out}}{H^{IN}} = 0 \tag{6-15}$$

where L^I, L^{II} and T are taken to be unknown variables.

Detailed procedures:

1. Set up vapor rate profile and composition.
2. Obtain the initial liquid rates and compositions of each stage from liquid-liquid calculation, using the assumed vapor values or assume K^I, K^{II}, L^I, L^{II} or give initial values of X^I, L^I, X^{II}, L^{II}.
3. Set up temperature profile, and put in the required physical properties data and specified values.
4. Obtain vapor profile from equation (6-13).
5. Evaluate equilibrium constants $K^I_{i,j}$ and $K^{II}_{i,j}$ from the equation, if assumed $x^I_{i,j}$, $x^{II}_{i,j}$ are given.

6. Solve for liquid composition $x^{I}_{i,j}$ from the tri-diagonal matrix method.
7. Normalize liquid composition $x^{I}_{i,j}$. Then repeat steps 5 and 6 until composition values before step 7 almost agree with that of step 7.
8. From equation (6-2, 3) obtain y and x^{II}.
9. Evaluate function values of equation (6-14).
10. Normalize y, x^{II} and obtain the enthalpy of vapor and liquid.
11. Evaluate the enthalpy function value of equation (6-15).
12. Adjust variables L^{I}, L^{II} and T by the Broyden method, and repeat steps 4 to 12 until the prescribed criterion is met.

A logical flow chart diagram is shown in Figure 27.

Results and Conclusions

For descriptions of a three-phase distillation problem, some of system equations are redundant. Several methods have been studied by varying combinations of system equations. The most successful one is the algorithm of combining equations which are for a conventional two-phase distillation and a liquid-liquid equilibrium. So far, the proposed method has been demonstrated successfully to treat the problem where the whole column is with heterogeneous

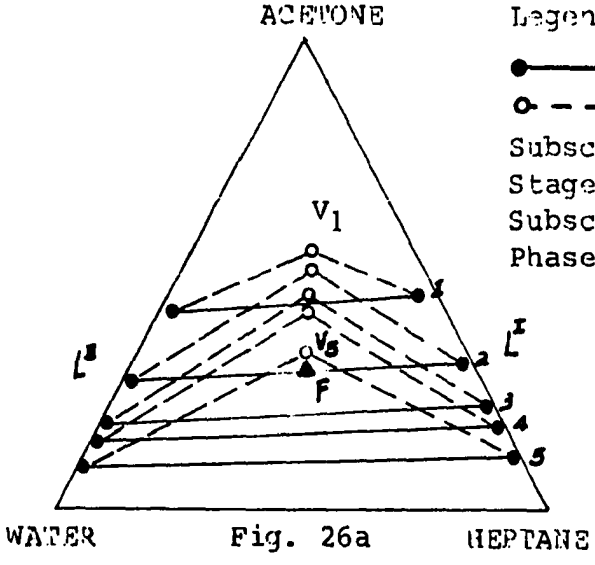


Fig. 26a

x_F = 0.35. 0.30, 0.35

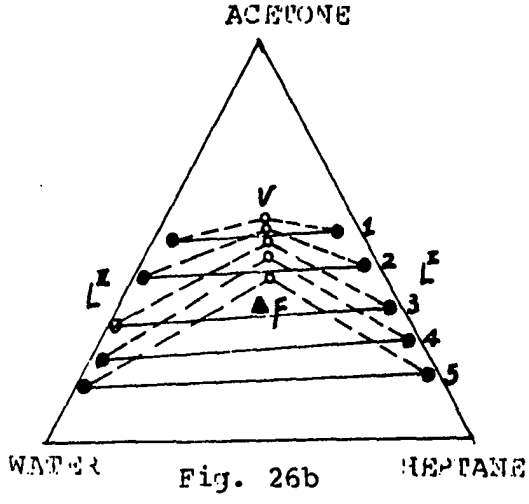


Fig. 26b

x_F = 0.32, 0.35, 0.33

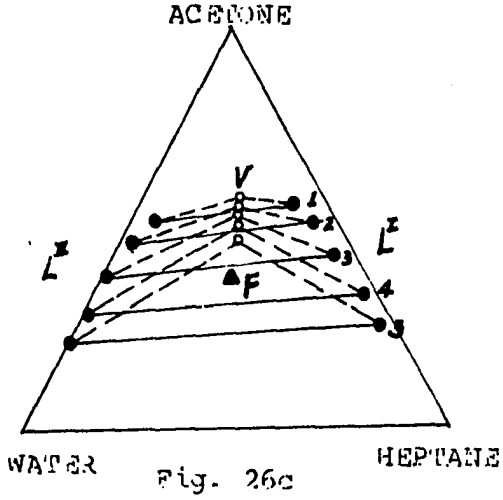


Fig. 26c

x_F = 0.30. 0.40, 0.30

Figure 26 Results of a Three-phase Five-Stage Distillation Calculation

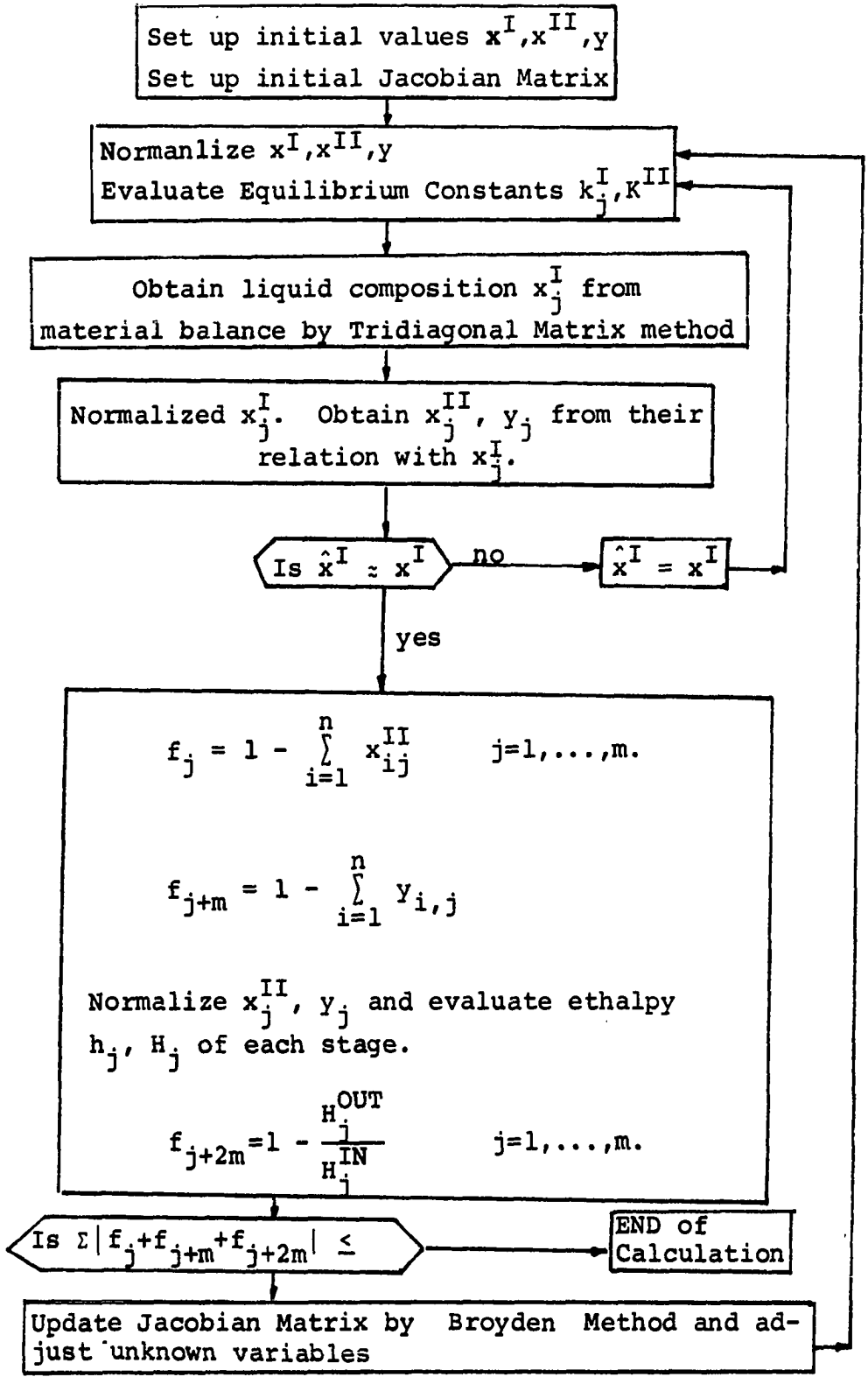


Figure 27. The Logical Diagram of a Three-Phase Distillation Method

TABLE 16. Variations of Function Residues with Iteration Number for a Three-Phase Distillation Problem

Iteration	Norm of Function Residues
1	0.8085 E-1
2	0.2826 E-1
3	0.2495 E-1
4	0.5779 E-2
5	0.7972 E-3
6	0.3694 E-3
7	0.3195 E-4
8	0.1933 E-4
9	0.2992 E-5
10	0.3608 E-6

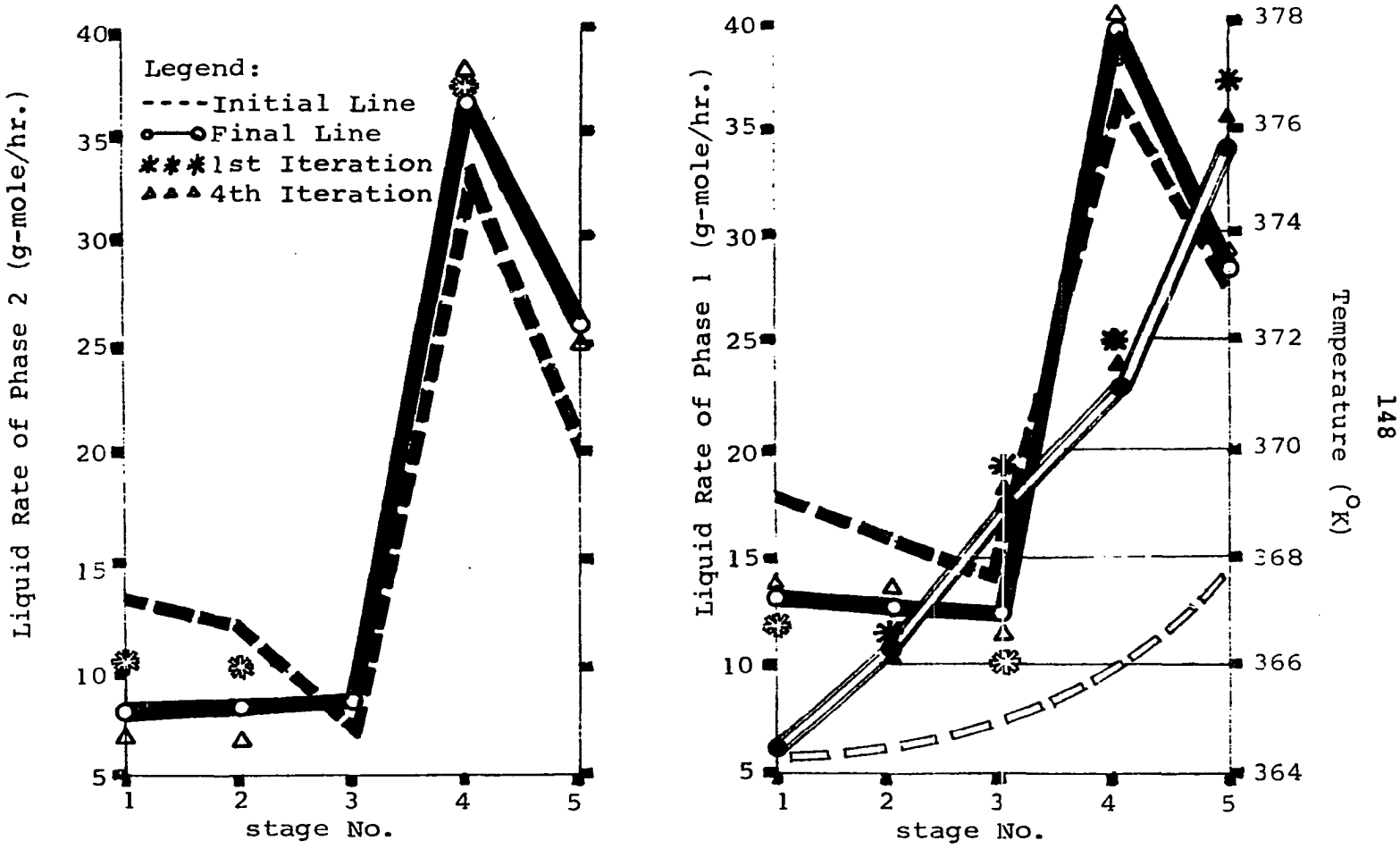


Figure 28 Analysis of Liquid Rate, Temperature with Iteration for a Three-phase Distillation Calculation

Table 17 SOLUTIONS OF A THREE-PHASE DISTILLATION PROBLEM

TRAY NUMBER 1
LIQUID 1 RATE = 13.45 MOLES/HR
LIQUID 2 RATE = 10.40 MOLES/HR
VAPOR RATE = 43.93 MOLES/HR

T = 366.34 DEG K P = 43.93 ATM	LIQUID 1	LIQUID 2	VAPOR
WATER	.0389	.5564	.2091
ACETONE	.4583	.4199	.5571
HEPTANE	.5029	.0240	.2339

TRAY NUMBER 2
LIQUID 1 RATE = 12.65 MOLES/HR
LIQUID 2 RATE = 10.68 MOLES/HR
VAPOR RATE = 67.78 MOLES/HR

T = 368.40 DEG K P = 67.78 ATM	LIQUID 1	LIQUID 2	VAPOR
WATER	.0162	.7163	.2286
ACETONE	.3151	.2756	.5163
HEPTANE	.6687	.0079	.2550

TRAY NUMBER 3
LIQUID 1 RATE = 12.24 MOLES/HR
LIQUID 2 RATE = 10.85 MOLES/HR
VAPOR RATE = 67.26 MOLES/HR

T = 371.08 DEG K P = 67.26 ATM	LIQUID 1	LIQUID 2	VAPOR
WATER	.0091	.8083	.2533
ACETONE	.2200	.1878	.4669
HEPTANE	.7709	.0037	.2298

TRAY NUMBER 4
LIQUID 1 RATE = 39.92 MOLES/HR
LIQUID 2 RATE = 38.88 MOLES/HR
VAPOR RATE = 67.03 MOLES/HR

T = 373.20 DEG K P = 67.03 ATM	LIQUID 1	LIQUID 2	VAPOR
WATER	.0037	.8426	.2695
ACETONE	.1825	.1545	.4357
HEPTANE	.8102	.0028	.2947

TRAY NUMBER 5
LIQUID 1 RATE = 27.80 MOLES/HR
LIQUID 2 RATE = 28.27 MOLES/HR
VAPOR RATE = 22.73 MOLES/HR

T = 377.67 DEG K P = 22.73 ATM	LIQUID 1	LIQUID 2	VAPOR
WATER	.0047	.9084	.3183
ACETONE	.1076	.0896	.3417
HEPTANE	.8877	.0015	.3399

TABLE 18. Sensitivities of Changes of Function Residues to Compositions

Iteration A			Iteration B		
	Variables	Function Residues		Variables	Function Residues
	366.15	-0.49 E-3		366.15	-0.50 E-3
	367.33	-0.128 E-2		367.33	-0.247 E-2
T	368.65	-0.83 E-3	T	368.65	-0.245 E-2
	370.31	-0.11 E-3		370.31	-0.42 E-3
	372.32	0.23 E-3		372.32	-0.4 E-4
	14.23	-0.2 E-2		14.23	-0.128 E-2
	14.26	-0.387 E-2		14.26	-0.676 E-2
L^I	13.36	-0.298 E-2	L_1^I	13.37	-0.650 E-2
	39.76	-0.66 E-3		39.76	-0.121 E-2
	26.26	0.3 E-4		26.65	-0.35 E-3
	9.97	0.43 E-3		9.97	-0.61 E-3
	9.75	0.18 E-3		9.75	0.14 E-3
L^{II}	10.29	-0.45 E-3	L_1^{II}	10.29	-0.62 E-3
	36.99	-0.19 E-3		36.99	-0.19 E-3
	26.31	-0.00007			
	Norm of Function Residues	0.2885 E-4			0.10445E-3

liquids. The Figure 26 shows results of a five-stage three-phase distillation calculation with different feed compositions for the system of water-acetone-heptane. A typical output is shown in Table 17.

Since the method is not successful to deal with the problem where miscible liquid as well as immicible liquid phases are coexisted in a distillation column it was failed for problems with more than five stages. Part of failures might be indebted to the Renon constants which are not able to describe the V-L equilibrium behavior for homogeneous regions as well as heterogeneous phase region. Some prospect areas in calculating this type of problems is still left for further developments.

We have shown in the section of liquid-liquid equilibrium that values of activity coefficients are very sensitive to minor changes of liquid compositions. At the current study, this special characteristic also accounts for the occasional failure of convergence. A set calculated values are given in Table 18 to interpret this point.

Compared with a two-phase distillation calculation, selections of initial values are much restricted in a three-phase distillation calculation. It will be better to take a look at the material balance of the partial condenser.

$$(L_1^I + D^I)x_1^I + (L_1^{II} + D^{II})x_1^{II} = V_2y_2 - V_1y_1 = z$$

For the above equations, the given improper vapor rate values

will bring values, z, to be compositions in a miscible region. Accordingly, it implies that solutions of x^I, x^{II} will be a set of trivial solutions. If such case happens, then the problem will never go back to a heterogeneous liquid solution, thus a convergence solution cannot be expected. For the narrow selection of initial values, feasibilities of the proposed method are very restrained with the existence of one more liquid phase. However, the method is proved very efficiently, if a set of reasonable initial values is given. Figure 28 and Table 16 are shown this point.

A possible way to obtain a set of proper initial values is to solve material balance as a liquid-liquid equilibrium problem stage-by-stage. Then adjust temperature and vapor profile by Broyden method, until a rough convergence criterion is reached.

Based on the same number of column stages results of this study suggest a more efficient separation between two liquid phases can be accomplished by a three-phase distillation method than a counter-current extraction method of which results will be shown later.

Azeotropic Distillation

Now we want to show that the proposed method can also be applied to the highly-nonideal solution, two-phase equilibrium process calculation, such as the azeotropic distillation.

As it was introduced by Smith (50), the rigorous method for azeotropic processes is the stage-by-stage method, and this method is known to be unstable and inefficient. Therefore, the current study should be considered to be a new, efficient method.

System Equations and the Proposed Algorithm

Although our proposed method is designed especially for three-phase distillation calculations, it should be able to extend to two-phase nonideal solution equilibrium process problems. All of the system equations are the same as we described in equations (6-1, 7), by only letting $L_j^{II} = 0$, $j = 1,...m$. The method can be followed as we described in Figure 27.

Results and Discussion

In order to demonstrate the proposed method, we have the ethylacetate-methanol-water and ethylacetate-ethanol-water systems as illustrative examples. Based on one hundred mole feed, we give problems as follows: The distillation column with a partial condenser is operated under one atmosphere condition and the feed composition is given

1. 0.38, 0.25, 0.37
2. 0.2, 0.6, 0.2
3. 0.1, 0.8, 0.1

Table 19 SOLUTIONS OF AN AZEOTROPIC DISTILLATION PROBLEM

TRAY NUMBER 1
LIQUID 1 RATE =346.06 MOLES/HR
VAPOR RATE = 36.70 MOLES/HR

T = 35.09 DEG K P = 1.00 ATM	LIQUID	VAPOR	K-VALUE
WATER	.2580	.3719	1.4414
ACETONE	.5831	.4888	.8383
HEPTANE	.1588	.1366	.8601

TRAY NUMBER 2
LIQUID 1 RATE =346.88 MOLES/HR
VAPOR RATE = 36.33 MOLES/HR

T = 71.79 DEG K P = 1.00 ATM	LIQUID	VAPOR	K-VALUE
WATER	.1959	.3137	1.6010
ACETONE	.6274	.5370	.8559
HEPTANE	.1766	.1479	.8376

TRAY NUMBER 3
LIQUID 1 RATE =347.34 MOLES/HR
VAPOR RATE = 36.13 MOLES/HR

T = 71.42 DEG K P = 1.00 ATM	LIQUID	VAPOR	K-VALUE
WATER	.1668	.2826	1.6941
ACETONE	.6432	.5597	.8702
HEPTANE	.1900	.1571	.8265

TRAY NUMBER 4
LIQUID 1 RATE =347.56 MOLES/HR
VAPOR RATE = 36.02 MOLES/HR

T = 71.22 DEG K P = 1.00 ATM	LIQUID	VAPOR	K-VALUE
WATER	.1537	.2680	1.7435
ACETONE	.6461	.5674	.8781
HEPTANE	.2002	.1638	.8180

TRAY NUMBER 5
LIQUID 1 RATE =347.65 MOLES/HR
VAPOR RATE = 35.95 MOLES/HR

T = 71.11 DEG K P = 1.00 ATM	LIQUID	VAPOR	K-VALUE
WATER	.1476	.2614	1.7707
ACETONE	.6442	.5684	.8823
HEPTANE	.2082	.1688	.8107

Table 19 SOLUTIONS OF AN AZEOTROPIC DISTILLATION PROBLEM (continued)

TRAY NUMBER 6
LIQUID 1 RATE =347.69 MOLES/HR
VAPOR RATE = 35.89 MOLES/HR

T = 71.04 DEG K	LIQUID	VAPOR	K-VALUE
P = 1.00 ATM	--------	--------	-------
WATER	.1444	.2582	1.7876
ACETONE	.6409	.5670	.8848
HEPTANE	.2147	.1727	.8045

TRAY NUMBER 7
LIQUID 1 RATE =347.71 MOLES/HR
VAPOR RATE = 85.74 MOLES/HR

T = 70.98 DEG K	LIQUID	VAPOR	K-VALUE
P = 1.00 ATM	--------	--------	-------
WATER	.1425	.2565	1.7995
ACETONE	.6374	.5650	.8864
HEPTANE	.2200	.1759	.7992

TRAY NUMBER 8
LIQUID 1 RATE =347.75 MOLES/HR
VAPOR RATE = 85.71 MOLES/HR

T = 20.83 DEG K	LIQUID	VAPOR	K-VALUE
P = 1.00 ATM	--------	--------	-------
WATER	.1398	.2529	1.8085
ACETONE	.6397	.5680	.8880
HEPTANE	.2204	.1762	.7992

TRAY NUMBER 9
LIQUID 1 RATE =347.92 MOLES/HR
VAPOR RATE = 85.62 MOLES/HR

T = 20.80 DEG K	LIQUID	VAPOR	K-VALUE
P = 1.00 ATM	--------	--------	-------
WATER	.1315	.2419	1.8391
ACETONE	.6460	.5774	.8939
HEPTANE	.2225	.1778	.7993

TRAY NUMBER 10
LIQUID 1 RATE =348.53 MOLES/HR
VAPOR RATE = 64.91 MOLES/HR

T = 20.71 DEG K	LIQUID	VAPOR	K-VALUE
P = 1.00 ATM	--------	--------	-------
WATER	.1070	.2085	1.9478
ACETONE	.6591	.6050	.9180
HEPTANE	.6339	.1868	.7986

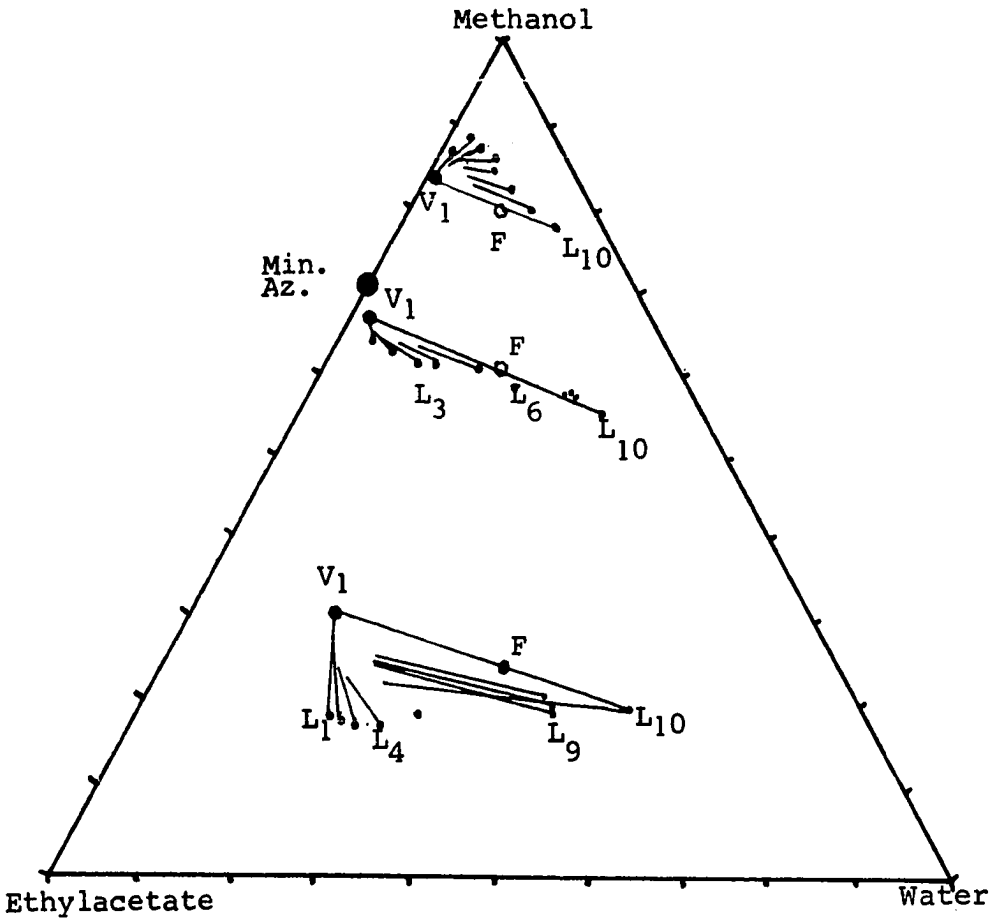


Figure 29a Results of Three Azeotropic Distillation Calculations for Ethylacetate - Methanol-Water system

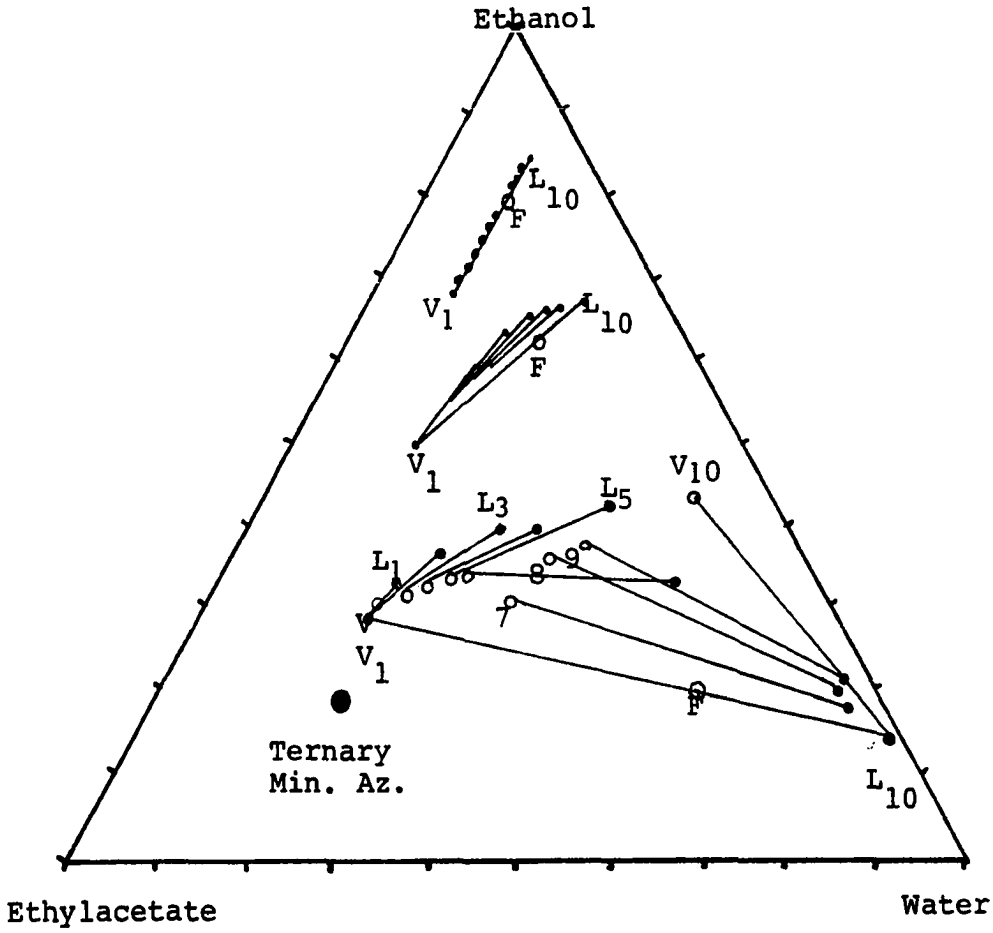


Figure 29b Results of Three Azeotropic Distillation Calculations for Ethylacetate-Ethanol - Water system

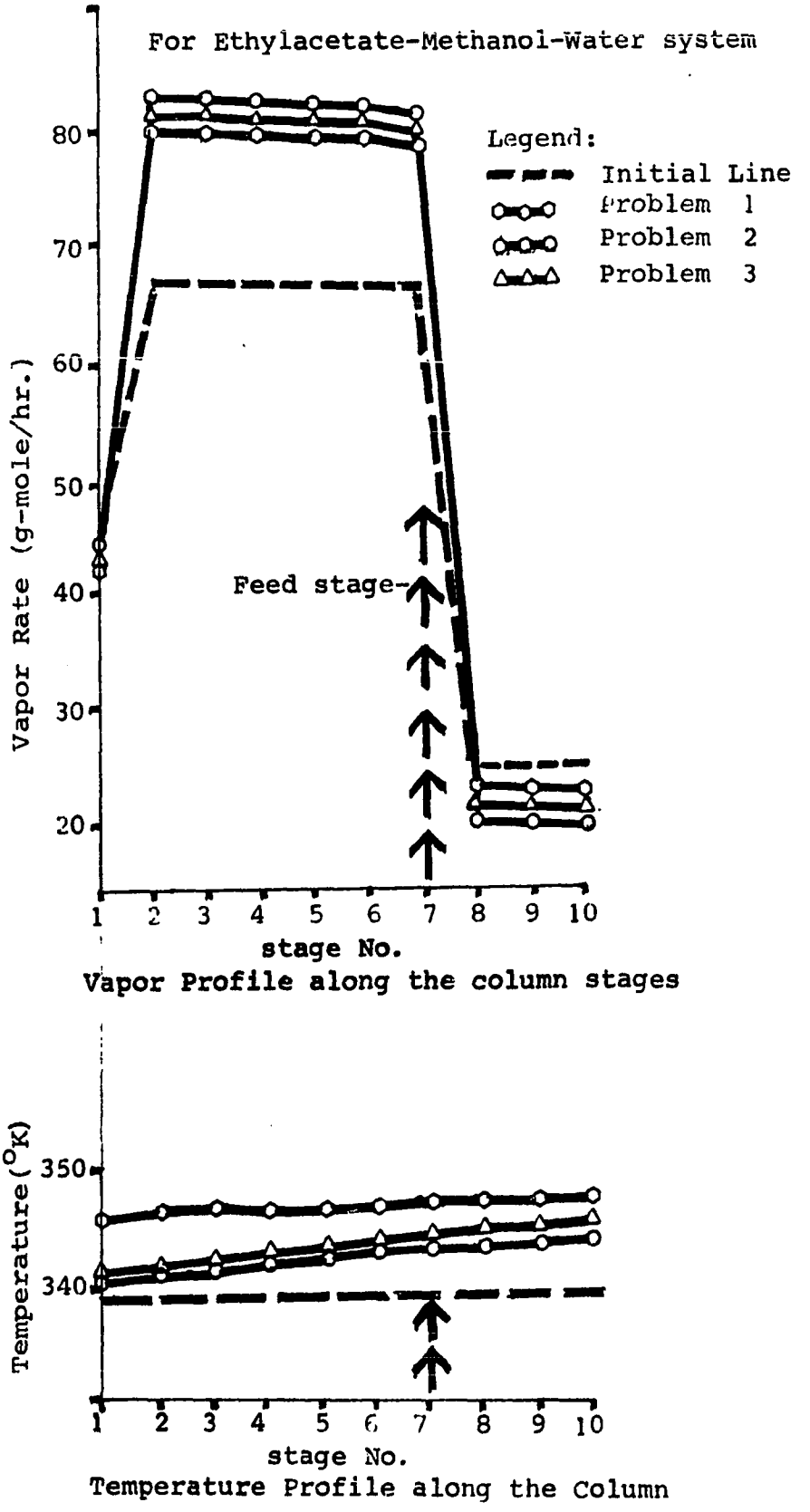
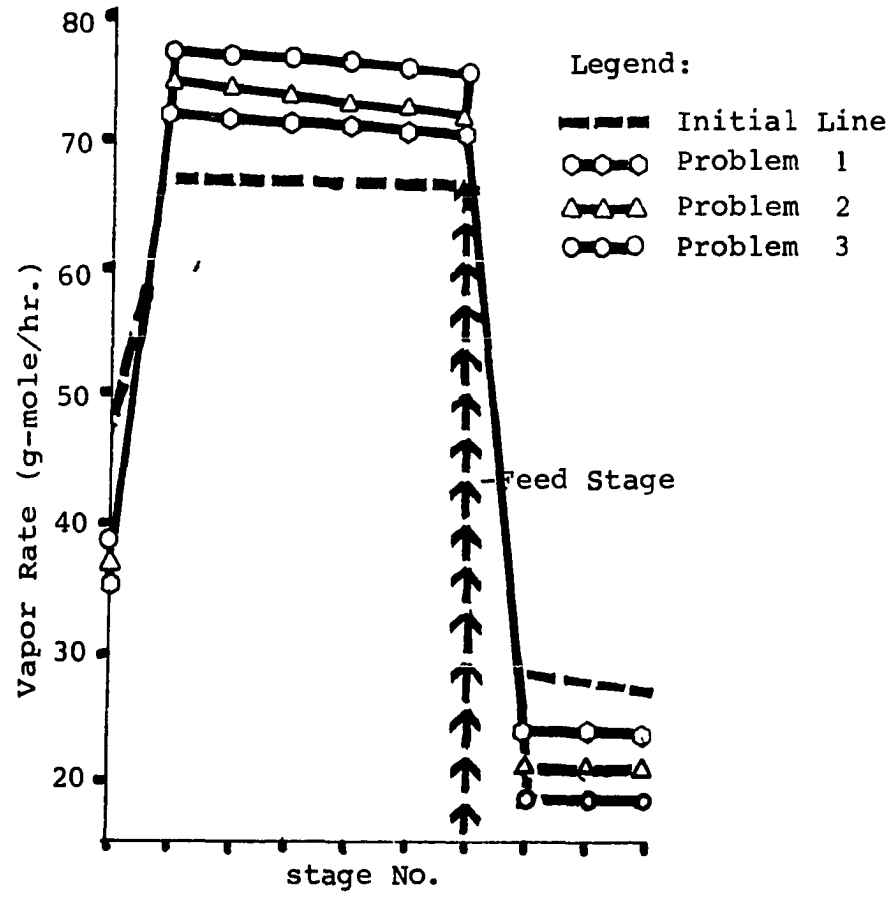
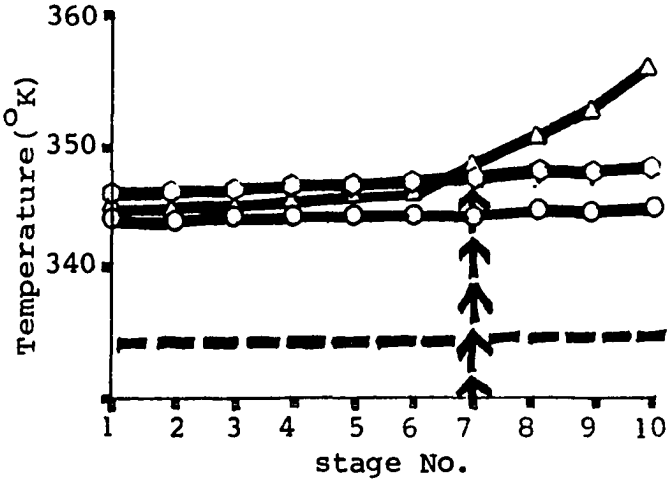


Figure 30.a Results of a Ten-stage Azeotropic Distillation

For Ethylacetate-Ethanol-Water System



Vapor Profile along the column stages



Temperature Profile along the Column

Figure 30b Results of a Ten-stage Azeotropic Distillation

for three different runs respectively. There are ten stages in the column and feed is fed at the 7th stage. Partial condenser duty is 35 Kcal/hr. The total liquid of the partial condenser is assumed to return to the column. Results are shown in Figure (29-a, 30-a). A typical output print is listed in Table 19. A better separation is obtained above the feed stage, rather than in the stages below the feed stage, since liquid rates of the 7th, 8th, and 9th stages are almost the same.

With the same specifications, we run the case for the E-E-W system. The results are shown in Figure (30-b, 29-b). The specified stage number is not given enough for an overproduct to reach the minimum azeotrope, but the distillation lines show the tendency toward an azeotrope for each feed. Therefore, the method is reliable. The efficiency of the method can be seen in Table 20, which shows the norm of function values at each iteration.

Initial Values to the Convergence Rate

It is found that accurate estimates for unknown variables, such as temperature profile and vapor profile are the more significant initial values than that of the composition profile of vapor and liquid in affecting the convergence. Some ill-conditioned initial unknown variables might lead to nonconvergence of the inner-loop iteration for which the liquid composition should agree. This would make the entire calculation fail. Most of the time, however, the method works very well.

Liquid-Liquid Extraction Calculation

The same algorithm can also be applied to a counter-current liquid-liquid extraction calculation for which the system figure is shown below. For this process calculation, the solvent is fed from the top stage, and the separated feed is from the bottom stage. The extraction column is always at isothermal and isobaric conditions. In this case the liquid rate L^I is considered as the vapor rate was in the two phase distillation problem, and L^{II} as the liquid rate. The problem is supposed to adjust variable L_j^{II}, such that the following equations are satisfied:

$$f_j = \sum_{i=1}^{n} x_{i,j}^{II} - 1 = \Sigma x_{ij}^{I} \beta_{ij} - 1 \qquad j=1,\ldots m$$

where distribution factor $\beta_i = \dfrac{\gamma_i^I}{\gamma_i^{II}}$

Composition of liquid phase I, x_i^I, is calculated from the tridiagonal method, with constants of

$$A_j = L_{j-1}^{II} \beta_{j-1}$$

$$B_j = -L_j^I - L_j^{II} \beta_{ij}$$

$$C_j = L_{j+1}^I \qquad \text{and } D_j = -S$$

and the liquid rate of phase I is evaluated from the following

total material balance:

$$L_j^I = F_2 - L_m^{II} + L_{j-1}^I \qquad j=1,\ldots m$$

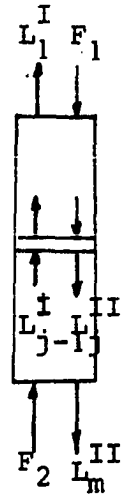


Figure 31. A Countercurrent Extraction System Model.

Results and Conclusions

A method for countercurrent extraction calculations has been proposed to solve the required system equations simultaneously. It is demonstrated successfully with several example problems. A typical outprint of results is shown in Table 21. Results of a ten-stage and a fifteen-stage problem are shown in Figure 32. Liquid profiles of phase I at the initial, 4th, 8th, and final iteration are shown in Figure 33-a for the ten-stage problem and of the initial, 4th and final iteration are shown in Figure 33-b for the fifteen stage problem. The norm of function residues at each iteration are given in Table 22 for the studied problems. From these results, the method is proved to be very efficient to improve the initial profile to the final profile. However, it suffers the same problem as we have

TABLE 20. Variations of Norm of Function Residuals with Iteration Number for Azeotropic Distillation Calculations

1. System: Ethylacetate-Ethanol-Water

Iteration	Problem Number		
	1	2	3
1	0.1096	0.3527 E-2	0.3515 E-2
2	0.9377 E-3	0.164 E-4	0.248 E-4
3	0.3775 E-4	0.1953 E-5	0.1817 E-5
4	0.642 E-6	0.2061 E-6	0.2489 E-7

Problem 1 Feed = 20,60,20
Problem 2 Feed = 37,25,38
Problem 3 Feed = 20,20,60

2. System: Ethylacetate-Methanol-Water

1	0.6474	0.288	0.115 E-1
2	0.3237	0.35 E-2	0.127 E-4
3	0.3572 E-1	0.8645 E-4	0.661 E-8
4	0.2172 E-2	0.24 E-5	
5	0.8374 E-4	0.246 E-7	
6	0.1222 E-4		
7	0.1665 E-5		
8	0.172 E-6		

Problem 1 Feed = 37,25,38
Problem 2 Feed = 20,60,20
Problem 3 Feed = 10,80,10

Table 21 SOLUTIONS OF A COUNTERCURRENT EXTRACTION PROBLEM

TRAY NUMBER 1
LIQUID 1 RATE = 61.04 MOLES/HR
LIQUID 2 RATE = 55.69 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0023	.9003
ACETONE	.1213	.0991
HEPTANE	.8765	.0005

TRAY NUMBER 2
LIQUID 1 RATE = 66.74 MOLES/HR
LIQUID 2 RATE = 60.17 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0040	.8358
ACETONE	.1937	.1630
HEPTANE	.8023	.0013

TRAY NUMBER 3
LIQUID 1 RATE = 71.22 MOLES/HR
LIQUID 2 RATE = 63.88 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0058	.7897
ACETONE	.2417	.2081
HEPTANE	.7525	.0022

TRAY NUMBER 4
LIQUID 1 RATE = 74.92 MOLES/HR
LIQUID 2 RATE = 67.16 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0074	.7534
ACETONE	.2763	.2432
HEPTANE	.7163	.0033

TRAY NUMBER 5
LIQUID 1 RATE = 78.21 MOLES/HR
LIQUID 2 RATE = 69.80 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0091	.7270
ACETONE	.3036	.2692
HEPTANE	.6873	.0043

Table 21 SOLUTIONS OF A COUNTERCURRENT EXTRACTION PROBLEM (Continued)

TRAY NUMBER 6
LIQUID 1 RATE = 80.85 MOLES/HR
LIQUID 2 RATE = 72.37 MOLES/HR

T = 298. DEG K	LIQUID 1	LIQUID 2
P = 1. ATM	---	---
WATER	.0105	.7030
ACETONE	.3239	.2919
HEPTANE	.6656	.0053

TRAY NUMBER 7
LIQUID 1 RATE = 83.41 MOLES/HR
LIQUID 2 RATE = 74.51 MOLES/HR

T = 298. DEG K	LIQUID 1	LIQUID 2
P = 1. ATM	---	---
WATER	.0119	.6845
ACETONE	.3420	.3097
HEPTANE	.6462	.0063

TRAY NUMBER 8
LIQUID 1 RATE = 85.55 MOLES/HR
LIQUID 2 RATE = 77.16 MOLES/HR

T = 298. DEG K	LIQUID 1	LIQUID 2
P = 1. ATM	---	---
WATER	.0131	.6630
ACETONE	.3561	.3292
HEPTANE	.6308	.0076

TRAY NUMBER 9
LIQUID 1 RATE = 88.20 MOLES/HR
LIQUID 2 RATE = 79.49 MOLES/HR

T = 298. DEG K	LIQUID 1	LIQUID 2
P = 1. ATM	---	---
WATER	.0146	.6458
ACETONE	.3720	.3455
HEPTANE	.6133	.0088

TRAY NUMBER 10
LIQUID 1 RATE = 90.53 MOLES/HR
LIQUID 2 RATE = 81.78 MOLES/HR

T = 298. DEG K	LIQUID 1	LIQUID 2
P = 1. ATM	---	---
WATER	.0160	.6297
ACETONE	.3852	.3605
HEPTANE	.5988	.0100

Table 21 SOLUTIONS OF A COUNTERCURRENT EXTRACTION PROBLEM

(continued)

TRAY NUMBER 11
LIQUID 1 RATE = 92.83 MOLES/HR
LIQUID 2 RATE = 84.02 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0174	.6150
ACETONE	.3973	.3741
HEPTANE	.5852	.0113

TRAY NUMBER 12
LIQUID 1 RATE = 95.06 MOLES/HR
LIQUID 2 RATE = 86.11 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0188	.6019
ACETONE	.4084	.3861
HEPTANE	.5727	.0125

TRAY NUMBER 13
LIQUID 1 RATE = 97.16 MOLES/HR
LIQUID 2 RATE = 88.35 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0202	.5886
ACETONE	.4183	.3979
HEPTANE	.5616	.0138

TRAY NUMBER 14
LIQUID 1 RATE = 99.39 MOLES/HR
LIQUID 2 RATE = 90.93 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0216	.5743
ACETONE	.4281	.4105
HEPTANE	.5503	.0153

TRAY NUMBER 15
LIQUID 1 RATE =101.97 MOLES/HR
LIQUID 2 RATE = 88.96 MOLES/HR

T = 298. DEG K P = 1. ATM	LIQUID 1	LIQUID 2
WATER	.0232	.5605
ACETONE	.4386	.4226
HEPTANE	.5382	.0169

TABLE 22. Variation of Norm of Function Residues with Iteration Number for Extraction Calculation

Iteration Number	Problem 1	Problem 2
0	0.1625 E-1	0.924
1	0.1 E-3	0.517 E-1
2	0.999 E-4	0.223 E-1
3	0.614 E-4	0.440 E-2
4	0.1527 E-4	0.358 E-2
5	0.2366 E-5	0.124 E-2
6	0.2029 E-5	0.974 E-3
7	0.1703 E-5	0.278 E-4
8	0.1249 E-5	0.223 E-4
9	0.8720 E-6	0.2065 E-4
10		0.8725 E-5
11		0.2693 E-5
12		0.2397 E-5
13		0.679 E-6

Problem 1 with 15 stage and f_1 = 0,45,55.

Problem 2 with 10 stage and f_1 = 0,40,60

mentioned in three-phase distillation calculation, that is, the norm of function residues is significantly affected by minor changes of liquid rates. It has been shown that in Figure 33 the rate profile of the 8th iteration is very close to the final profile, but the function values is 0.233E-4 compared with 0.679E-6 of the final convergence. The same conclusion can be observed for the fifteen-stage problem, the value of 0.154E-4 at the 4th iteration compared with the value of 0.872E-6 at the final result. This characteristic will hinder the convergence of a problem when the liquid rate of phase I is improved to some extent. Results shown in Figure 32 confirm that an efficient separation between two liquid phases can be obtained from a three-phase distillation method than a counter-current extraction method.

Uniform Approach for Nonideal Solution Separation Calculation

It has been shown that the three-phase distillation algorithm can be applied to the other related highly-nonideal solution separation processes calculations. Since in a mathematical sense, the difference among those processes is their unknown variables and function equations involved in calculations. It is desirable to have a general purpose and compact computer program by putting them together. A summary

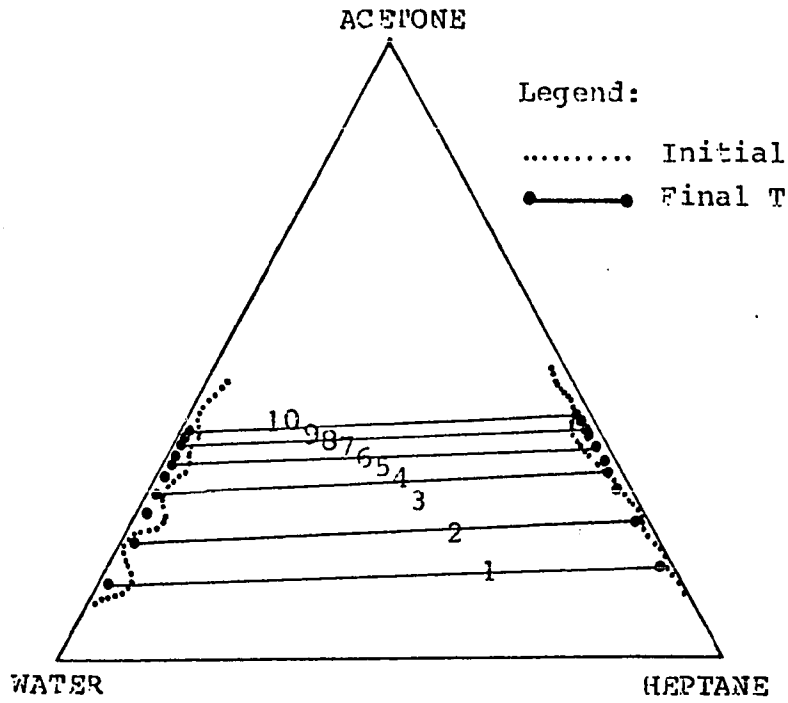


Fig. 32a Ten-Stage

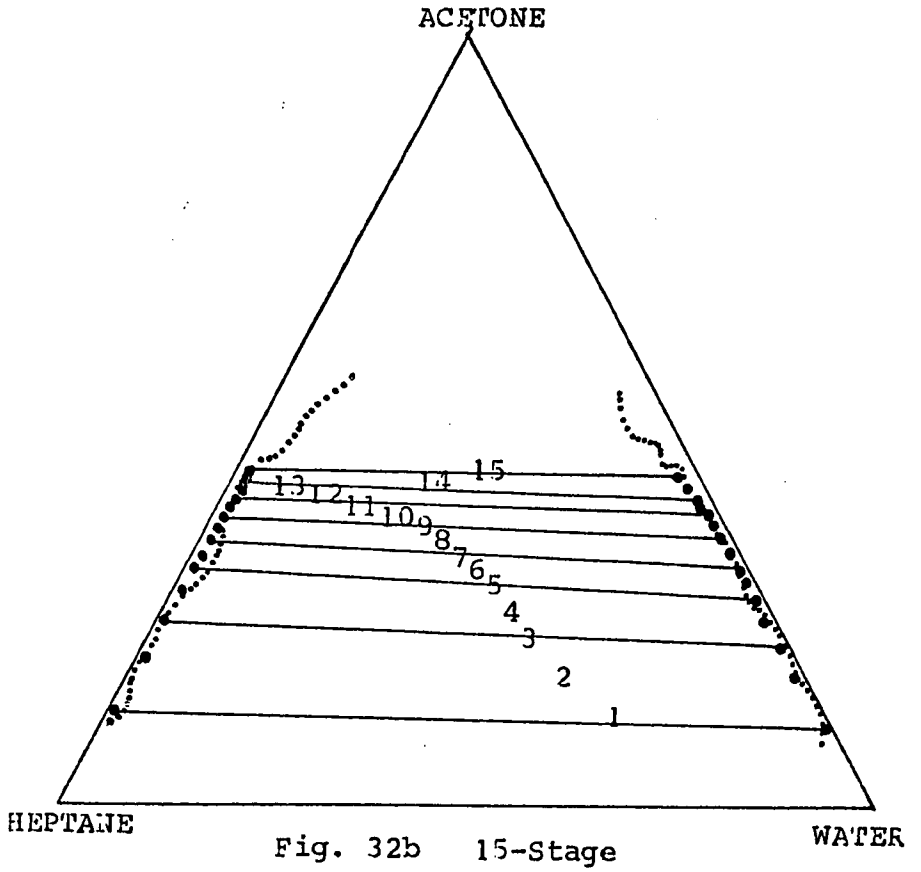


Fig. 32b 15-Stage

Figure 32 Results of Countercurrent Extraction Problems

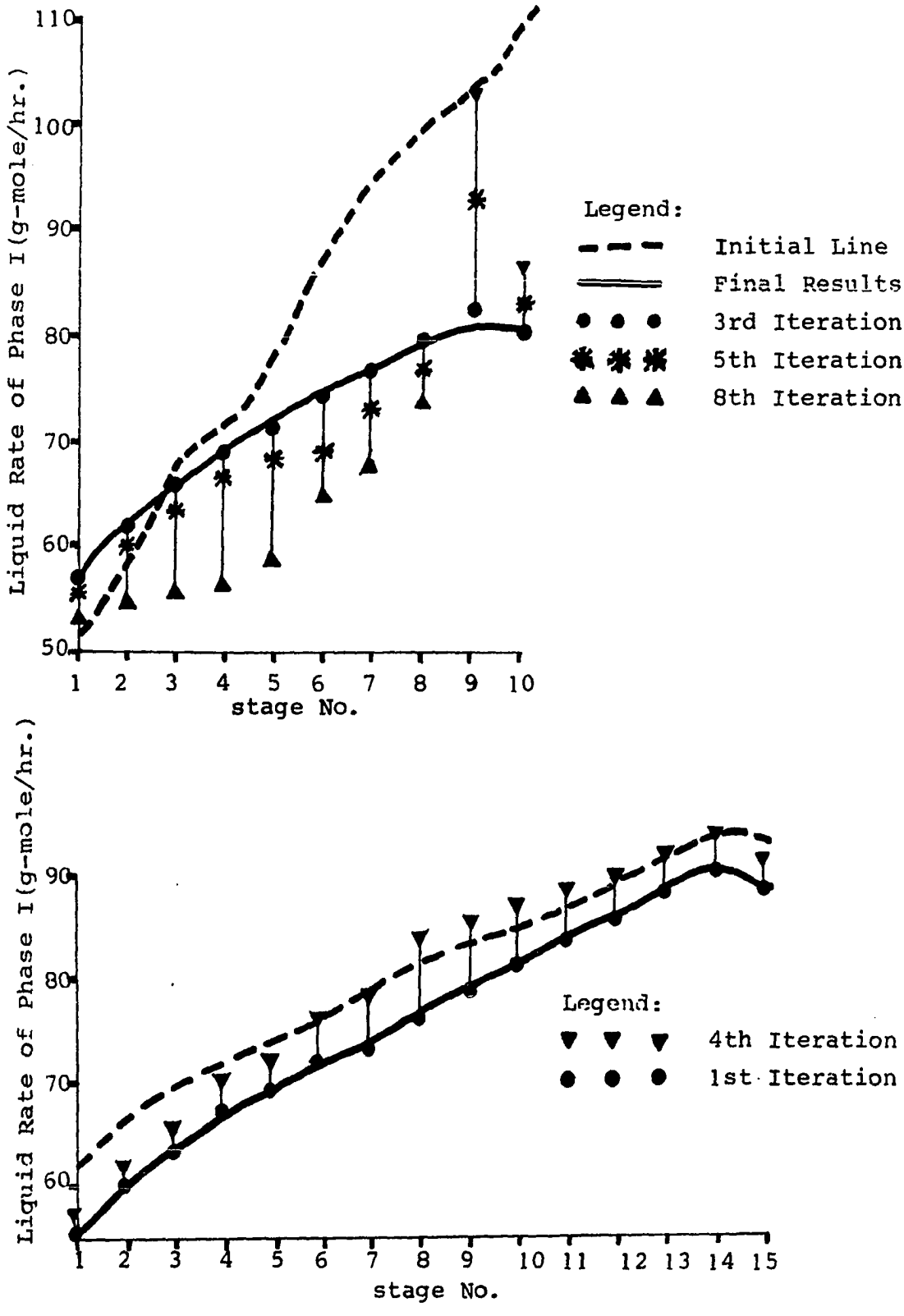


Figure 33 Analysis of Rate Profile with the Iteration Numbers for Countercurrent Extraction Problems

is given below to express the related variables and function equations for each m-stage processes.

PROCESSES CALCULATION	NO. OF VARIABLES	UNKNOWN VARIABLES	EQUATIONS
Countercurrent liquid-liquid	m	L_j^{II}	f_j
Azeotropic distillation	2m	L_j^{I}, T_j	f_j, f_{j+m}
Three-phase distillation	3m	L^{I}, L^{II}, T	f_j, f_{j+m}, f_{j+2m}

where $f_j = \sum_{i=1}^{n} x_i^{II} - 1$, $f_{j+m} = \sum_{i=1}^{n} x_i^{I} - 1$

$$f_{j+2m} = (H^{in} - H^{out})/H^{in}$$

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NOMENCLATURE

$a_i b_i$	Parameters of Redlich-Kwong equation of state
a	Parameters defined by $\sum_{i=1}^{n} y_i a_i$
b	Parameters defined by $\sum_{i=1}^{n} y_i b_i$
A_j, B_j, C_j, D_j	jth row elements of Tridiagonal Matrix
B_{ij}	Constants defined in Equation (6-9, 10)
$C_N^{(m)}$, $CN_N^{(m)}$, $N_N^{(m)}$	Number of saddle-type, complex type, and node type singular points corresponding to Nth dimension azeotropes in a mth dimension simplex.
${}_nC_m$	defined as $n!/m!(n-m)!$
G^+, G^-	Number of positive, negative singular points corresponding to a m^oth dimension azeotrope within a m-th dimension simplex.
G_b^+, G_b^-	Number of positive, negative singular points corresponding to azeotropes locating on the boundary of a mth dimension simplex.

G_i^+, G_i^-	Number of positive, negative singular points corresponding to i-th dimension azeotropes of a defined simplex.
h, H	Enthalpy of liquid, vapor [cal/hr.].
g_{ij}	Energies of interaction between an i-j pair of molecules [cal/mole].
G_{ij}	Coefficient as defined by $G_{ij} = \tau_{ij} \exp(-\alpha_{ij}\tau_{ij})$
f^k	Function values at kth iteration
f^L, f^V	fugacity of liquid and vapor
K_i	Equilibrium constant of pure component i
$\left\|\frac{\partial K_i}{\partial x_j}\right\|$	Determinant of a Matrix which element is $\frac{\partial K_i}{\partial x_j}$
L_j^I, L_j^{II}	Liquid rate of phase I, II at the jth stage [g-moles/hr.]
n	Number of component
m	Number of stages
Mi, Ma	Binary minimum, and maximum boiling azeotropes
M_j	Number of jth azeotropes in a simplex
p_i	Vapor pressure of pure component i [atm]
P	System pressure [atm]
R	Gas constant [1.987 cal/mole °K]

S	Numbers of liquid moles in a batch distillation still
t	Defined as $t = d\ln S$
T	Absolute temperature [°K]
v_i	Molar volume of component i [cc/gmole]
V_j	Vapor rate at jth stage [g-moles/hr.]
x_i^I, x_j^{II}	Liquid compositions of component i at phase I, II. [mole fraction]
y_i	Vapor compositions of component i [mole fraction]
z_i	Feed composition of component i [mole-fraction]
z	Compressibility factor
α_{ij}	Nonrandomness constant for a binary i-j interaction
β_{ij}	Distribution factor between two liquid phases
γ_i	Activity coefficient of component i
ρ_i	Density of component i g/c.c.
δ_{ij}	$\delta_{ij}=1$, if $i=j$; $\delta_{ij}=0$, $i\neq j$
λ_i	ith eigenvalues of a characteristic equation
ϕ	Split fraction of the overall liquid into the liquid phase I
τ_{ij}	Coefficient as defined by $\tau_{ij} = (g_{ij}-g_{jj})/RT$

APPENDIX A

To demonstrate that determinations of singular points corresponding to a vertex of a triangle diagram can be done by using relations of boiling points instead of equilibrium constants.

For a pure component of ternary systems, the following cases are considered and demonstrated separately with conditions of binary azeotropic formations, that is:
If a binary azeotropy formed from component 1 and 2, then

$$\left|\lim_{x_1 \to 1} \ln\gamma_2\right| > \left|\ln(p_1(T_1)/p_2(T_1))\right| \qquad (1)$$

if no binary azeotropy formed from components 1 and 2, then

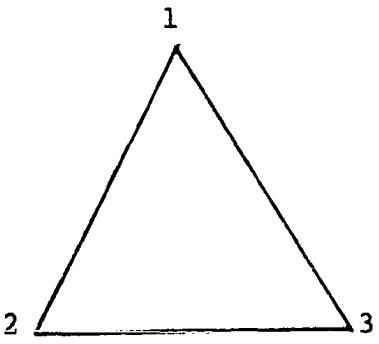
$$\left|\lim_{x_1 \to 1} \ln\gamma_2\right| < \left|\ln(p_1(T_1)/p_2(T_1))\right| \qquad (2)$$

where

$p_i(T_j)$ = vapor pressure of component i at boiling point temperature of component j

T_j = Boiling point temperature of component j

and each of the following cases is referred to the vertex 1 of the sketch shown on the following page.



Usually, determination of singular points corresponding to a vertex 1 is determined by the values of equilibrium constants of K_2, K_3 at T_1, P and x = (1,0,0). However, an alternative derived from relations of boiling points of related components is shown here.

I. No bianry azeotropy formed on the sides of vertex 1.

a. If $T_1 > T_2 > T_3$ then $p_1 < p_2(T_1) < p_3(t_1)$

$p_1/p_2 < 1$ $\ln(p_1/p_2) < 0$

From conditions (2), we have $\gamma_2 > p_1/p_2(T_1)$ for $\ln\gamma_2 > 0$, or $\ln\gamma_2 < 0$;

thus $K_2 = \gamma_2 p_2/p_1 > 1$.

In the same manner, we can have $K_3 > 1$; therefore, vertex 1 is a node point.

b. If $T_1 < T_2 < T_3$ so $p_1 > p_2(T_1) > p_3(T_1)$

$p_1/p_2 > 1$, $\ln(p_1/p_2) > 0$.

From conditions 2, $\gamma_2 < p_1/p_2$. Thus,

$K_2 = \gamma_2 p_2/p_1 < 1$; the same as $K_3 < 1$. So vertex 1 is a node point.

c. If $T_2 > T_1 > T_3$, then from the result of Ia we have $K_3 > 1$ and from result of I-b, we have $K_2 < 1$ so vertex 1 is a saddle point.

II. <u>One Binary Azeotrope Form from Components 1 and 2</u>

a. If $T_1 > T_{12}, T_3$, thus for the existence of minimum azeotrope

$\gamma_2 > 1$, so $\ln\gamma_2 > 0$,

from condition 1, there always exists

$\gamma_2 > p_1/p_2$ so $K_2 > 1$

and from results of I-a, $K_3 > 1$. Therefore vertex 1 is a node.

b. If $T_3 > T_1 > T_{12}$

thus summing up the results of (I-b) and (II-a), we have

$K_2 > 1$; and $K_3 < 1$

so vertex 1 is a saddle point.

c. If $T_{12} > T_1 > T_3$

since for the existence of a maximum azeotrope, there $\gamma_2 < 1$, $\ln\gamma_2 < 0$, so by condition (1),

$\gamma_2 < p_1/p_2$ for $p_1/p_2 > 1$, or $p_1/p_2 < 1$

so

$K_2 < 1$, and from results of I-a, $K_3 > 1$

so vertex 1 is a saddle point.

d. If T_{12}, $T_3 > T_1$

summing up the results of (II-c), and (I-b), we have

$K_3 < 1$, and $K_2 < 1$

so vertex 1 is a saddle point.

III. Two Binary Azeotropes Formed from Component 1 and 2, and 1 and 3.

There are four different cases which results are summarized in the table shown on the following page, and obtained by summing up results of (II-a) and (II-b).

Summaries of Relations of Singular Points with Boiling Points for Ternary System

Catalog	Relations of Boiling Points	Singular Point
I	a. $T_1 > T_2, T_3$	Node
	b. $T_1 < T_2, T_3$	Node
	c. $T_2 > T_1 > T_3$	Saddle
II	a. Min. and $T_3 > T_1$	Saddle
	b. Min. and $T_3 < T_1$	Node
	c. Max. and $T_3 > T_1$	Node
	d. Max. and $T_3 < T_1$	Saddle
III	a. Min. and Max.	Saddle
	b. Max. and Max.	Node
	c. Min. and Min.	Node

APPENDIX B. List of Wilson Constants

Binary System		$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	Ref.
ACETONE	Benzene	494.92	-167.91	18
ACETONE	Carbon Tetr[illegible]	[illegible]1.76	- 12.67	18
ACETONE	Chlorofor[illegible]	[illegible]20	-332.23	18
ACETONE	2,3-Dime[illegible]	[illegible]	234.96	18
ACETONE	Ethanol[illegible]	[illegible]	418.96	18
ACETONE	Methan[illegible]	[illegible]	664.09	18
ACETONE	Methyl[illegible]	[illegible]	161.26	22
ACETONE	Cl-IC4[illegible]	[illegible]	-657.72	38
ACETONE	N-Pent[illegible]	[illegible]	262.74	18
ACETONE	2-Prop[illegible]	[illegible]	284.99	18
ACETONE	Water	[illegible]	1405.49	18
ACETONITRILE	Water	[illegible]	1610.07	18
BENZENE	1-Butanol[illegible]	[illegible]2	817.67	18
BENZENE	Carbon Tet[illegible]	[illegible]00	400.00	32
BENZENE	Carbon Tetra[illegible]	[illegible]3.41	204.82	18
BENZENE	Chloroform	141.62	-204.22	18
BENZENE	Cyclohexane	187.23	80.02	18
BENZENE	Cyclopentane	266.56	- 24.18	18
BENZENE	Ethanol	131.47	1297.90	18
BENZENE	N-Hexane	173.93	169.92	18
BENZENE	Methanol	153.86	1620.36	18
BENZENE	Methylacetate	229.25	- 23.84	18
BENZENE	MethylcycloC6	- 4.15	360.92	18
BENZENE	MethlcycloC5	161.44	97.33	18
BENZENE	I-Octane	201.75	277.47	38
BENZENE	N-Heptane	171.50	200.94	18
BENZENE	1-Propanol	- 73.91	1370.32	18
BENZENE	2-Propanol	160.53	1007.94	18
BENZENE	Toluene	75.4	- 88.83	56
1-BUTANOL	Toluene	887.80	104.68	18

Appendix B (Continued)

Binary System		$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	Ref.
ETHANOL	Methanol	-511.39	598.44	18
ETHANOL	Methylcyclo-C5	2221.47	161.53	18
ETHANOL	Water	382.30	955.45	18
ETHYL ACETATE	Methanol	-200.36	985.69	18
ETHYL ACETATE	1-Propanol	-198.72	661.24	18
ETHYL ACETATE	2-Propanol	60.99	289.68	18
ETHYLBENZENE	N-Octane	304.31	-134.87	18
METHANOL	Methyl Acetate	834.06	- 78.81	18
Methanol	2-Propanol	88.02	- 30.19	18
METHYLACETATE	2-Propanol	207.00	301.00	18
METHANOL	Toluene	1899.00	102.00	44
METHANOL	Water	205.30	482.16	18
METHYLCYCLO-C5	Toluene	-451.61	957.61	18
C1-C2-KETONE	2-Propanol	-164.951	527.542	44
C-C2-KETONE	Toluene	588.00	-240.00	44
C1-C2 KETONE	Water	1069.42B	2071.917	44

APPENDIX B. List of Wilson Constants

Binary System		$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	Ref.
ACETONE	Benzene	494.92	-167.91	18
ACETONE	Carbon TetraCl	651.76	- 12.67	18
ACETONE	Chloroform	- 72.20	-332.23	18
ACETONE	2,3-DimethylC4	948.29	234.96	18
ACETONE	Ethanol	38.17	418.96	18
ACETONE	Methanol	-214.85	664.09	18
ACETONE	Methylacetate	- 65.21	161.26	22
ACETONE	Cl-IC4-Ketone	882.39	-657.72	38
ACETONE	N-Pentane	996.75	262.74	18
ACETONE	2-Propanol	127.43	284.99	18
ACETONE	Water	439.64	1405.49	18
ACETONITRILE	Water	694.08	1610.07	18
BENZENE	1-Butanol	160.12	817.67	18
BENZENE	Carbon Tetra-CL	-250.00	400.00	32
BENZENE	Carbon TetraCL	-103.41	204.82	18
BENZENE	Chloroform	141.62	-204.22	18
BENZENE	Cyclohexane	187.23	80.02	18
BENZENE	Cyclopentane	266.56	- 24.18	18
BENZENE	Ethanol	131.47	1297.90	18
BENZENE	N-Hexane	173.93	169.92	18
BENZENE	Methanol	153.86	1620.36	18
BENZENE	Methylacetate	229.25	- 23.84	18
BENZENE	MethylcycloC6	- 4.15	360.92	18
BENZENE	MethlcycloC5	161.44	97.33	18
BENZENE	I-Octane	201.75	277.47	38
BENZENE	N-Heptane	171.50	200.94	18
BENZENE	1-Propanol	- 73.91	1370.32	18
BENZENE	2-Propanol	160.53	1007.94	18
BENZENE	Toluene	75.4	- 88.83	56
1-BUTANOL	Toluene	887.80	104.68	18

Appendix B (Continued)

Binary System		$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	Ref.
ETHANOL	Methanol	-511.39	598.44	18
ETHANOL	Methylcyclo-C5	2221.47	161.53	18
ETHANOL	Water	382.30	955.45	18
ETHYL ACETATE	Methanol	-200.36	985.69	18
ETHYL ACETATE	1-Propanol	-198.72	661.24	18
ETHYL ACETATE	2-Propanol	60.99	289.68	18
ETHYLBENZENE	N-Octane	304.31	-134.87	18
METHANOL	Methyl Acetate	834.06	- 78.81	18
Methanol	2-Propanol	88.02	- 30.19	18
METHYLACETATE	2-Propanol	207.00	301.00	18
METHANOL	Toluene	1899.00	102.00	44
METHANOL	Water	205.30	482.16	18
METHYLCYCLO-C5	Toluene	-451.61	957.61	18
C1-C2-KETONE	2-Propanol	-164.951	527.542	57
C-C2-KETONE	Toluene	588.00	-240.00	44
C1-C2-KETONE	Water	1060.428	2071.937	57
I-OCTANE	Toluene	61.19	148.58	38
2-PROPANOL	2,2,4-Tri-C1-C5	1231.69	183.12	18
2-PROPANOL	Water	725.886	1260.437	57

Appendix B (Continued)

Binary System		$\lambda_{12}-\lambda_{11}$	$\lambda_{21}-\lambda_{22}$	Ref.
N-HEPTANE	Methanol	2478.00	662.00	44
N-HEPTANE	C-C2-Ketone	988.00	3.00	44
N-HEPTANE	I-Octane	32.66	- 22.27	38
N-HEPTANE	Toluene	282.00	- 67.00	44
N-HEXANE	Hexene-1	415.18	-279.86	18
N-HEXANE	Methylcyclo-C5	272.09	-175.70	18
N-HEXANE	1-Propanol	834.85	812.66	18
N-HEXANE	1,2,3-Tri-CL-C3	116.39	1106.39	18
N-HEXANE	Toluene	-121.00	383.89	56
HEXENE-1	1,2,3-Tri-CL-C3	156.93	570.31	18
CARBON TETRA-CL	Cyclohexane	70.00	40.00	32
CARBON TETRA-CL	Methylacetate	-140.00	540.00	32
CHLOROFORM	2,3-Dimethyl-C4	213.88	223.69	18
CHLOROFORM	Ethyl Acetate	-367.50	- 92.50	18
CHLOROFORM	Methanol	-373.30	1703.68	18
CHLOROFORM	Methyl Acetate	-451.09	113.248	18
CHLOROFORM	C-C2-Ketone	-231.61	-235.12	18
CHLOROFORM	C-IC4-Ketone	-324.23	11.95	38
CYCLOHEXANE	Ethanol	303.42	2151.01	18
CYCLOHEXANE	Hexane	-230.57	496.96	56
CYCLOHEXANE	C-C2-Ketone	35.00	870.00	33
CYCLOHEXANE	Methyl Acetate	345.11	691.651	18
CYCLOHEXANE	Methylcyclo-C5	-247.40	327.06	56
CYCLOHEXANE	2-Propanol	69.02	1734.12	18
CYCLOHEXANE	Toluene	-414.68	909.362	18
2,3-DMB	Methanol	449.08	2771.84	18
1,4-DIOXANE	Hexene-1	495.15	176.39	18
ETHANOL	Ethyl-Acetate	844.69	-178.81	18
ETHANOL	N-Heptane	2096.50	617.571	18
ETHANOL	N-Hexane	2281.99	283.62	18

APPENDIX C. List of Constants of Vapor Pressure Equations (38)

Vapor equation is $\ln p_i^o = C_1 + C_2/T + C_4T + C_6 \ln T$

	C_1	C_2	C_4	C_6
ACETONE	3.2157	-3969.2218	-0.0084	2.0
ACETONITRILE	-27.3365	-3168.5819	-0.0136	7.0
BENZENE	133.3128	-8026.2913	0.0239	-20.29
CARBON TETRA-C6	43.7312	-5270.9369	0.0018	- 5.00
CHLOROFORM	129.7988	-7443.2153	0.0260	-20.00
CYCLOHEXANE	98.5856	-6943.3635	0.0152	-14.37
ETHANOL	123.9120	-8754.0896	0.0202	-18.10
HEPTANE	122.7654	-8141.3862	0.0196	-18.27
N-HEXANE	113.2828	-7151.4899	0.0200	-17.00
METHANOL	49.9513	-5970.8229	0.0042	- 5.79
METHYLACETATE	115.5246	-7240.8314	0.0204	-17.30
METHYLCYCLO-C6	114.3107	-7694.6047	0.0186	-17.00
C-IC4-KETONE	162.0805	-10040.5873	0.0251	-24.49
N-OCTANE	33.9438	-6144.6379	-0.0037	- 2.85
ISO-OCTANE	105.5669	-7434.5352	0.0162	-15.49
TOLUENE	115.9659	-8111.7556	0.0179	-17.09
WATER	70.4347	-7362.6981	0.0070	- 9.00

Appendix C (Continued)

Vapor Equation is $\log_{10} p_i^o = A - B/C+t(°C)$ (18)

	A	B	C
1 Butanol	8.27488	1873.9	230.0
Cyclopentane	6.88676	1124.162	231.361
2,3-DMB	6.80983	1127.187	228.9
1,4-Dioxane	7.8642	1866.7	273.0
Ethylacetate	7.09808	1238.71	217.0
C2-Cyclohexane	6.87041	1384.036	215.128
Hexene-1	6.8657	1152.97	225.85
Methylcyclo-C5	6.86283	1186.05	226.042
MEK	6.97421	1209.6	216.0
N-Pentane	6.85021	1064.63	232.0
1-Propanol	7.99733	1569.70	209.5
2-Propanol	6.66040	8130.55	132.93
1,2,3,TRI Cl-C3	6.98716	1502.3	209.0
2,2,4-TRI-Cl-C5	6.81189	1257.840	220.735

APPENDIX D. List of Molar Volume Data

	T(°K)	cc/gmole	T(°K)	cc/gmole	T(°K)	cc/gmole	Ref
ACETONE	228.15	67.380	273.15	71.483	323.15	76.826	18
ACETONITRILE	273.15	51.092	303.15	53.214	355.15	57.4	18
BENZENE	273.15	86.783	323.15	92.263	373.15	98.537	22
1-BUTANOL	273.15	89.873	343.15	97.8	413.15	108.7	18
CARBON TETRAC6	293.15	96.518	353.15	104.192	413.15	114.379	18
CHLOROFORM	273.15	78.218	303.15	81.185	333.15	84.5	18
CYCLOHEXANE	288.15	107.47	306.30	109.841	352.35	116.63	18
CYCLOPENTANE	273.15	91.9	333.15	99.4	373.15	105.23	18
2,3-DIMETHYL C4	273.15	126.80	303.15	132.06	333.15	138.03	18
1,4-DIOXANE	293.15	85.24	333.15	89.3	373.15	93.90	18
ETHANOL	273.15	57.141	323.15	60.356	373.15	64.371	18
ETHYL ACETATE	273.15	95.3	323.15	102.1	373.15	110.5	18
ETHYLBENZENE	273.15	120.02	343.15	129.09	413.15	140.29	18
ETHYLCYCLOC6	293.15	142.48	353.15	152.1	413.15	163.9	18
N-HEPTANE	273.15	143.045	323.15	152.303	373.15	163.619	18
N-HEXANE	273.15	127.301	323.15	136.388	373.15	148.211	18
HEXENE-1	273.15	121.62	303.15	126.8	333.15	132.45	18
METHANOL	273.15	39.556	373.15	44.874	473.15	57.939	22
METHYLACETATE	273.15	77.221	373.15	90.111	473.15	121.443	18
METHYLCCYLOC6	303.15	129.116	333.85	133.833	372.65	140.609	18
METHYLCYCLOC5	273.15	109.67	303.15	113.91	373.15	126.2	18
C-C2-KETONE	273.15	87.3	333.15	94.5	373.15	100.0	18
C-IC4-KETONE	303.15	129.116	333.85	133.833	372.65	140.609	38
N-OCTANE	273.15	158.97	333.15	170.63	393.15	185.182	18
I-OCTANE	273.15	161.373	303.15	167.062	323.15	171.270	38
N-PENTANE	273.15	111.8	333.15	122.9	373.15	131.4	18
N-PROPANOL	293.15	74.785	343.15	78.962	393.15	84.515	18
2-PROPANOL	293.15	77.0	333.15	80.5	373.15	86.1	18
TOLUENE	303.15	107.415	353.15	113.717	400.00	120.879	18
1,2,3-REIXL-C3	293.15	106.22	353.15	112.6	433.15	124.1	18
2,2,4-TRI-C-C5	273.15	161.26	323.15	171.24	373.15	183.66	18
WATER	277.13	18.060	323.15	18.278	373.15	18.844	18

APPENDIX E

List of Renon Constants

SYSTEM: Chloroform(1)-Acetone(2)-Water(3)-(25°C)(13)

i-j	1-2	1-3	2-3
α_{ij}	0.466	0.2389	0.3
C_{ij}	255.	1862.	537.
C_{ji}	-579.	3050.	746.

SYSTEM: Water(1)-ethanol(2)-Butanol(3)-(25°C)(13)

i-j	1-2	1-3	2-3
α_{ij}	0.104	0.4188	0.05
C_{ij}	1579	2223.	-225.
C_{ji}	-621.	4934.	491.

SYSTEM: Water(1)-Methanol(2)-Benzene(3)-(25°C)(13)

i-j	1-2	1-3	2-3
α_{ij}	0.3369	0.223	0.0239
C_{ij}	332.	3645.	2325.
C_{ji}	-897.6	2640.	-1342.

SYSTEM: Diethyl-glycol(1)-Benzene(2)-heptane(3)-(100°C)(13)

i-j	1-2	1-3	2-3
α_{ij}	0.386	0.2	0.3
C_{ij}	614	1956	780
C_{ji}	1440	2517.5	-382.

SYSTEM: Water(1)-Acetone(2)-Heptane(3)-(25°C)(5)

i-j	1-2	1-3	2-3
α_{ij}	0.393	0.15	0.222
C_{ij}	980	4100	16
C_{ji}	230	2800	1030

APPENDIX E

List of Renon Constants(Continued)

SYSTEM: Ethylacetate(1)-Ethanol(2)-Water(3)-(B.P.)(58)

i-j	1-2	1-3	2-3
α_{ij}	0.1	0.3	0.3
C_{ij}	1148.848	611.817	-53.732
C_{ji}	-480.377	1869.89	1166.524

SYSTEM: Ethylacetate(1)-Methanol(2)-Water(3)-(B.P.)(58)

i-j	1-2	1-3	2-3
α_{ij}	0.1	0.1	0.3
C_{ij}	129.125	611.817	-1141.564
C_{ji}	564.522	1869.89	1914.641

SYSTEM: Water(1)-Methanol(2)-Aniline(3)-(25°C)(13)

i-j	1-2	1-3	2-3
α_{ij}	.3369	.3356	.424
C_{ij}	332.	2484.	2453.
C_{ji}	-897.6	731.9	-1458

SYSTEM: Phenol-n-Butylacetate-water-(44°C)(13)

i-j	1-2	1-3	2-3
α_{ij}	.122	.5183	0.1493
C_{ij}	-1155	332.7	4351
C_{ji}	64.6	2204	13.3

SYSTEM: N-hexane(1)-5-nonanone(3)-DMSO(4)-(25°C)(44)

	1-2	1-3	1-4	2-3	2-4	3-4
α_{ij}	0.3	0.3	0.355	0.3	0.375	0.4
C_{ij}	31	256	2263	605	2057	646
C_{ji}	31	54.	2199	-269	1672	1111

APPENDIX E

List of Renon Constants(Continued)

n-Hexane(1)-Hexene(2)-5-Nonane(3)-DMSO(4)-(60°C)(44)

i-j	1-2	1-3	1-4	2-3	2-4	3-4
C_{ij}	31	793	2100	780	1753	447
C_{ji}	31	-270	1942	-381	1511	1163

SYSTEM: Methanol(1)-Water(2)-Aniline(3)-Benzene(4)-(25°C)(13)

i-j	1-2	1-3	1-4	2-3	2-4	3-4
α_{ij}	0.3369	0.424	0.0239	0.3356	0.223	0.543
C_{ij}	-897.6	2453.0	2325.0	2484.0	3645.	1660
C_{ji}	332.0	-1458.0	-1342.0	732.0	2640.	4760

SYSTEM: Heptane(1)-DMFA(2)-Water(3)-Benzene(4)-(25°C)(5)

i-j	1-2	1-3	1-4	2-3	2-4	3-4
α_{ij}	0.25	0.15	0.30	0.253	0.425	0.203
C_{ij}	1113.0	2800.0	-207.0	-1240.0	394.0	3350.
C_{ji}	1186.0	2100	697	1460.0	-140.0	2120

SYSTEM: i-Octane(1)-Cyclohexane(2)-Benzene(3)-Furfural(4) (25°C)(5)

i-j	1-2	1-3	1-4	2-3	2-4	3-4
α_{ij}	0.3	0.3	0.3	0.3	0.35	0.3
C_{ij}	-262	-207	1284	-37	1420.	434
C_{ji}	428.	824.	1400.	45.0	9790	197.0

SYSTEM: Water(1)-Ethanol(2)-Butanol(3)-Acetone(4)-Benzene(5) (25°C) (13)

i-j	1-2	1-3	1-4	1-5	2-3
α_{ij}	0.104	0.44	0.214	0.223	-0.1
C_{ij}	1579.	216.3	769.	3645.	25
C_{ji}	-621	757.7	452.	2640.0	286.0

APPENDIX E

List of Renon Constants(Continued)

i-j	2-4	2-5	3-4	3-5	4-5
α_{ij}	0.3	0.5086	0.188	0.6363	0.3
C_{ij}	325.	486.	1347.	463.0	-69.4
C_{ji}	210.	1244.0	-546.5	1085.0	390.0

SYSTEM: Water(1)-Ethanol(2)-Butanol(3)-Methanol(4)-Benzene(5)

i-j	1-2	1-3	1-4	1-5	2-3
α_{ij}	0.104	0.4188	0.0286	0.223	0.05
C_{ij}	1579	2223.	138.0	3645.	-225.
C_{ji}	-621.	493.4	133.8	2640.0	219.0

i-j	2-4	2-5	3-4	3-5	4-5
α_{ij}	0.225	0.5086	0.4	0.6363	0.0372
C_{ij}	-173.0	486.0	-126.0	483.0	2800.
C_{ji}	219.0	1244.0	381.0	1085.0	-1430

SYSTEM: Water(1)-Ethanol(2)-Butanol(3)-Methanol(4)-Acetone(5)-Benzene(6)-(25°C)(13)

i-j	1-2	1-3	1-4	1-5	1-6
α_{ij}	0.104	0.4188	0.0286	0.214	0.223
C_{ij}	1579.0	2223.0	138.0	769.0	3645.0
C_{ji}	-621.0	493.4	133.8	452.0	2640.0

i-j	2-3	2-4	2-5	2-6	3-4
α_{ij}	0.05	0.225	0.3	0.5086	0.4
C_{ij}	-225.0	-173.0	325.0	486.0	-126.
C_{ji}	219.0	219.0	210.0	1244.0	381.0

	3-5	3-6	4-5	4-6	5-6
α_{ij}	0.188	0.6363	0.2199	0.0372	0.3
C_{ij}	1347.0	483	471.0	2800.0	-69.4
C_{ji}	-546.5	1085.0	-45.4	-1430.0	390.0

where $C_{ij} = \tau_{ij} - \tau_{ii}$

$C_{ji} = \tau_{ji} - \tau_{jj}$

APPENDIX F

Detailed Results of the Proposed Liquid-Liquid Method

System: Heptane DMFA Water

1.	O.V.:	0.095	0.888	0.017	P.P.:	one		N.F.:	4
		Phase I				Phase II			ϕ
	I.V.:	0.062	0.888	0.050	0.128	0.888	-0.0156		0.5
	F.R.:	0.094	0.889	0.017	0.096	0.887	0.017		0.500
2.	O.V.:	0.178	0.790	0.032	P.P.:	two		N.F.:	46
		Phase I				Phase II			ϕ
	I.V.:	0.160	0.790	0.050	0.196	0.790	0.014		0.5
	F.R.:	0.050	0.913	0.037	0.938	0.062	0.000		0.855
3.	O.V.:	0.314	0.658	0.028	P.P.:	two		N.F.	31
		Phase I				Phase II			ϕ
	I.V.:	0.292	0.658	0.050	0.336	0.658	0.006		0.5
	F.R.:	0.049	0.911	0.040	0.938	0.062	0.000		0.702
4.	O.V.:	0.317	0.625	0.057	P.P.:	two		N.F.:	28
		Phase I				Phase II			ϕ
	I.V.:	0.325	0.626	0.050	0.310	0.626	0.064		0.5
	F.R.:	0.943	0.057	0.000	0.040	0.878	0.082		0.307
5.	O.V.:	0.425	0.524	0.051	P.P.:	two		N.F.:	16
		Phase I				Phase II			ϕ
	I.V.:	0.426	0.524	0.050	0.423	0.526	0.051		0.5
	F.R.:	0.943	0.057	0.000	0.039	0.872	0.089		0.428
6.	O.V.:	0.429	0.493	0.077	P.P.:	two		N.F.:	17
		Phase I				Phase II			ϕ
	I.V.	0.457	0.494	0.050	0.402	0.493	0.104		0.5
	F.R.:	0.949	0.051	0.000	0.031	0.833	0.136		0.434
7.	O.V.:	0.517	0.414	0.070	P.P.:	two		N.F.:	22
		Phase I				Phase II			ϕ
	I.V.:	0.536	0.414	0.050	0.497	0.414	0.088		0.5
	F.R.:	0.950	0.050	0.000	0.029	0.823	0.148		0.530

Appendix F (Continued)

8.	O.V.:	0.521	0.385	0.094	P.P.: two		N.F.: 21	
		Phase I				Phase II		ϕ
	I.V.:	0.565	0.385	0.050	0.478	0.385	0.137	0.5
	F.R.:	0.955	0.045	0.000	0.022	0.778	0.201	0.535
9.	O.V.:	0.598	0.295	0.107	P.P.: two		N.F.: 18	
		Phase I				Phase II		ϕ
	I.V.:	0.655	0.295	0.050	0.541	0.295	0.164	0.5
	F.R.:	0.963	0.037	0.000	0.015	0.706	0.279	0.615
10.	O.V.:	0.658	0.243	0.089	P.P.: two		N.F.: 31	
		Phase I				Phase II		ϕ
	I.V.:	0.707	0.243	0.050	0.610	0.243	0.147	0.5
	F.R.:	0.965	0.035	0.000	0.013	0.682	0.305	0.678

System: Heptane Benzene DMFA

1.	O.V.:	0.120	0.770	0.110	P.P.: one		N.F.: 4	
		Phase I				Phase II		ϕ
	I.V.:	0.180	0.770	0.050	0.060	0.770	0.169	0.5
	F.R.:	0.120	0.770	0.110	0.120	0.770	0.110	0.500
2.	O.V.:	0.120	0.717	0.164	P.P: one		N.F.: 4	
		Phase I				Phase II		ϕ
	I.V.:	0.050	0.717	0.233	0.189	0.717	0.094	0.5
	F.R.:	0.120	0.717	0.164	0.120	0.717	0.164	0.500
3.	O.V.:	0.161	0.673	0.166	P.P.: one		N.F.: 5	
		Phase I				Phase II		ϕ
	I.V.:	0.050	0.673	0.277	0.272	0.673	0.054	0.5
	F.R.:	0.161	0.673	0.166	0.161	0.673	0.166	0.500
4.	O.V.:	0.376	0.107	0.516	P.P.: two		N.F.: 17	
		Phase I				Phase II		ϕ
	I.V.:	0.050	0.108	0.843	0.703	0.108	0.190	0.5
	F.R.:	0.094	0.109	0.796	0.786	0.105	0.109	0.592
5.	O.V.:	0.378	0.162	0.460	P.P.: two		N.F.: 20	
		Phase I				Phase II		ϕ
	I.V.:	0.050	0.162	0.788	0.706	0.162	0.133	0.5
	F.R.:	0.121	0.166	0.714	0.703	0.157	0.140	0.558

Appendix F (Continued)

6.	O.V.:	0.332	0.213	0.455	P.P.: two			N.F.: 48	
		Phase I			Phase II				ϕ
	I.V.:	0.050	0.213	0.737	0.614	0.213	0.173		0.5
	F.R.:	0.157	0.217	0.626	0.615	0.206	0.179		0.619
7.	O.V.:	0.314	0.266	0.420	P.P.: two			N.F.:	
		Phase I			Phase II				ϕ
	I.V.:	0.050	0.266	0.684	0.579	0.266	0.155		0.5
	F.R.:	0.324	0.266	0.410	0.302	0.266	0.432		0.555
8.	O.V.:	0.297	0.296	0.407	P.P.: one			N.F.:	
		Phase I			Phase II				ϕ
	I.V.:	0.050	0.296	0.654	0.544	0.297	0.160		0.5
	F.R.:	0.272	0.296	0.432	0.313	0.297	0.391		0.385

System: Water Acetone Heptane

1.	O.V.:	0.555	0.345	0.100	P.P.: two			N.F.: 28	
		Phase I			Phase II				ϕ
	I.V.:	0.605	0.345	0.050	0.506	0.345	0.150		0.5
	F.R.:	0.651	0.341	0.008	0.014	0.367	0.619		0.849
2.	O.V.:	0.619	0.288	0.093	P.P.: two			N.F.: 28	
		Phase I			Phase II				ϕ
	I.V.:	0.662	0.288	0.050	0.576	0.288	0.136		0.5
	F.R.:	0.711	0.284	0.005	0.010	0.315	0.676		0.869
3.	O.V.:	0.624	0.271	0.105	P.P.: two			N.F.: 35	
		Phase I			Phase II				ϕ
	I.V.:	0.679	0.271	0.050	0.569	0.271	0.160		0.5
	F.R.:	0.736	0.266	0.604	0.009	0.300	0.691		0.853
4.	O.V.:	0.631	0.248	0.121	P.P.: two			N.F.: 27	
		Phase I			Phase II				ϕ
	I.V.:	0.702	0.248	0.050	0.560	0.248	0.192		0.5
	F.R.:	0.755	0.242	0.003	0.008	0.277	0.715		0.834
5.	O.V.:	0.740	0.144	0.117	P.P.: two			N.F.: 35	
		Phase I			Phase II				ϕ
	I.V.:	0.807	0.144	0.050	0.673	0.144	0.183		0.5
	F.R.:	0.859	0.140	0.001	0.003	0.168	0.829		0.860

Appendix F (Continued)

6.	O.V.:	0.749	0.116	0.135	P.P.: two		N.F.: 30	
		Phase I			Phase II			ϕ
	I.V.:	0.834	0.116	0.050	0.664	0.116	0.220	0.5
	F.R.:	0.887	0.112	0.001	0.003	0.137	0.861	0.844
7.	O.V.:	0.428	0.303	0.269	P.P.: one		N.F.: 58	
		Phase I			Phase II			ϕ
	I.V.:	0.563	0.370	0.067	0.294	0.235	0.471	0.5
	F.R.:	0.435	0.305	0.260	0.424	0.301	0.275	0.376
8.	O.V.:	0.353	0.292	0.355	P.P.: one		N.F.: 68	
		Phase I			Phase II			ϕ
	I.V.:	0.576	0.370	0.540	0.130	0.214	0.656	0.5
	F.R.:	0.367	0.300	0.333	0.346	0.288	0.366	0.330

System: Ethylacetate Ethanol H_2O

1.	O.V.:	0.315	0.075	0.610	P.P.: two		N.F. 8	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.075	0.876	0.580	0.075	0.345	0.5
	F.R.:	0.080	0.051	0.870	0.531	0.096	0.373	0.478
2.	O.V.:	0.344	0.052	0.604	P.P.: two		N.F.:	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.052	0.898	0.638	0.052	0.310	0.5
	F.R.:	0.069	0.034	0.898	0.604	0.069	0.328	0.485
3.	O.V.:	0.283	0.107	0.610	P.P.: two		N.F.:	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.107	0.843	0.515	0.107	0.378	0.5
	F.R.:	0.103	0.077	0.821	0.416	0.129	0.454	0.426
4.	O.V.:	0.301	0.074	0.625	P.P.: two		N.F.:	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.074	0.876	0.552	0.074	0.376	0.5
	F.R.:	0.081	0.052	0.867	0.531	0.097	0.372	0.512
5.	O.V.:	0.300	0.043	0.657	P.P.:	N.F.:		
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.043	0.907	0.550	0.063	0.407	0.5
	F.R.:	0.067	0.030	0.902	0.625	0.061	0.314	0.583

Appendix F (Continued)

6.	O.V.:	0.301	0.107	0.592	P.P.: two		N.F.:	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.107	0.843	0.552	0.107	0.341	0.5
	F.R.:	0.106	0.077	0.816	0.435	0.128	0.438	0.407
7.	O.V.:	0.051	0.227	0.722	P.P.: one		N.F.:	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.227	0.723	0.051	0.228	0.721	0.5
	F.R.:	0.051	0.227	0.722	0.051	0.227	0.722	0.500
8.	O.V.:	0.712	0.266	0.022	P.P.: one		N.F.:	
		Phase I			Phase II			ϕ
	I.V.:	0.684	0.266	0.050	0.740	0.266	-0.006	0.5
	F.R.:	0.712	0.266	0.022	0.712	0.266	0.022	0.500
9.	O.V.:	0.154	0.214	0.632	P.P.: one		N.F.:	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.214	0.736	0.258	0.214	0.528	0.5
	F.R.:	0.154	0.214	0.632	0.154	0.214	0.631	0.500
10.	O.V.:	0.723	0.178	0.099	P.P.:	N.F.:		
		Phase I			Phase II			ϕ
	I.V.:	0.772	0.178	0.050	0.674	0.178	0.148	0.5
	F.R.:	0.723	0.178	0.099	0.723	0.178	0.099	0.500

System: Ethylacetate Methanol Water

1.	O.V.:	0.368	0.028	0.604	P.P.: two		N.F.: 7	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.029	0.922	0.685	0.029	0.287	0.5
	F.R.:	0.049	0.026	0.924	0.723	0.031	0.246	0.528
2.	O.V.:	0.345	0.060	0.595	P.P.: two		N.F.: 4	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.060	0.890	0.640	0.060	0.300	0.5
	F.R.:	0.061	0.056	0.883	0.661	0.064	0.275	0.526
3.	O.V.:	0.361	0.039	0.600	P.P.: two		N.F.: 7	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.039	0.911	0.672	0.039	0.289	0.5
	F.R.:	0.053	0.036	0.911	0.702	0.042	0.255	0.526

Appendix F (Continued)

4.	O.V.:	0.327	0.086	0.587	P.P.: two		N.F.: 15	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.086	0.865	0.605	0.086	0.309	0.5
	F.R.:	0.074	0.081	0.846	0.606	0.091	0.303	0.524
5.	O.V.:	0.274	0.113	0.613	P.P.: two		N.F.: 22	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.114	0.837	0.497	0.114	0.389	0.5
	F.R.:	0.094	0.109	0.798	0.539	0.120	0.340	0.596
6.	O.V.:	0.047	0.228	0.725	P.P.: one		N.F.: 3	
		Phase I			Phase II			ϕ
	I.V.:	0.050	0.228	0.722	0.046	0.226	0.728	0.5
	F.R.:	0.047	0.228	0.725	0.047	0.228	0.725	0.500
7.	O.V.:	0.703	0.125	0.172	P.P.: one		N.F.: 6	
		Phase I			Phase II			ϕ
	I.V.:	0.825	0.125	0.050	0.587	0.125	0.294	o.5
	F.R.:	0.703	0.525	0.172	0.703	0.125	0.172	0.502
8.	O.V.:	0.709	0.236	0.055	P.P.: one		N.F.: 3	
		Phase I			Phase II			ϕ
	I.V.:	0.714	0.236	0.050	0.704	0.236	0.060	0.5
	F.R.:	0.709	0.236	0.055	0.709	0.236	0.055	0.500

System: N-Hexane 5 - Nonanedsmo

1.	O.V.:	0.381	0.198	0.421	P.P.: two		N.F.: 33	
		Phase I			Phase II			ϕ
	I.V.:	0.741	0.221	0.038	0.022	0.175	0.804	0.5
	F.R.:	0.609	0.294	0.096	0.019	0.045	0.935	0.614
2.	O.V.:	0.344	0.278	0.379	P.P.:		N.F.: 32	
		Phase I			Phase II			ϕ
	I.V.:	0.602	0.357	0.041	0.085	0.198	0.717	0.5
	F.R.:	0.485	0.358	0.188	0.343	0.277	0.380	0.537
3.	O.V.:	0.340	0.261	0.400	P.P.: two		N.F.: 22	
		Phase I			Phase II			ϕ
	I.V.:	0.483	0.474	0.043	0.197	0.047	0.756	0.5
	F.R.:	0.517	0.318	0.166	0.338	0.260	0.602	0.010

Appendix F (Continued)

4.	O.V.:	0.359	0.245	0.396	P.P.: two		N.F.: 13	
		Phase I			Phase II			ϕ
	I.V.:	0.604	0.329	0.067	0.114	0.160	0.72	0.5
	F.R.:	0.572	0.299	0.132	0.357	0.244	0.398	0.715
5.	O.V.:	0.374	0.213	0.413	P.P.: two		N.F.: 22	
		Phase I			Phase II			ϕ
	I.V.:	0.649	0.286	0.065	0.099	0.141	0.760	0.5
	F.R.:	0.583	0.310	0.102	0.019	0.048	0.933	0.626
6.	O.V.:	0.381	0.198	0.421	P.P.:		N.F.: 37	
		Phase I			Phase II			ϕ
	I.V.:	0.538	0.434	0.028	0.225	-0.038	0.813	0.5
	F.R.:	0.668	0.293	0.096	0.019	0.045	0.936	0.614
7.	O.V.:	0.427	0.162	0.412	P.P.:		N.F.: 21	
		Phase I			Phase II			ϕ
	I.V.:	0.643	0.331	0.027	0.211	-0.008	0.797	0.5
	F.R.:	0.694	0.244	0.071	0.018	0.036	0945	0.611
8.	O.V.:	0.416	0.126	0.458	P.P.:		N.F.: 26	
		Phase I			Phase II			ϕ
	I.V.:	0.733	0.205	0.062	0.099	0.047	0.855	0.5
	F.R.:	0.742	0.204	0.050	0.617	0.036	0.953	0.548
9.	O.V.:	0.416	0.126	0.458	P.P.:		N.F.: 22	
		Phase I			Phase II			ϕ
	I.V.:	0.819	0.168	0.012	0.011	0.084	0.905	0.5
	F.R.:	0.742	0.204	0.050	0.017	0.030	0.953	0.548
10.	O.V.:	0.347	0.295	0.358	P.P.:		N.F.: 57	
		Phase I			Phase II			ϕ
	I.V.:	0.675	0.261	0.064	0.020	0.328	0.651	0.5
	F.R.:	0.434	0.334	0.233	0.300	0.273	0.427	0.358

System: Water, Ethanol, Butanol, Methanol Benzene

1.	O.V.:	0.820	0.050	0.10	0.020	P.P.: two	N.F.: 20
		Phase I				Phase II	
	I.V.:	0.90	0.04	0.04	0.5	0.015	
		0.74	0.06	0.16	0.015	0.025	
	F.R.	0.928	0.035	0.026	0.010	0.001	
		0.319	0.122	0.441	0.010	0.108	