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LOCAL MOLE FRACTION EQUATIONS
FOR THE EXCESS FREE ENERGY OF MIXING

BY

JOSE MARIO MARINA

A DISSERTATION
PRESENTED IN PARTIAL FULFILLMENT OF
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APPROVAL OF DISSERTATION

LOCAL MOLE FRACTION EQUATIONS FOR THE EXCESS FREE ENERGY OF MIXING

BY

JOSE MARIO MARINA

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________ CHAIRMAN

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NEWARK, NEW JERSEY

To My Wife

For her love, patience and understanding

ABSTRACT

LOCAL MOLE FRACTION EQUATIONS FOR THE EXCESS FREE ENERGY OF MIXING

An extensive study of local mole fraction equations aimed at obtaining a two parameter expression for the Excess Free Energy of miscible and immiscible systems has been undertaken.

Initially our approach was to modify existing equations by substituting those parameters reflecting interaction between like molecules by the pure component energies of vaporization. This resulted in a one parameter modification of the three parameter Wilson equation, which correlates data poorly and a two parameter modification of the NRTL equation which correlates binary miscible data with fair accuracy. A modification of the Scatchard-Hildebrand equation, where mole fractions are substituted by local mole fractions yields also a fairly good correlation for binary miscible systems.

The most significant result, however, was obtained when it was found that the substitution $\alpha = -1$, in the NRTL equation, results in an improved correlation for the excess free energy of mixing and consequently for the activity coefficients. A study of partially miscible systems, 5 binaries and 7 ternaries, shows that the new two parameter expression predicts binary vapor-liquid equilibrium from mutual solubility data and ternary liquid-liquid equilibrium

from binary data with better accuracy than the NRTL equation with the value of α set according to the rules of Renon and Prausnitz. In predicting binary immiscible behavior from vapor-liquid equilibrium data, both equations offer practically the same accuracy. A similar study conducted on miscible systems, 55 binaries and 11 ternaries, shows that both equations correlate binary data and predict ternary vapor-liquid equilibrium, from binary data, with about the same accuracy.

The importance of this finding is that now it becomes possible to use the NRTL equation, without the uncertainty involved in making the right choice for α, for predicting vapor-liquid and liquid-liquid equilibrium from either mutual solubility or azeotropic data. This modification, therefore, combines in a single expression the advantages of both the Wilson and NRTL equations.

Considering that a value of $\alpha = -1$ is inconsistent with Renon's derivation of the NRTL equation, a new model is proposed in which a distinction is made between bound and free molecules in a cell. Equating the ratio of local mole fractions of free molecules, what we call Effective Mole Fractions, to fugacities, leads to the desired two constant expression hereafter referred to as the LEMF equation.

During the course of this study a computational technique for the prediction of ternary liquid-liquid equilibria was developed. This technique makes use of a Fortran subroutine for function minimization to find the composition of phases in equilibrium.

Another result of this study was the finding that more than one set of parameters can be obtained, for either the NRTL or LEMF equation, depending on the initial values chosen to initiate the search. From a study of this phenomena we concluded that a 0-0 set of initial values generally yields the best set of binary parameters.

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INTRODUCTION

For a quantitative treatment of separation techniques such as distillation and extraction we must rely heavily on the phase equilibria relationships. There arises, therefore, the necessity of a functional expression between activity coefficient, temperature and composition. Throughout the years several such expressions have been proposed. Among these, the equations of VanLaar (39), Margules (17), and Wohl (45), are probably the best known. Rather recently Wilson (43) introduced the concept of local mole fractions through an analog to the expression for the partition function of independent localized systems. In a later publication Wilson (44) describes local mole fractions as those existing in cells composed of a central molecule and its immediate neighbors. Introducing the local mole fractions into the Flory-Huggins equation, Wilson obtains his equation for the Excess Free energy of mixing and from this by differentiation the activity coefficients are obtained.

The resulting two-parameter expression provides a very good representation of miscible systems but fails to describe immiscible behavior. Later Renon and Prausnitz (29), based on the concept of Local Mole Fractions and Scott's (33) two-liquid theory, developed the Non Random Two Liquid (NRTL) equation, a three parameter expression which describes with good accuracy miscible and immiscible systems. Both of these expressions seem to represent the data with a greater degree of accuracy than the previously proposed expressions. Our purpose in this work was to fill the gap between these two equations, that is to develop a two-constant expression for miscible and immiscible systems.

Such an expression would combine the advantages of both the Wilson and NRTL expressions thus allowing not only prediction of vapor-liquid equilibrium from azeotropic data but also prediction of vapor-liquid equilibrium from mutual solubility data and viceversa. Both of these areas lie at the threshold of either expression since the Wilson equation is incapable of describing immiscible behavior and the NRTL equation, being a 3 parameter, requires at least three data points for proper evaluation of the same.

Renon had some success in trying to overcome this problem by proposing rules for evaluation of the parameter α from qualitative considerations on the nature of the system and its components. However, at times, these rules are ambiguous and difficult to apply. The expression proposed here, a modification of the NRTL equation, eliminates the parameter α. The resulting correlation not only yields the same accuracy as the NRTL equation for miscible systems, but improves data prediction for immiscible systems.

II

BASIC PRINCIPLES

Under this heading we summarize the basic thermodynamic relations necessary for the study of vapor liquid equilibrium. The derivations that follow were obtained from treatises on the subject of thermodynamics of non electrolyte solutions by workers such as Van Ness (40) Hougen et.al. (13), Dodge (4) and Prausnitz (25).

PARTIAL MOLAL PROPERTIES

Let us assume M stands for the value of a property of a solution on a molar basis. Then for the entire solution we have

$$nM = n_1\bar{M}_1 + n_2\bar{M}_2 + n_3\bar{M}_3 + \dots \qquad \text{(II-1)}$$

where

$n = n_1 + n_2 + n_3 + \dots$

n_i = number of moles of component i

and $\bar{M}_i$ is the partial molal property of component i defined as follows

$$\bar{M}_i = \left[\frac{\partial (nM)}{\partial n_i}\right]_{T,\,P,\,n_{j \neq i}} \qquad \text{(II-2)}$$

If Eq. (II-1) is divided by n we get

$$M = X_1\bar{M}_1 + X_2\bar{M}_2 + X_3\bar{M}_3 + \dots \qquad \text{(II-3)}$$

where we must have

$$\sum_{i=1}^{n} X_i = 1 \qquad \text{(II-4)}$$

eliminating X_j **from Eqs. (II-3) and (II-4) we get** a new function in which all the X_i $i \neq j$ are independent i.e.

$$M = M(X_1, X_2, X_3 \dots X_{j-1}, X_{j+1}, \dots X_n) \qquad \text{(II-5)}$$

Taking now the total derivative with respect to n_j we have

$$\frac{\partial M}{\partial n_j} = \sum_{i=1}^{n} \left[\frac{\partial M}{\partial X_i} \frac{\partial X_i}{\partial n_j} \right] \qquad i \neq j \qquad \text{(II-6)}$$

and since $X_i = \dfrac{n_i}{n}$

then $$\frac{\partial X_i}{\partial n_j} = \frac{1}{n}\frac{\partial n_i}{\partial n_j} - \frac{n_i \partial n}{n^2 \partial n_j}$$

But $$\frac{\partial n_i}{\partial n_j} = 0 \quad \text{and} \quad \frac{\partial n}{\partial n_j} = 1$$

$$\therefore \quad \frac{\partial X_i}{\partial n_j} = -\frac{n_i}{n^2} = -\frac{X_i}{n} \qquad \text{(II-7)}$$

and introducing Eq. (II-7) into Eq. (II-6)

$$\frac{\partial M}{\partial n_j} = -\sum_{i-1}^{n} \left[\frac{\partial M}{\partial X_i} \frac{X_i}{n} \right] \qquad \text{(II-8)}$$

$$\therefore \quad n \frac{\partial M}{\partial n_j} = -\sum_{i=1}^{n} X_i \frac{\partial M}{\partial X_i} \qquad \text{(II-9)}$$

Now, Eq (II-2) can be put in the following form

$$\bar{M}_j = M + n \frac{\partial M}{\partial n_j} \qquad \text{(II-10)}$$

And combining equations (II-9) and (II-10)

$$\bar{M}_j = M - \sum_{\substack{i=1 \\ i \neq j}}^{n} X_i \frac{\partial M}{\partial X_i} \qquad \text{(II-11)}$$

This relation is of great importance since it gives the value of the partial molal property as a function of the total property and composition.

THE GIBBS-DUHEM EQUATION

Let G stand for the total value of a property in an n component system. Therefore in general we will have

$$G = G(T, P, n_1, n_2, \ldots n_n) \qquad \text{(II-12)}$$

Differentiating at constant T and P

$$dG = \frac{\partial G}{\partial n_1} dn_1 + \frac{\partial G}{\partial n_2} dn_2 + \ldots \frac{\partial G}{\partial n_n} \partial n_n \qquad \text{(II-13)}$$

And since $\frac{\partial G}{\partial n_i} = \bar{G}_i$, a partial molal property,

$$dG = \bar{G}_1 \, dn_1 + \bar{G}_2 \, dn_2 + \ldots\ldots \bar{G}n \, dn_n \qquad \text{(II-14)}$$

Integrating at constant T, P and composition, from a state of zero mass to a state of finite mass

$$G = \bar{G}_1 n_1 + \bar{G}_2 n_2 + \ldots\ldots \bar{G}_n n_n \qquad \text{(II-15)}$$

If equation (II-15) is now differentiated without the restriction of constant composition we obtain

$$dG = \bar{G}_1\, dn_1 + \bar{G}_2\, dn_2 + \ldots \bar{G}_n\, dn_n$$

$$+ n_1\, d\bar{G}_1 + n_2\, d\bar{G}_2 + \ldots n_n\, d\bar{G}_n \qquad \text{(II-16)}$$

and comparing Eqs. (II-14) and (II-16) we conclude

$$n_1\, d\bar{G}_1 + n_2\, d\bar{G}_2 + \ldots n_n\, d\bar{G}_n = 0 \qquad \text{(II-17)}$$

which is the Gibbs-Duhem equation for a multicomponent system constrained to changes at constant T and P.

THE CRITERIA OF EQUILIBRIUM

The most useful thermodynamic property in the study of equilibrium is the free energy (G). For a closed system of n components in two phases we have

$$G = \sum_{i=1}^{n} (n_i' \bar{G}_i' + n_i'' \bar{G}_i'') \qquad \text{(II-18)}$$

Differentiating at constant T and P,

$$dG = \sum_{i=1}^{n} (\bar{G}_i' dn_i' + \bar{G}_i'' dn_i'' + n_i' d\bar{G}_i' + n_i'' d\bar{G}_i'') = 0 \qquad \text{(II-19)}$$

And after comparing with the Gibbs-Duhem equation
we conclude

$$dG = \sum_{i=1}^{n} (\bar{G}_i^{'} dn_i^{'} + \bar{G}_i^{''} dn_i^{''}) = 0 \qquad \text{(II-20)}$$

Since the system is closed we must have

$$dn_i^{'} = - dn_i^{''} \qquad \text{(II-21)}$$

$$\therefore \quad \sum_{i=1}^{n} dn_i \; (\bar{G}_i^{'} - \bar{G}_i^{''}) = 0 \qquad \text{(II-22)}$$

Therefore, considering that the dn_i are independent variables, we must conclude

$$\bar{G}_i^{'} = \bar{G}_i^{''} \qquad \text{(II-23)}$$

i.e., the criteria for equilibrium is that the Partial Molal free energy of component i must be the same in both phases.

DEFINITION OF FUGACITY

Equilibrium between phases is better dealt with in terms of fugacities. For isothermal changes the free energy change of an ideal gas is given by

$$dG = RT\ d \ln P.$$

The fugacity of pure component i is defined as the quantity for which P must be substituted to obtain the free energy change dG_i of a real gas. That is for a real gas we write

$$dG_i = RT\ d \ln f_i \qquad \text{(II-24)}$$

Since for low pressure all real gases approach ideal gas behavior, the definition is completed by stating

$$\lim_{P \to 0} \left(\frac{f_i}{P}\right) = 1 \qquad \text{(II-25)}$$

Equation (II-24) may be extended to solutions in which case we write

$$d\bar{G}_i = RT\ d\ \ln \hat{f}_i \qquad \text{(II-26)}$$

In this case the definition is completed by stating

$$\lim_{P \to 0} \frac{\hat{f}_i}{P_i} = \lim \frac{\hat{f}_i}{Y_i P} = 1 \qquad \text{(II-27)}$$

where Y_i =mole fraction of component i

$\hat{f}_i$ = fugacity of component i in solution

P_i = partial pressure of component i

P = total pressure.

The condition of equilibrium presented in eq (II-23) can now be stated in terms of fugacities as follows

$$\hat{f}_i^{\,\prime} = \hat{f}_i^{\,\prime\prime} \qquad \text{(II-28)}$$

ACTIVITY AND ACTIVITY COEFFICIENTS

The activity of component i in solution is defined from the following equation

$$f_i = \gamma_i \ X_i \ f_i^{\circ} = a_i f_i^{\circ} \qquad \text{(II-29)}$$

where a_i = activity of component i

f_i° = fugacity of component i at standard state conditions

γ_i = activity coefficient of component i

X_i = mole fraction of component i

A very common std. state is that of the pure component at the temperature and pressure of the solution and in the same physical state.

When correlating activity coefficients it is convenient to eliminate the effect of pressure through the introduction of a pressure correction term. Thus we rewrite Eq. (II-29) as follows

$$f_i = \gamma_i^{(\circ)} X_i f_i^{(\circ)} e^{\frac{v^L(P-P^{\circ})}{RT}} \qquad \text{(II-30)}$$

where both $\gamma_i^{(\circ)}$ and $f_i^{(\circ)}$ are evaluated at P°. For convenience, throughout this work, P° is taken as zero.

ACTIVITY COEFFICIENTS AND EXCESS PROPERTIES

Excess properties are defined as the difference between the value of a property in a real mixture and the value this property would have should the mixture behave ideally. Accordingly the excess free energy of a mixture is given by

$$G^E = G^M - G^M_* \tag{II-31}$$

G^E = excess Gibbs Energy

G^M = Gibbs energy of mixing

G^M_* = Gibbs energy of mixing for an ideal solution

And since

$$G^M = \sum_{i=1}^{n} (X_i \bar{G}_i - X_i G_i)$$

And

$$G^M_* = RT \sum_{i=1}^{n} X_i \ln X_i$$

We have that

$$G^E = \sum_{i=1}^{n} (X_i\bar{G}_i - X_iG_i - RT\, X_i \ln X_i) \qquad \text{(II-32)}$$

$$G^E = RT \sum_{i=1}^{n} X_i(\ln \frac{\hat{f}_i}{f_i} - \ln X_i) \qquad \text{(II-33)}$$

$$G^E = RT \sum_{i=1}^{n} X_i \ln \gamma_i \qquad \text{(II-34)}$$

where

$\bar{G}_i$ = partial molal Gibbs energy of component i

and G_i = Gibbs energy of pure component i

Now, since we have that

$$G^E = \sum_{i=1}^{n} X_i\, \bar{G}_i^E \qquad \text{(II-35)}$$

Comparing with Eq (II-32) we define the partial molal excess Gibbs energy as follows

$$\bar{G}_i^E = \bar{G}_i - G_i - RT \ln X_i \qquad \text{(II-36)}$$

$$\therefore\ \bar{G}_i^E = RT \ln \gamma_i \qquad \text{(II-37)}$$

Equation (II-37) offers a convenient way of relating the activity coefficients to excess properties. Making use of Eq. (II-11), we can write

$$\bar{G}_j^E = RT \ln \gamma_j = G^E - \sum_{\substack{i=1 \\ i \neq j}}^{n} X_i \frac{\partial G^E}{\partial X_i} \qquad \text{(II-38)}$$

THE VIRIAL EQUATION

The only equation of state which has been shown to have physical significance in terms of molecular dimensions is the VIRIAL equation, which gives the compresibility factor Z as a power series in 1/V.

$$\frac{PV}{RT} = Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots. \qquad \text{(II-39)}$$

where the coefficients B, C, D, etc. are known as the second, third, fourth, etc. VIRIAL coefficients. For a given substance, these coefficients are a function of temperature only. From statistical mechanics we learn that the VIRIAL coefficients reflect the molecular interactions between a particular number of molecules, thus the second VIRIAL coefficient reflects interactions between pairs of molecules, the third between triplets and so on. The second VIRIAL coefficient for the gas phase is given in terms of the various components as follows

$$B = \sum_{i}^{n} \sum_{j}^{n} Y_i \; Y_j \; B_{ij} \qquad \text{(II-40)}$$

For a binary solution this becomes

$$B = Y_1^2 \; B_{11} + 2 \; Y_1 \; Y_2 \; B_{12} + Y_2^2 \; B_{22} \qquad \text{(II-41)}$$

where Y_i represents the mole fraction of component i in the gas phase, B_{11} and B_{22} are the second VIRIAL coefficients of pure component 1 and 2 and B_{12} is the second VIRIAL cross coefficient. All are functions of temperature only.

As as matter of convenience a new coefficient δ_{12} may be defined as follows

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \qquad \text{(II-42)}$$

And combining (II-41) and (II-42) we get

$$B = Y_1 B_{11} + Y_2 B_{22} + Y_1 Y_2 \delta_{12} \qquad \text{(II-43)}$$

The third VIRIAL coefficient can be represented in terms of the components as

$$C = \sum_{i}^{n} \sum_{j}^{n} \sum_{k}^{n} Y_i Y_j Y_k C_{ijk} \qquad \text{(II-44)}$$

For a binary solution this equation takes the following form.

$$C = Y_1^3 C_{111} + 3Y_1^2 Y_2 C_{112} + 3Y_1 Y_2^2 C_{122} + Y_2^3 C_{222} \qquad \text{(II-45)}$$

Where the coefficients C_{111} and C_{222} are the third VIRIAL coefficients for pure components 1 and 2 and C_{112} and C_{122} are the third VIRIAL cross coefficients.

One could continue defining higher order VIRIAL coefficients, but little is known about the fourth and higher order VIRIAL coefficients. Fortunately, however, the VIRIAL equation truncated to only 3 terms is accurate to moderate pressures. Truncated to two terms, the equation is highly reliable for low pressures.

THE FUGACITY COEFFICIENT

The fugacity coefficient is defined as the ratio f/P and can be conveniently expressed in terms of the compresibility factor as follows

$$\ln \phi = \int_0^P (Z - 1) \frac{dP}{P} \qquad \text{(II-46)}$$

where the integration is to be carried out at constant temperature.

Since the VIRIAL equation is explicit in P, it must be rearranged in order to perform the integration. We have that

$$PV = ZRT \qquad \text{(II-47)}$$

therefore at constant T

$$PdV + VdP = RT\ dZ \qquad \text{(II-48)}$$

dividing by PV = ZRT

$$\frac{dP}{P} = \frac{dZ}{Z} - \frac{dV}{V} \qquad \text{(II-49)}$$

$$\therefore \quad (Z - 1) \frac{dP}{P} = dZ - d \ln Z + (Z - 1)\ V\ d\left(\frac{1}{V}\right) \qquad \text{(II-50)}$$

But from eq (II-39) truncated to two terms we can see that

$$(Z - 1)\ V = B \qquad \text{(II-51)}$$

Hence, substituting (II-50) and (II-51) into (II-46) and performing the integration we obtain

$$\ln \phi = Z - 1 - \ln Z + \frac{B}{V} \qquad \text{(II-52)}$$

and substituting (Z−1) from eq (II-39) into eq (II-52) gives

$$\ln \phi = - \ln Z + \frac{2B}{V} \qquad \text{(II-53)}$$

a very accurate expression for low pressures. Its only disadvantage is that being implicit in V, it is difficult to calculate volumes and other thermodynamic properties at constant T and P.

The fugacity coefficient of component i in solution, $\hat{\phi}_i$ is obtained from the fugacity coefficient of the solution ϕ by application of Eq. (II-11). That is

$$\ln \hat{\phi}_i = \ln\phi - \sum_{\substack{j=1\\ j\neq i}}^{n} X_j \frac{\partial \ln\phi}{\partial X_j} \tag{II-54}$$

For a binary solution, Eq. (II-54) in terms of gaseous mole fractions becomes

$$\ln \hat{\phi}_i = \ln \phi - Y_j \frac{\partial \ln\phi}{\partial Y_j} \tag{II-55}$$

And after introducing Eq. (II-53) we obtain

$$\ln \hat{\phi}_i = \frac{2B}{V} - \ln Z - Y_j \frac{\partial}{\partial Y_j} \left(\frac{2B}{V} - \ln Z\right) \tag{II-56}$$

$$\therefore \ln\hat{\phi}_i = \frac{2B}{V} - \ln Z - Y_j \left[\frac{2}{V} \left(\frac{\partial B}{\partial Y_j}\right) + 2B \frac{\partial}{\partial Y_j} \left(\frac{1}{V}\right) - \frac{1}{Z} \left(\frac{\partial Z}{\partial Y_j}\right)\right] \tag{II-57}$$

$$\therefore \ln\hat{\phi}_i = \frac{2B}{V} - \ln Z - Y_j \left[\frac{2}{V} \left(\frac{\partial B}{\partial Y_j}\right) - \frac{2B}{V^2}\left(\frac{\partial V}{\partial Y_j}\right) - \frac{1}{Z}\left(\frac{1}{V} \frac{\partial B}{\partial Y_j} - \frac{B}{V^2} \frac{\partial V}{\partial Y_j}\right)\right] \tag{II-58}$$

$$\therefore \ln \hat{\phi}_i = \frac{2B}{V} - \ln Z - \frac{Y_j}{Z}\left[\frac{1}{V}\,\frac{\partial B}{\partial Y_j}\left(2Z-1\right) - \frac{B}{V^2}\,\frac{\partial V}{Y_j}\left(2Z-1\right)\right] \qquad \text{(II-59)}$$

Now, from Eq. (II-39) truncated after the second term we get

$$\frac{PV}{RT} = 1 + \frac{B}{V} \qquad \text{(II-60)}$$

And taking the partial derivative with respect to Y_j

$$\frac{P}{RT}\left(\frac{\partial V}{\partial Y_j}\right) = \frac{1}{V}\left(\frac{\partial B}{\partial Y_j}\right) - \frac{B}{V^2}\left(\frac{\partial V}{\partial Y_j}\right) \qquad \text{(II-61)}$$

$$\therefore \quad \frac{\partial V}{\partial Y_j} = \frac{\partial B}{\partial Y_j}\left(\frac{1}{2Z - 1}\right) \qquad \text{(II-62)}$$

Now substituting Eq. (II-62) into Eq. (II-59) we get

$$\ln \hat{\phi}_i = \frac{2B}{V} - \ln Z - \frac{Y_j}{Z}\left[\frac{1}{V}\left(\frac{\partial B}{\partial Y_j}\right)\left(2Z-1\right) - \frac{B}{V^2}\left(\frac{\partial B}{\partial Y_j}\right)\right] \qquad \text{(II-63)}$$

$$\therefore \ln \hat{\phi}_i = \frac{2B}{V} - \ln Z - \frac{Y_j}{ZV}\left(\frac{\partial B}{\partial Y_j}\right)\left[2Z - 1 - \frac{B}{V}\right] \qquad \text{(II-64)}$$

$$\therefore \ln \hat{\phi}_i = \frac{2B}{V} - \ln Z - \frac{Y_j}{V}\left(\frac{\partial B}{\partial Y_j}\right) \qquad \text{(II-65)}$$

And substituting for B from Eq. (II-41)

$$\ln \hat{\phi}_i = \frac{1}{V}\left(2\ Y_i^2\ B_{ii} + 4\ Y_iY_jB_{ij} + 2Y_j^2\ B_{jj}\right) - \ln Z$$

$$- \frac{1}{V}\left(-\ 2Y_iY_jB_{ii} - 2Y_j^2\ B_{ij} + 2Y_iY_jB_{ij} + 2\ Y_j^2B_{jj}\right) \quad \text{(II-66)}$$

$$\therefore \ln \hat{\phi}_i = \frac{2}{V}\left(Y_iB_{ii} + Y_jB_{ij}\right) - \ln Z \quad \text{(II-67)}$$

which gives the fugacity coefficient $\hat{\phi}_i$ as a function of the virial coefficients.

For pure component i, we obtain from Eq. (II-67)

$$\ln \phi_i = \frac{2B_{ii}}{V} - \ln Z \quad \text{(II-68)}$$

LOW PRESSURE VAPOR-LIQUID EQUILIBRIUM

At low pressures, up to several atmospheres, equation (II-67) can be used with good accuracy. This will allow us to calculate activity coefficients for the liquid phase from vapor-liquid equilibrium data. As indicated by Eq.(II-28) the condition for equilibrium between phases is

$$\hat{f}_i^L = \hat{f}_i^V \qquad \text{(II-69)}$$

where $\hat{f}_i^V = YP \hat{\phi}_i$ and $\hat{f}_i^L$ is given by Eq. (II-30).

Making these substitutions in Eq. (II-69) we obtain

$$\gamma_i^{(o)} X_i f_i^{(o)} e^{\frac{V^L P}{RT}} = Y \hat{\phi}_i P \qquad \text{(II-70)}$$

where the reference fugacity $f_i^{(o)}$ is given by that of the vapor, in equilibrium with the liquid, after the necessary pressure correction is made, i.e.

$$f_i^{(o)} = f_i^s e^{-\frac{V^L P^s}{RT}} \qquad \text{(II-71)}$$

Now introducing Eq. (II-68) into Eq. (II-71) we obtain

$$f_i^{(o)} = P^s e^{\left[\frac{2B_{ii}}{V^v} - \ln Z - \frac{V^L P^s}{RT}\right]} \qquad \text{(II-72)}$$

But from Eq. (II-39) truncated to two terms we get

$$Z = 1 + \frac{B_{ii}}{V^V}$$

$$\therefore \ln Z = \ln\left(1 + \frac{B_{ii}}{V^V}\right) \qquad \text{(II-73)}$$

And after expanding in series and dropping higher order terms

$$\ln Z = \frac{B_{ii}}{V^V} \qquad \text{(II-74)}$$

If we now substitute $\frac{1}{V^V} = \frac{P^s}{RT}$ in Eqs. (II-74) and (II-72) we obtain

$$f_i^{(o)} = P^s e^{\left[\frac{B_{ii}P^s}{RT} - \frac{V^L P^s}{RT}\right]} \qquad \text{(II-75)}$$

And introducing Eq. (II-75) into (II-70) we obtain the expression for the liquid phase activity coefficient.

$$\gamma_i^{(o)} = \frac{Y\hat{\phi}_i\ P}{X_i\ P^s\ e^{[B_{ii}P^s + V^L(P-P^s)]/RT}} \qquad \text{(II-76)}$$

CORRELATION FOR 2ND VIRIAL COEFFICIENTS

In order to correlate pure component 2nd VIRIAL coefficients B_{ii} it is necessary to have accurate volumetric data of the pure gas. To correlate second VIRIAL cross coefficients, it is necessary to have accurate volumetric data on the gas mixture. Since this data is seldom available it is necessary to estimate the desired VIRIAL coefficients from correlations. In general it is possible to estimate with good accuracy 2nd VIRIAL coefficients of non polar gases and mixtures. 2nd VIRIAL coefficients for polar gases and mixtures can be estimated with only fair accuracy. Here we present the correlation of Pitzer and Curl for non polar gases and mixtures and Prausnitz extension to polar gases and mixtures.

For pure non polar gases Pitzer and Curl (22, 23) suggests the following relation

$$\frac{P_{c_i}\, B_{ii}}{R\, T_{c_i}} = f_B^{(o)}\,(T_r) + W_i\, f_B^{(1)}\,(T_r) \qquad \text{(II-77)}$$

where Pc_i = critical pressure of i

Tc_i = critical temperature of i

T_r = reduced temperature, T/Tc_i

$$W_i = \text{accentric factor of } i = -\log_{10}\left(\frac{P_i^s}{P_{c_i}}\right) - 1.0 \qquad \text{(II-78)}$$

where P_i^S is the saturation vapor pressure of i at $T_r = 0.7$

And the empirical functions $f_B^{(o)}(T_r)$ and $f_B^{(1)}\,(T_r)$ are

$$f_B^{(o)}\,(T_r) = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^{\,2}} - \frac{0.0121}{T_r^{\,3}} \qquad \text{(II-79)}$$

$$f_B^{(1)}\,(T_r) = 0.073 + \frac{0.46}{T_r} - \frac{0.50}{T_r^{\,2}} - \frac{0.097}{T_r^{\,3}} - \frac{0.0073}{T_r^{\,8}} \qquad \text{(II-80)}$$

For pure polar gases Prausnitz et. al. (25) recommend the following correlation

$$\frac{Pc_i\;\; B_{ii}}{R\;\; Tc_i} = f_B^{(o)}\,(T_r) + W_{Hi}\;\; f_B^{(1)}\,(T_r) + f_\mu\;(\mu, T_r) + \eta_i f_a\,(T_r) \qquad \text{(II-81)}$$

where W_{Hi} = accentric factor of Polar component's homomorph

$f_B^{(o)}$ (T_r) and $f_B^{(1)}$ (T_r) are as defined above, Eqs. (II-79) and (II-80)

μ_r = reduced dipole moment = $\dfrac{10^5\;\; \mu_i^2\;\; P_{c_i}}{T c_i^2}$

η_i = vapor phase association constant

$$f\mu\ (\mu_r\ , T_r) = -\ 5.237220 + 5.665807\ \ln \mu_r - 2.133816\ (\ln \mu_r)^2 + 0.2525373\ (\ln \mu_r)^3 + \frac{1}{T_r}\left[5.769770 - 6.181427\ \ln \mu_r + 2.283270\ (\ln \mu_r)^2 - 0.2649074\ (\ln \mu_r)^3\right] \quad \text{(II-82)}$$

$$f_a\ (T_r) = \exp\left[6.6\ (0.7 - T_r)\right] \quad \text{(II-83)}$$

The Polar contributions of eq. (II-82) and (II-83) should be neglected for reduced temperatures higher than 0.95. If $\mu_r < 4$, Eq (II-82) does not apply and the polar contributions should be neglected.

For gas mixtures the cross coefficient B_{ij} is estimated from the previously presented correlations by using suitable mixing rules for the various parameters.

For the case where i and j are both nonpolar, Eqs. (II-77), (II-79) and (II-80) are used as presented except for the replacement of B_{ii}, Pc_i, Tc_i and W_i by the corresponding mixtures properties B_{ij}, Pc_{ij}, Tc_{ij} and W_{ij}.

The following mixing rules are recommended

$$Tc_{ij} = (Tc_i\ Tc_j)^{1/2} \quad \text{(II-84)}$$

$$W_{ij} = 1/2(W_i + W_i) \quad \text{(II-85)}$$

$$Pc_{ij} = 4\ Tc_{ij}\left[\frac{Pc_i\ Vc_i}{Tc_i} + \frac{Pc_j\ Vc_j}{Tc_j}\right] / \left(Vc_i^{1/3} + Vc_j^{1/3}\right)^3 \quad \text{(II-86)}$$

where V_C is the critical volume.

These mixing rules give good results whenever components i and j have similar molecular size and volatility. Otherwise empirical modifications may be required.

For a Polar-nonpolar mixture of gases equations (II-77), (II-79) and (II-80) are used after replacing B_{ii}, T_C, W_i, and Pc_i by the corresponding mixtures properties B_{ij}, Tc_{ij} W_{ij} and Pc_{ij} as per equations (II-84), (II-87) and (II-86).

$$W_{ij} = 1/2\,(WH_i + W_j) \qquad \text{(II-87)}$$

For the case of a polar-polar mixtures, eq. (II-81) is used after replacing B_{ii}, Tc_i, Pc_i, WH_i and η_i by the corresponding mixture properties B_{ij} Tc_{ij}, Pc_{ij} WH_{ij}, and η_{ij} as per equation(II-84), (II-86), (II-88) and (II-89).

$$WH_{ij} = 1/2(WH_i + WH_j) \qquad \text{(II-88)}$$

$$\eta_{ij} = 1/2\,(\eta_i + \eta_j) \qquad \text{(II-89)}$$

And the reduced dipole moment μ_r by the expression

$$\frac{10^5\,\mu_i\;\mu_j\,Pc_{ij}}{Tc_{ij}^{\;2}}$$

The mixing rules presented above are approximations and should be used only when no other data is available.

The Reference Fugacity

As required by the condition of equilibrium, Eq. (II-28), the fugacity of a pure saturated liquid must equal that of the vapor in equilibrium with it, that is ,

$$f_i^{(P_i^s)} = \phi_i^s P_i^s \qquad \text{(II-90)}$$

where ϕ_i^s is the fugacity coefficient of pure vapor i at temperature T and saturation pressure P_i^s . For low pressures Eq. (II 67) may be used, or alternatively Eq. (II-53) , that is

$$\ln \phi_i^s = \frac{2}{V_i^s} B_{ii} - \ln Z_i^s \qquad \text{(II-91)}$$

For Tr <0.56

$$\text{where} \quad Z_i^s = \frac{P_i^s V_i^s}{RT} = 1 + \frac{B_{ii}}{V_i^s} \qquad \text{(II-92)}$$

Another alternative is the correlation by Lyckman, Eckert and Prausnitz (25) which allows calculation of ϕ_i^s at temperatures much closer to the critical temperature.

$$\ln \phi_i^s = (\log \phi_i^s)^{(o)} + W_i (\log \phi_i^s)^{(1)} \text{ for } 0.56 < Tr < 1.0 \qquad \text{(II-93)}$$

where W_i is the accentric factor and where $(\log \phi_i^s)^{(o)}$ and $(\log \phi_i^s)^{(1)}$ are generalized functions of T_r. An analytic form of (II-93) is used in the present work. See Program ATHENA, Subroutine RSTATE. The reference fugacity is the fugacity of pure liquid i at Temp T and a reference pressure arbitrarily chosen as zero.

Therefore since

$$\left[\frac{\partial \ln f_i^{l}}{\partial P}\right]_T = \frac{V_i^L}{RT} \qquad \text{(II-94)}$$

$$f_i^{(Po)} = \phi_i^s P_i^s \exp - \frac{V_i^L P_i^s}{RT} \qquad \text{(II-95)}$$

- III -

CORRELATIONS FOR THE EXCESS FREE ENERGY OF MIXING

THE WOHL EQUATION

Throughout the years many different expressions have been proposed for correlation of activity coefficients. Usually these expressions take the form of polynominals in X, the mole fraction, with temperature dependent coefficients. In these expressions, as many terms as required to fit the data are used and although in some cases the fit may be good, there is little physical meaning for the constants found.

One of these polynomial-type expression was suggested by Wohl

$$\frac{G^E}{RT(\Sigma q_i X_i)} = \sum_{ih} Z_i Z_h \, a_{ih} + \sum_{ihj} Z_i Z_h Z_j \, a_{ihj} + \sum_{ihjl} Z_i Z_h Z_j Z_l \, a_{ihjl} + \ldots\ldots \quad \text{(III-1)}$$

where for component i

X_i = mole fraction of i

q_i = effective molal volume

Z_i = effective volume fraction

i,h, j refer to the different components

a_{ih}, a_{ihj} ..... = empirical constants.

And

$$Z_i = \frac{X_i}{X_i + \Sigma q_j X_j / q_i}$$

In these equations the number of terms used depends on the complexity of the mixture and the degree of accuracy desired. The term $\Sigma \; Z_i Z_h \; a_{ih}$ represents the contributions due to unlike components in groups of 2. The term $\Sigma \; Z_i Z_h Z_j \; a_{ihj}$ represents contributions in group of 3 and so on, each term reflecting deviations not accounted for by the previous term.

THE WILSON EQUATION

The concept of local mole fractions was first introduced by Wilson (40), who proposed a two-parameter equation that represents with great accuracy the behavior of binary miscible systems. According to Wilson, the distribution of molecules of component 2 around a molecule of component 1, see Fig. (1), is given by

$$\frac{X_{21}}{X_{11}} = \frac{X_2}{X_1} \; e^{-(\lambda 21 - \lambda 11)/RT} \qquad \text{(III-2)}$$

where

X_{21} = local mole fraction of component 2 around a center molecule of component 1
X_{11} = local mole fraction of component 1 around a molecule of component 1
X_2 = mole fraction of component 2 in the mixture
X_1 = mole fraction of component 1 in the mixture
λ_{21} and λ_{11} are constants proportional to the energy of interaction in a 2-1 and a 1-1 pair, respectively.

From Eq. (III-2) Wilson obtained an expression for the partial volumes of components 1 and 2 in the mixture and introducing them into the Flory Huggins equation, he obtained the following expression for the excess free energy of mixing.

$$\frac{G^E}{RT} = -\sum_i X_i \ln \left(1 - \sum_j X_j A_{ji}\right) \qquad \text{(III-3)}$$

where

$$A_{ji} = 1 - \frac{V_j}{V_i} e^{-(\lambda_{ji} - \lambda_{ii})/RT}$$

V_j = pure component volume of component j

V_i = pure component volume of component i

The above expression can readily be expanded to multicomponent systems and prediction of multicomponent vapor liquid equilibrium follows from binary data alone.

As previously mentioned, the Wilson equation represents with great accuracy the vapor-liquid equilibrium of miscible systems. The equation, however, fails to represent **immiscible behavior.**

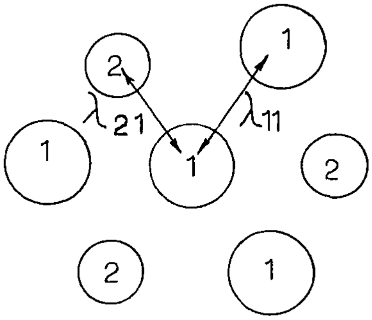

FIGURE 1

THE NRTL EQUATION

In 1968 Renon and Prausnitz (29) modified Wilson's equation for local mole fractions by introducing the constant α to account for the non randomness of liquid solutions.

$$\frac{X_{21}}{X_{11}} = \frac{X_2 \exp\left[-\alpha(g_{21} - g_{11})/RT\right]}{X_1} \qquad \text{(III-4)}$$

Making use of this expression and Scott's (23) two liquid theory they developed the "Non Random Two Liquid" equation (NRTL) a three parameter equation capable of describing vapor-liquid equilibrium of miscible and immiscible systems with remarkable accuracy.

$$\frac{G^E}{RT} = \frac{X_1X_2}{RT}\left[\frac{(g_{21} - g_{11}) \exp -\alpha(g_{21} - g_{11})/RT}{X_1 + X_2 \exp -\alpha(g_{21} - g_{11})/RT} + \frac{(g_{12} - g_{22}) \exp -\alpha(g_{12} - g_{22})/RT}{X_2 + X_1 \exp -\alpha(g_{12} - g_{22})/RT}\right] \qquad \text{(III-5)}$$

where

g_{ij} = residual Gibb energies

X_1 and X_2 = mole fractions of components 1 and 2

In the above expression the differences $(g_{ij} - g_{jj})$ are fitted to the data and the third constant, α , may either be fitted to the data or evaluated a priori from the nature of the system.

According to Renon, binary mixtures can be classified into eight different types from considerations on the polarity and self association characteristics of the pure components and the value of the excess free energy of the mixture. Each of these mixture types is associated with a value of α in the range 0.2 to 0.47, therefore the value of α follows from the type of binary mixture under consideration. These rules, however, constitute an approximation and better correlations may be obtained by curve fitting .

In general this equation correlates binary data and predicts multicomponent phase equilibria with good accuracy. The NRTL equation although a 3 parameter equation, represents an improvement over the Wilson equation because of its ability to predict phase immiscibility.

THE MODIFIED WILSON EQUATION

According to Tassios (38), fairly good results are obtained when the constants $-\lambda_{11}$ and $-\lambda_{22}$ in the Wilson equation are substituted for the heat of vaporization of the pure components. The result is a one constant equation that allows the prediction of activity coefficients for a binary system from one infinite dilution determination. However, this correlation is bound by the same limitations of the original Wilson equation in that it will not represent inmiscible behavior.

Scatchard and Wilson (32) showed that this limitation could be eliminated if the equation for the excess free energy is multiplied by a constant as follows

$$\frac{G^E}{RT} = -c \sum_i X_i \ln (1 - \sum_j X_j \quad A_{ji}) \qquad \text{(III-6)}$$

where as before

$$A_{ji} = 1 - \left(\frac{V_j}{V_i}\right) e^{-(\lambda_{ji} - \lambda_{ii})/RT}$$

V_i and V_j are molal volumes

λ_{ii} and λ_{ij} are constants proportional to the energy of interaction in an ii – and ij pair respectively.

We proposed them to express the constant C as a function of λ_{11} and λ_{22} while at the same time λ_{11} and λ_{22} would be substituted for pure component heats of vaporization. This would result in a one constant equation for miscible and inmiscible systems. The advantage would the ability to predict vapor-liquid or liquid-liquid equilibria from a single infinite dilution or solubility point. Several different functional relations for C have been investigated. The results are presented in Table I,

TABLE I

STANDARD DEVIATIONS OF CALCULATED ACTIVITY COEFFICIENTS WITH THE MODIFIED WILSON EQUATION					
		STANDARD DEVIATION			
		MODIFIED WILSON EQ.			
-- SYSTEM --	DATA POINTS	$C = C_1$	$C = C_2$	$C = C_3$	WILSON EQUATION
Nitromethane-carbon tetrachloride at 45°C.	12	0.246	0.286	0.290	0.0202
Acetone-toluene at 45°C.	20	0.249	0.268	0.272	0.0017
Nitromethane-toluene at 45°C.	12	0.036	0.035	0.033	0.0105
Acetonitrile-toluene at 45°C.	18	0.541	0.631	0.634	0.0328
2-Propanol-ethyl acetate at 60°C.	19	0.243	0.227	0.248	0.0376
1-Propanol-ethyl acetate at 60°C.	13	0.239	0.210	0.224	0.0322

where

$$C_1 = 1.5 + \frac{\text{SLOPE } 2}{\text{SLOPE } 1 - \text{SLOPE } 2}$$

SLOPE 1 and SLOPE 2 refer to the SLOPE of the G^E/RT vs. X curve at X = 0 and X = 1, respectively, i.e.

$$\text{SLOPE } 1 = -\ln(1 - A_{21}) + A_{12}$$

$$\text{SLOPE } 2 = \ln(1 - A_{12}) - A_{21}$$

the constant C_1 is a measure of the symmetry of the system, i.e. for a symmetric system SLOPE 1 = − SLOPE 2 and $C_1 = 1$

$$C_2 = (\sqrt{\lambda_{11}\ \lambda_{22}} - \lambda_{12})\ /RT$$

$$C_3 = \left|\left(\frac{\lambda_{11} + \lambda_{22}}{2} - \lambda_{12}\right)\right| /RT$$

The standard deviation is defined as follows

$$\text{STD. DEV.} \sqrt{\frac{(\gamma_1\text{cal} - \gamma_1\text{obs})^2 + (\gamma_2\text{cal} - \gamma_2\text{obs})^2}{2n - 1}} \qquad \text{(III-7)}$$

where γ ical = calculated activity coefficient of component i

γ iobs = observed activity coefficient of component i

n = number of points.

Work along these lines was discontinued due to erratic behavior of the equation for some systems. A two constant form of this modification was not investigated.

THE MODIFIED SCATCHARD–HILDEBRAND EQUATION

The original Scatchard–Hildebrand (30) equation for the Excess Gibbs Energy of regular solution is:

$$G^E = \Phi_1 \Phi_2 (X_1V_1 + X_2V_2)\ (C_{11} + C_{22} - 2C_{12}) \qquad \text{(III-8)}$$

where X_1 and X_2 are liquid composition, V_1 and V_2 are molar volumes, C_{11} and C_{22} are pure components cohesive energies, C_{12} is the interaction cohesive energy and Φ_1 and Φ_2 are volume fractions.

Weimer and Prausnitz (41) extended this equation to include the effect of a polar solvent by expressing the energy of vaporization **as a function of polar and non polar solubility parameters.**

$$\frac{\Delta U}{V_1} = \frac{\Delta U_1}{V_1}\text{(nonpolar)} + \frac{\Delta U_2}{V_1}\text{(polar)} = \beta_1^2 + \tau_1^2 \qquad \text{(III-9)}$$

where β_i is the non polar and τ_i the polar solubility parameter. The extended form of Scatchards equation according to Weimer and Prausnitz is:

$$G^E = \Phi_1 \Phi_2 (X_1V_1 + X_2V_2)\left[(\beta_1 - \beta_2)^2 + \tau_1^2 - 2\,\psi_{12}\right] \text{(III-10)}$$

where the energy term ψ_{12} was introduced to account for the induction effect between a polar and non polar molecule.

Helpinstill and Van Winke (11) further generalized this equation by introducing polar solubility parameters for the solute, in addition to those of the solvent, and by adding Flory Huggins correction terms.

$$G^E = \Phi_1 \Phi_2 (X_1V_1 + X_2V_2) \left[(\beta_1 - \beta_2)^2 + (\tau_1 - \tau_2)^2 - 2\psi_{12}\right]$$

$$- RT \left(X_1 \ln \frac{X_1}{\Phi_1} + X_2 \ln \frac{X_2}{\Phi_2}\right) \qquad \text{(III-11)}$$

Continuing with our search for a new correlation we substituted the volume fractions Φ_1 and Φ_2 by Wilson's "Local" Volume fractions, and following Tassios (38) made the substitution $\lambda_{ii} = - \Delta U_i$. With these changes the equation takes the form

$$G^E = \Phi'_1 \Phi'_2 (X_1V_1 + X_2V_2) \left[\frac{\lambda_{21} - \lambda_{11}}{V_1} + \frac{\lambda_{12} - \lambda_{22}}{V_2}\right]$$

$$- RT \left(X_1 \ln \frac{X_1}{\Phi'_1} - X_2 \ln \frac{X_2}{\Phi'_2}\right) \qquad \text{(III-12)}$$

where

$$\Phi'_1 = \frac{X_1V_1 e^{-(\lambda_{11}/RT)}}{X_1V_1 e^{-\lambda_{11}/RT} + X_2V_2 e^{-\lambda_{21}/RT}} \qquad \text{(III-13)}$$

$$\Phi'_2 = \frac{X_2V_2 e^{-(\lambda_{22}/RT)}}{X_1V_1 e^{-\lambda_{12}/RT} + X_2V_2 e^{-\lambda_{22}/RT}} \qquad \text{(III-14)}$$

$$\beta_1^2 + \tau_1^2 = - \frac{\lambda_{11}}{V_1} \qquad \text{(III-15)}$$

$$\beta_2^2 + \tau_2^2 = - \frac{\lambda_{22}}{V_2} \qquad \text{(III-16)}$$

and $$- 2\beta_1\beta_2 - 2\tau_1\tau_2 - 2\psi_{12} = \frac{\lambda_{21}}{V_1} + \frac{\lambda_{12}}{V_2} \qquad \text{(III-17)}$$

where $\lambda_{21} = \lambda_{12}$

Although according to Tassios suggestion $-\frac{\lambda_{11}}{V_1} = \frac{\Delta U_1}{V_1}$

and $-\frac{\lambda_{22}}{V_2} = \frac{\Delta U_2}{V_2}$, we chose to keep these as adjustable parameters. It should be noted that the last term in Eq. (III-12) is in effect Wilson's expression for G^E.

The activity coefficients are obtained by differentiations and are given by

$$\begin{aligned} RT \ln \gamma_1 = {} & \left[\frac{\lambda_{21}-\lambda_{11}}{V_1} + \frac{\lambda_{12}-\lambda_{22}}{V_2}\right]\Phi'_1\Phi'_2 V_1 \\ & - X_2(X_1V_1 + X_2V_2)\left[\frac{\lambda_{21}-\lambda_{11}}{V_1} + \frac{\lambda_{12}-\lambda_{22}}{V_2}\right]\left[\Phi'_1\frac{\partial\Phi'_2}{\partial X_2} + \Phi'_2\frac{\partial\Phi'_1}{\partial X_2}\right] \\ & - X_2RT\left[\frac{X_1}{\Phi'_1}\frac{\partial\Phi'_1}{\partial X_2} + \frac{X_2}{\Phi'_2}\frac{\partial\Phi'_2}{\partial X_2} - \frac{1}{X_2}\ln\frac{\Phi'_1}{X_1}\right] \qquad \text{(III-18)} \end{aligned}$$

$$RT \ln \gamma_2 = \left[\frac{\lambda_{21} - \lambda_{11}}{V_1} + \frac{\lambda_{12} - \lambda_{22}}{V_2} \right] \Phi'_1 \Phi'_2 V_2$$

$$- X_1 (X_1 V_1 + X_2 V_2) \left[\frac{\lambda_{21} - \lambda_{11}}{V_1} + \frac{\lambda_{12} - \lambda_{22}}{V_2} \right] \left(\Phi'_2 \frac{\partial \Phi'_1}{\partial X_1} + \Phi'_1 \frac{\partial \Phi'_2}{\partial X_1} \right)$$

$$- X_1 RT \left[\frac{X_2 \partial \Phi'_2}{\Phi'_2 \partial X_1} + \frac{X_1 \partial \Phi'_1}{\Phi'_1 \partial X_1} - \frac{1}{X_1} \ln \frac{\Phi'_2}{X_2} \right] \qquad \text{(III-19)}$$

where

$$\frac{\partial \Phi'_i}{\partial X_i} = \frac{\Phi'_i}{X_i} - \Phi'_i \left[\frac{\Phi'_i}{X_i} - \frac{1}{X_i \left(\frac{V_i}{V_j}\right) \exp \left(g_{ji} - g_{ii}\right)/RT + X_j} \right] \qquad \text{(III-20)}$$

and $$\frac{\partial \Phi_i}{\partial X_j} = - \frac{\partial \Phi_i}{\partial X_i} \qquad \text{(III-21)}$$

The data for several binary systems has been correlated with this equation. A summary of the results is presented in table II. A comparison with other equations is presented in table VI.

Unless otherwise specified, from here on the std. deviation is defined as follows

$$\text{Std. Dev.} = \sqrt{\frac{\left[\frac{\gamma_1 \text{cal} - \gamma_1 \text{obs}}{\gamma_1 \text{obs}}\right]^2 + \left[\frac{\gamma_2 \text{cal} - \gamma_2 \text{obs}}{\gamma_2 \text{obs}}\right]^2}{2n - 1}} \qquad \text{(III-7a)}$$

TABLE II

STANDARD DEVIATION OF CALCULATED ACTIVITY COEFFICIENTS WITH THE MODIFIED SCATCHARD-HILDEBRAND EQUATION

SYSTEM	STD. DEV.	$\lambda_{21} - \lambda_{11}$	$\lambda_{12} - \lambda_{22}$
Acetone-chloroform at 50°C.	0.0277	87.23	-166.98
Acetone-methanol at 50°C.	0.0337	-164.73	142.18
Acetone-methyl acetate at 50°C.	0.0314	172.72	-168.52
Acetone-toluene at 45°C.	0.0013	119.16	-101.90
Acetonitrile-toluene at 45°C.	0.0306	186.85	-205.89
Carbon tetrachloride-benzene at 760 mm. Hg.	0.0040	- 16.17	28.22
Chloroform-methanol at 50°C.	0.0295	-559.02	393.80
n-Heptane-toluene at 760 mm. Hg.	0.0439	-233.68	229.79
n-Heptane-toluene at 760 mm. Hg.	0.0403	207.04	-312.39
Methanol-benzene at 55°C.	0.0483	388.67	-526.71
Methanol-carbon tetrachloride at 55°C.	0.1286	411.58	-572.20
Methanol-n-heptane at 760 mm. Hg.	0.1447	298.88	-413.40
Methanol-toluene at 760 mm. Hg.	0.0585	346.53	-458.79
Methyl acetate-methanol at 50°C.	0.0258	-236.22	201.65
Methylethylketone-toluene at 760 mm. Hg.	0.0668	283.64	-482.81
Nitroethane-toluene at 45°C.	0.0110	187.99	-194.02
Nitromethane-carbon tetrachloride at 45°C.	0.0617	254.69	-225.68
1-Propanol-ethyl acetate at 60°C.	0.0225	197.92	-251.88
1-Propanol-water at 60°C.	0.0640	-221.73	195.23
2-Propanol-ethyl acetate at 60°C.	0.0236	233.16	-317.08

THE MODIFIED NRTL EQUATION

Another possibility of using the substitution $\Delta U_i = -\lambda_{ii}$ presents itself with the NRTL equation. In this case if we substitute g_{11} for $-\Delta U_1$ and g_{22} for $-\Delta U_2$ we are left with only two constants g_{12} and α .

Development of this modification requires the following substitution

$$g_{ii} = -\Delta U_i \qquad \text{(III-22)}$$

which may seem arbitrary. However, Renon and Prausnitz (29), implicitly made the substitution $\lambda_{jj} = g_{ii}$ when using Eq. (III-2) as the starting point in the derivation of the NRTL equation. Therefore Eq. (III-22) follows from this substitution and the substitution $\lambda_{ii} = -\Delta U_i$ which as already indicated was previously suggested by Tassios (38).

As the reader may verify from the results in table III, the equation fits the data with fairly good accuracy. These results are compared with those of other equations in table VI.

TABLE III

STANDARD DEVIATION OF CALCULATED ACTIVITY COEFFICIENTS WITH THE MODIFIED NRTL EQUATION

SYSTEM	STD. DEV.	G_{12}	α
Acetone-chloroform at 50°C.	0.0281	-6940.08	1.487
Acetone-methanol at 50°C.	0.0447	-6227.55	1.165
Acetone-methyl acetate at 50°C.	0.0312	-6861.18	-2.496
Acetone-toluene at 45°C.	0.0704	-6383.05	1.302
Acetonitrile-toluene at 45°C.	0.1420	-6618.33	1.030
Carbon tetrachloride-benzene at 760 mm. Hg.	0.0082	-6885.94	-9.528
Chloroform-methanol at 50°C.	0.0210	-6882.29	0.297
n-Heptane toluene at 760 mm. Hg.	0.0545	-6929.87	4.289
n-Heptane-toluene at 760 mm. Hg.	0.0477	-7367.67	3.775
Methanol-benzene at 55°C.	0.0237	-6969.65	0.276
Methanol-carbon tetrachloride at 55°C.	0.0836	-6653.82	0.297
Methanol-n-heptane at 760 mm. Hg.	0.0427	-6106.51	0.447
Methanol-toluene at 760 mm. Hg.	0.0136	-7092.97	0.489
Methylethylketone-n-heptane at 760 mm. Hg.	0.1153	-7146.36	0.975
Methylethylketone-toluene at 760 mm. Hg.	0.0421	-7577.25	2.422
Nitroethane-toluene at 45°C.	0.0083	-8277.58	0.241
1-Propanol-ethyl acetate at 60°C.	0.0696	-6707.95	1.349
1-Propanol-water at 60°C.	0.0745	-9015.76	0.567
2-Propanol-ethyl acetate at 60°C.	0.0839	-6612.82	1.395

STUDY OF THE VALUE OF ALPHA IN THE NRTL EQUATION

As previously mentioned Renon and Prausnitz (29) suggested a set of rules for evaluation of the parameter α in the NRTL equation. However, in following these rules one finds situations in which the rules are ambiguous or lack specificity. Examples of these are the binaries nitroethane-carbon tetrachloride and nitromethane-carbon tetrachloride. Although these systems are quite similar one finds that the recommended values of α are 0.3 and 0.47, respectively. Another case in point is the partially miscible system water-ethyl acetate for which Renon and Prausnitz (28) recommend $\alpha = 0.4$, even though a value of $\alpha = 0.2$ is generally recommended for these type of systems (27).

These type of difficulties present no problem when there is enough data and α can be curve fitted. However, when trying to predict vapor-liquid equilibrium from azeotropic or mutual solubility data, a fit of α is not possible and it becomes necessary to estimate its value. In view of these it was decided to study the effect of the value of α on the accuracy of the correlations. For this purpose 18 systems were chosen for study and a plot of α vs. the standard deviation of calculated activity coefficients* was made. For each system α was assigned values between -2.0 and +0.7, and the corresponding activity coefficients and standard deviations were calculated.

Results representative of the 18 systems studied are presented in Figs. (2) and (3). Fig. (4) is an extended study of the system methanol-benzene covering a range of α values from -10 to +10. Table IV shows how the std. deviation and the parameters A_{21} and A_{12} change as a function

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* As defined in Eq. III-7

of α for two different systems.

It can be seen that for some systems the equation is rather insensitive to the value of α, while for others two minimas are observed. A sharp one, dependent on the nature of the system, in the range of 0.2 to 0.5, and a gradually approached one, rather independent of the nature of the system, in the vicinity of $\alpha = -1$. Extension of this results to a number of other systems has shown that a value of $\alpha = -1$ consistently yields accuracies comparable to those obtained with α set at the values recommended by Renon. Furthermore the new value of α predicts phase immiscibility with better accuracy than the recommended value of 0.2.

This suggests that a true two parameter expression may be obtained by substituting α by -1. A total of 55 binary and 18 ternary systems, seven of them partially miscible, have been studied. In all cases the single value of $\alpha = -1$ yielded excellent results.

However, according to Renon, α was introduced into Wilson's expression for local mole fractions as a measure of the non-randomness of the solution, and as such its lower value should be zero, corresponding to the case of an ideal solution. Furthermore from comparison with Guggenheims Quasichemical theory (9), Renon concluded that α was the equivalent of $1/Z$, where Z is the coordination number. Therefore, the expected value of α was of the order of 0.1 to 0.3. From these observations it is concluded that a negative value of α, as defined by Renon, is meaningless, therefore a new derivation of the equation becomes necessary.

FIGURE 2. STANDARD DEVIATION VS. ALPHA.

● METHANOL-TOLUENE AT 760 mm. Hg.

⧳ METHANOL-BENZENE AT 55°C.

-●- ETHANOL-BENZENE AT 400 mm. Hg.

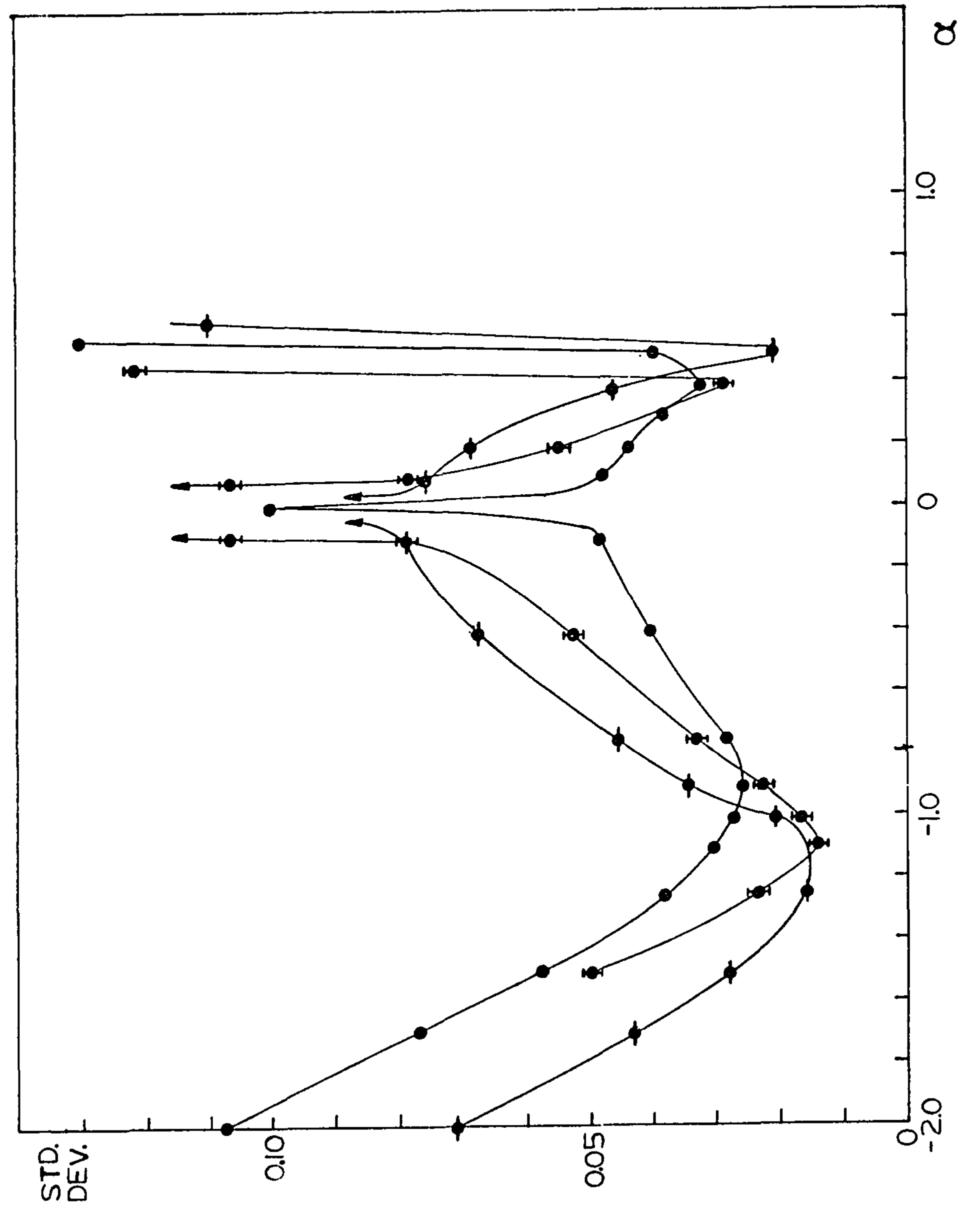

STD.
DEV.
0.10
0.05
0
-2.0
-1.0
0
1.0
α

FIGURE 3. STANDARD DEVIATION VS. ALPHA.

● METHANOL-BENZENE AT 35°C.

Φ CARBON TETRACHLORIDE-NITROMETHANE AT 45°C.

■ METHANOL-HEPTANE AT 760 mm. Hg.

○ ETHANOL-BENZENE AT 760 mm. Hg.

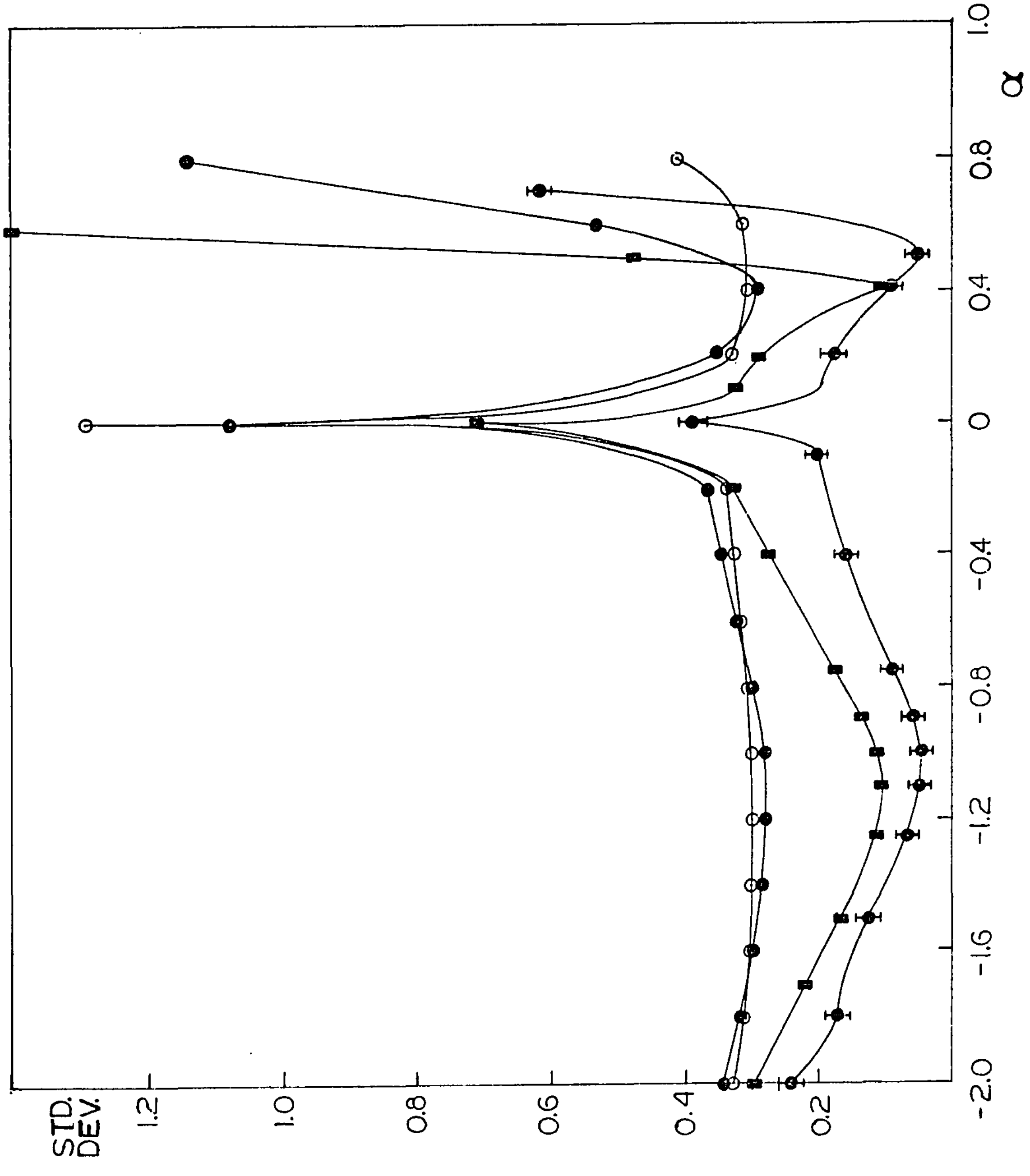
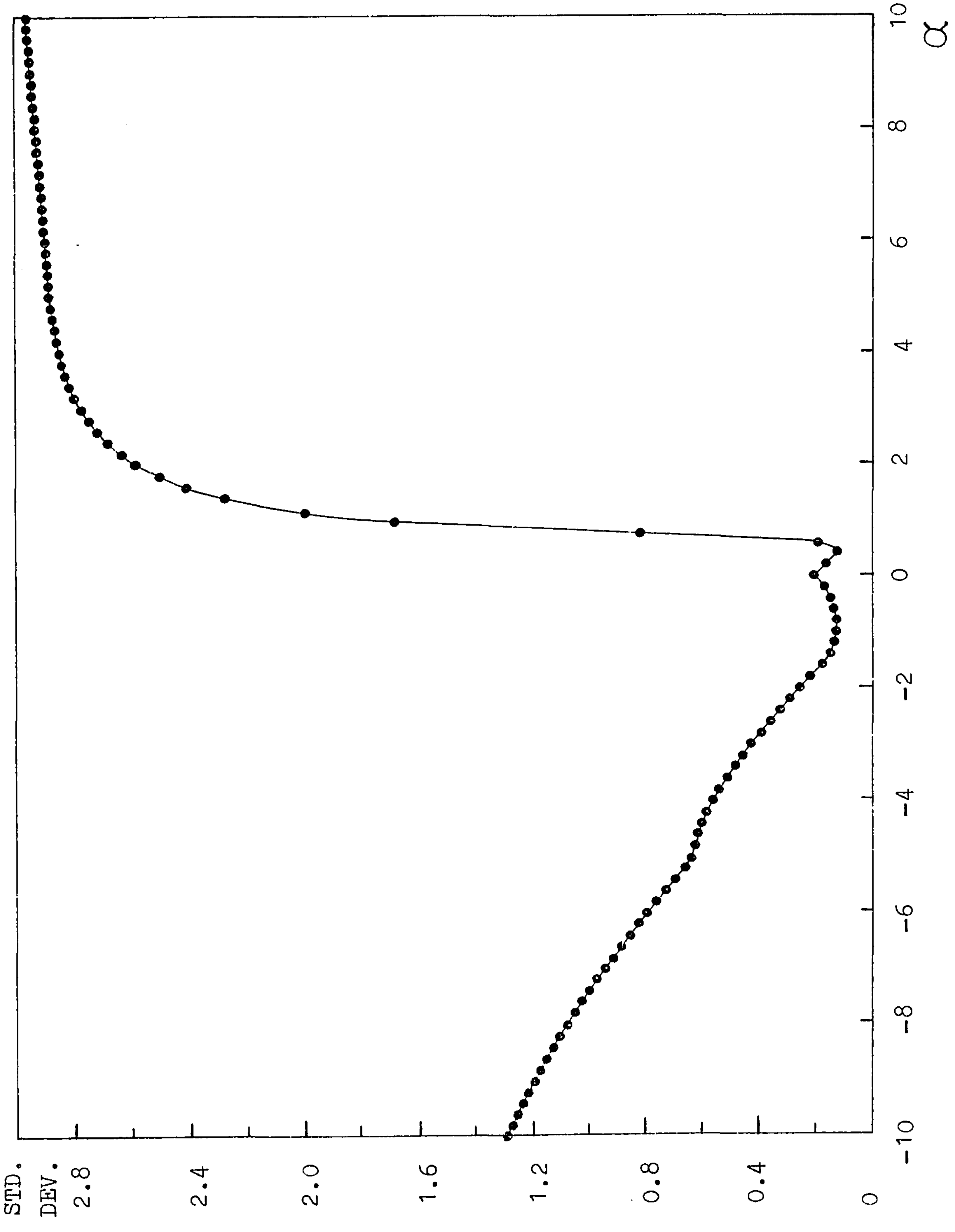

STD. DEV.
1.2
1.0
0.8
0.6
0.4
0.2
-2.0
-1.6
-1.2
-0.8
-0.4
0
0.4
0.8
1.0
α

FIGURE 4. STANDARD DEVIATION VS. ALPHA.
METHANOL-BENZENE AT 55°C.


STD.
DEV.
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2.4
2.0
1.6
1.2
0.8
0.4
0
−10
−8
−6
−4
−2
0
2
4
6
8
10
α

TABLE IV

VARIATION OF THE PARAMETERS A_{21} AND A_{12} AS A FUNCTION OF α

α	Benzene-n-heptane at 400 mm. Hg.			Methanol-n-heptane at 760 mm. Hg.		
	A_{21}	A_{12}	STD. DEV.	A_{21}	A_{12}	STD. DEV.
-2.0	200.57	53.22	0.0040	445.68	538.39	0.2943
-1.7	216.31	40.22	0.0038	481.65	533.13	0.2168
-1.5	229.94	27.81	0.0038	509.41	533.60	0.1632
-1.25	252.54	5.69	0.0038	550.76	536.73	0.1102
-1.10	270.87	-13.56	0.0038	580.73	538.73	0.1032
-1.00	286.09	-30.19	0.0038	603.64	539.52	0.1139
-0.90	204.61	-51.02	0.0039	629.67	539.60	0.1342
-0.75	342.00	-94.85	0.0039	676.56	536.43	0.1745
-0.40	557.68	-373.85	0.0045	865.23	474.91	0.2761
-0.10	1307.64	-1224.70	0.0155	1693.21	-281.20	0.3340
0.00	392.53	-72.58	0.0340	1055.82	695.11	0.7171
0.10	-973.61	1534.35	0.0021	-15.43	1924.53	0.3237
0.20	-454.02	928.16	0.0025	508.95	1488.21	0.2925
0.40	-161.72	578.36	0.0027	1130.01	1456.93	0.1033
0.50	-98.28	515.88	0.0027	1587.77	1790.05	0.4796
0.70	-21.45	434.53	0.0028	1071.23	1594.97	2.2673

THE "LOCAL EFFECTIVE MOLE FRACTION" MODEL

As previously indicated, Wilson (43) suggested the following relationship between the local mole fractions of component 2 and component 1 around a molecule of component 1

$$\frac{X_{21}}{X_{11}} = \frac{X_2}{X_1} \exp\left[-(\lambda_{21} - \lambda_{11})/RT\right] \qquad \text{(III-2)}$$

where

X_{21} and X_{11} are local compositions

X_2 and X_1 are average mixture compositions

and λ_{21} and λ_{11} are parameters proportional to the energies of interaction in 2-1 and 1-1 pairs respectively

This relation between local mole fractions and energies of interaction is at the very least qualitatively correct as can be seen by considering, as an example, a mixture with positive deviations from Raoults law. In this case the 1–2 interaction is weaker than the 1–1 interaction, i.e. $|\lambda_{21}| < |\lambda_{11}|$. Hence one would expect that a given molecule would be preferentially surrounded by molecules of its own kind, therefore $(X_{21}/X_{11}) < (X_2/X_1)$. The same conclusion could be reached from equation (III-2). Since both λ_{11} and λ_{21} are negative we have that

$$\lambda_{21} - \lambda_{11} > 0$$

and introducing this result into equation (III-2)

$$\frac{X_{21}}{X_{11}} < \frac{X_2}{X_1} \qquad \text{(III-23)}$$

Because of the existence of physical and chemical effects, Prausnitz and Anderson (24) suggested that the molecules in the cell are not equally free. We now propose to describe the macroscopic properties of the liquid in terms of the free molecules in the cell with mole fractions, referred to hereafter as "local effective mole fractions", X'_{21} and X'_{11} . Returning to the above example even though X_{21}/X_{11} is less than X_2/X_1, now we have that X'_{21}/X'_{11} will be larger than X_2/X_1. Taking this into consideration we now write for the local effective mole fractions

$$\frac{X'_{21}}{X'_{11}} = \frac{X_2}{X_1} \exp\left[(\lambda'_{21} - \lambda'_{11})/RT\right] \qquad \text{(III-24)}$$

and

$$X'_{21} + X'_{11} = 1 \qquad \text{(III-25)}$$

where λ'_{21} and λ'_{11} are parameters proportional to the interaction energies in 2–1 and 1–1 pairs but not the same as λ_{21} and λ_{11} because they refer to a cell described in terms of local effective mole fractions. It should be noticed that equation (III-24) is of the same type as Eq. (III-2) but the minus sign does not appear in the exponential. Following Tassios' (38) suggestion that λ_{ii} can be successfully approximated by the energy of vaporization and by similarity to Kincaid, Eyring and Stearn's (16) relation between free energy of activation and internal energy, equation (III-24) can be written as follows

$$\frac{X'_{21}}{X'_{11}} = \frac{X_2}{X_1} \exp\left[\alpha (g'_{21} - g'_{11})/RT\right] \qquad \text{(III-26)}$$

where g'_{ii} is the residual Gibbs free energy (with the cell described in terms of local effective mole fractions) and α' a proportionality constant between λ_{ij} and g_{ij}.

An alternative development of Eq.(III-26) is presented next for a better understanding of the quantities involved. Since the local effective mole fractions refer to the free molecules, and fugacities can be interpreted as "escaping tendencies", it is reasonable to postulate that

$$\frac{x'_{21}}{x'_{11}} = \frac{f_{21}}{f_{11}} = \frac{x_{21}\,\gamma_{21}\,f^{o}_{2}}{x_{11}\,\gamma_{11}\,f^{o}_{1}} \qquad \text{(III-27)}$$

where f_{21} and f_{11} are the fugacities of components 2 and 1 in a type 1 cell

γ_{21} and γ_{11} are the activity coefficients of components 2 and 1 in a type 1 cell

f^{o}_{2} and f^{o}_{1} are reference fugacities.

But

$$\ln\frac{\gamma_{21}f^{o}_{2}}{\gamma_{11}f^{o}_{1}} = \frac{(\bar{G}^{E}_{21} + G^{o}_{2} - G^{*}_{2})}{RT} - \frac{(\bar{G}^{E}_{11} + G^{o}_{1} - G^{*}_{1})}{RT}$$

(III-28)

$$= \frac{\bar{G}^{R}_{21} - \bar{G}^{R}_{11}}{RT} = \frac{(\partial G^{R}_{1}/\partial x_{21})}{RT}$$

where G^E_{21} and G^E_{11} are partial molal excess free energies of components 2 and 1 in a type 1 cell

G°_2 and G°_1 are Gibbs energies of pure components 2 and 1

G^*_2 and G^*_1 are Gibbs energies of pure components 2 and 1 in the ideal gas state.

G^R_{21} and G^R_{11} are partial molal residual Gibbs energies of components 2 and 1 in a type 1 cell.

G^R_1 is the total residual Gibbs energy of a type 1 cell.

Now according to Renon the residual Gibbs energies for types 1 and 2 cells are given by

$$G^R_1 = X_{11}g_{11} + X_{21}g_{21} \qquad \text{(III-29)}$$

$$G^R_2 = X_{22}g_{22} + X_{12}g_{12}$$

Similarly, in terms of local effective mole fractions, X'_{21} and X'_{11}, we could write

$$G^R_1 = X'_{11}g'_{11} + X'_{21}g'_{21}$$

$$G^R_2 = X'_{22}g'_{22} + X'_{12}g'_{12} \qquad \text{(III-30)}$$

If we now introduce Eqs. (III-2), (III-28), (III-29) into (III-27) we get

$$\frac{X'_{21}}{X'_{11}} = \frac{X_2}{X_1} \exp \; (g_{21} - g_{11})/RT - (\lambda_{21} - \lambda_{11})/RT \qquad \text{(III-31)}$$

and since the exponent in (III-31) is independent of composition, we could find a constant a' such that

$$(g_{21} - g_{11}) - (\lambda_{21} - \lambda_{11}) = a' \, (g'_{21} - g'_{11}) \qquad \text{(III-32)}$$

Finally introducing (III-32) into (III-31) we obtain

$$\frac{X'_{21}}{X'_{11}} = \frac{X_2}{X_1} \exp a' \, (g'_{21} - g'_{11})/RT \qquad \text{(III-33)}$$

A similar argument for a type two cell would give

$$\frac{X'_{12}}{X'_{22}} = \frac{X_1}{X_2} \exp a' \, (g'_{12} - g'_{22})/RT \qquad \text{(III-34)}$$

From now on we can parallel Renon's (29) development in introducing Scott's (33) two liquid theory, except that we will do so in terms of local effective mole fractions instead of local mole fractions.

According to Scott the actual value of G^R will be the average obtained by considering two liquids, one made of cells of type 1 and the other made of cells of type 2, that is

$$G^R = X_1(X'_{11}\,g'_{11} + X'_{21}\,g'_{21}) + X_2(X'_{22}\,g'_{22} + X'_{12}\,g'_{12}) \qquad \text{(III-35)}$$

And subtracting now the residual free energy corresponding to the pure components we obtain an expression for G^E that is

$$G^E = X_1X'_{21}\,(g'_{21} - g'_{11}) + X_2X'_{12}\,(g'_{12} - g'_{22}) \qquad \text{(III-36)}$$

Substitution of X'_{21} and X'_{12} from equations (III-33) and (III-34) yields

$$\frac{G^E}{RT} = \frac{X_1X_2}{RT}\left[\frac{(g'_{21} - g'_{11}) \exp \alpha'(g'_{21} - g'_{11})/RT}{X_1 + X_2 \exp \alpha'(g'_{21} - g'_{11})/RT} + \frac{(g'_{12} - g'_{22}) \exp \alpha'(g'_{12} - g'_{22})/RT}{X_2 + X_1 \exp \alpha'(g'_{12} - g'_{22})/RT}\right] \qquad \text{(III-37)}$$

Equation (III-37) is of the same form as equation (III-5) but the minus sign does not appear in the exponent. Furthermore, α does not represent a measure of the non-randomness of the solution, as is the case with the NRTL equation, but a proportionality constant in equation (III-32). If now α is substituted by +1 and $(g'_{21} - g'_{11})$ and $(g'_{12} - g'_{22})$ by A_{21} and A_{12} respectively, the following equation, hereafter referred to as the Local Effective Mole Fraction Equation (LEMF), is obtained.

$$\frac{G^E}{RT} = \frac{X_1X_2}{RT}\left[\frac{(A_{21} \exp (A_{21}/RT)}{X_1 + X_2 \exp (A_{21}/RT)} + \frac{A_{12} \exp (A_{12}/RT)}{X_2 + X_1 \exp (A_{12}/RT)}\right] \qquad \text{(III-38)}$$

The activity coefficients are obtained from (III-38) by differentiation, and are given by

$$\ln \gamma_1 = \frac{X_2^2}{RT}\left[\frac{A_{21} \exp (2A_{21}/RT)}{X_1 + X_2 \exp (A_{21}/RT)^{2}} + \right.$$

$$\left.\frac{A_{12} \exp (A_{12}/RT)}{X_2 + X_1 \exp (A_{12}/RT)^{2}}\right] \qquad \text{(III-39)}$$

$$\ln \gamma_2 = \frac{X_1^2}{RT}\left[\frac{A_{12} \exp (2A_{12}/RT)}{X_2 + X_1 \exp (A_{12}/RT)^{2}} + \right.$$

$$\left.\frac{A_{21} \exp (A_{21}/RT)}{X_1 + X_2 \exp (A_{21}/RT)^{2}}\right] \qquad \text{(III-40)}$$

Results obtained in correlating vapor-liquid equilibrium with the above equations are compared to those obtained with the NRTL equation in Table V.

It can be seen that the LEMF equation correlates binary miscible data with equal or better accuracy than the NRTL equation.

TABLE V

STANDARD DEVIATIONS OF CALCULATED ACTIVITY COEFFICIENTS WITH THE LEMF AND NRTL EQUATIONS

	DATA POINTS	LEMF EQUATION			NRTL EQUATION			
		A_{21}	A_{12}	STD. DEV.	$G_{21}-G_{11}$	$G_{12}-G_{22}$	α	STD.DEV.
Acetone-carbon tetrachloride at 50°C.	17	127.36	314.53	0.0230	657.95	-22.50	0.30	0.0235
Acetone-chloroform at 35.17°C.	20	-489.14	-258.40	0.0342	79.95	-526.02	0.30	0.0284
Acetone-chloroform at 50°C.	10	-399.92	-225.34	0.0282	36.85	-453.04	0.30	0.0277
Acetone-methanol at 50°C.	9	138.17	180.68	0.0323	251.62	125.85	0.30	0.0329
Acetone-methanol at 100°C.	14	498.70	-426.99	0.0601	-456.70	1089.65	0.30	0.0615
Acetone-methyl acetate at 50°C.	20	-180.45	203.59	0.0314	463.53	-310.73	0.30	0.0314
Acetone-toluene at 45°C.	20	187.21	177.36	0.0024	205.38	237.57	0.30	0.0003
Acetone-water at 25°C.	13	390.31	397.39	0.0759	802.35	432.02	0.30	0.0733
Acetone-water at 100°C.	12	285.86	617.96	0.0316	1474.95	174.26	0.30	0.0329
Acetone-water at 150°C.	12	192.52	709.91	0.0526	1780.58	-15.44	0.30	0.0518
Acetone-water at 200°C.	12	26.15	776.37	0.0627	2070.46	-283.14	0.30	0.0609
Acetonitrile-toluene at 45°C.	18	331.41	282.79	0.0109	358.59	507.90	0.30	0.0221
Benzene-n-heptane at 400 mm. Hg.	9	289.53	-35.37	0.0032	-266.97	710.82	0.30	0.0023
Butanol-water at 760 mm. Hg.	12	175.71	829.97	0.0749	2686.89	94.76	0.30	0.0754
Carbon tetrachloride-benzene at 49.99°C.	16	-250.73	249.11	0.0128	373.95	-233.49	0.30	0.0129
Carbon tetrachloride-benzene at 760 mm. Hg.	9	30.81	41.32	0.0040	56.74	18.06	0.30	0.0040
Chloroform-benzene at 760 mm. Hg.	14	- 49.93	-108.68	0.0271	823.30	-713.47	0.30	0.0289
Chloroform-ethyl acetate at 760 mm. Hg.	18	-230.62	-614.98	0.0141	-772.40	379.95	0.30	0.0095
Chloroform-methanol at 50°C.	9	553.01	38.73	0.0224	-167.43	1496.33	0.30	0.0210
Chloroform-methanol at 760 mm. Hg.	20	521.77	78.54	0.0206	-139.45	1358.98	0.30	0.0193

TABLE V (continued)

STANDARD DEVIATIONS OF CALCULATED ACTIVITY COEFFICIENTS WITH THE LEMF AND NRTL EQUATIONS

	DATA POINTS	LEMF EQUATION			NRTL EQUATION			
		A_{21}	A_{12}	STD. DEV.	$G_{21}-G_{11}$	$G_{12}-G_{22}$	α	STD. DEV.
Cyclohexane-n-heptane at 25°C.	11	137.43	- 94.63	0.0097	-205.71	306.45	0.30	0.0097
Ethanol-benzene at 400 mm. Hg.	10	332.34	503.89	0.0115	1052.08	543.79	0.47	0.0123
Ethanol-benzene at 40°C.	11	293.11	536.33	0.0450	1236.42	515.45	0.47	0.0435
Ethanol-ethyl acetate at 760 mm. Hg.	9	256.87	233.26	0.0143	248.94	370.78	0.30	0.0140
Ethanol-n-heptane at 400 mm. Hg.	16	504.48	550.41	0.0460	1345.51	1196.81	0.47	0.0314
Ethanol-water at 50 mm. Hg.	19	254.71	296.92	0.0965	483.55	279.26	0.30	0.0934
Ethanol-water at 380 mm. Hg.	20	41.15	527.03	0.0577	1341.39	-175.65	0.30	0.0584
Ethanol-water ar 760 mm. Hg.	20	64.30	544.80	0.0154	1391.87	-177.37	0.30	0.0166
Ethanol-water at 760 mm. Hg.	10	76.39	544.27	0.0175	1360.70	-147.58	0.30	0.0188
n-Heptane-toluene at 760 mm. Hg.	19	135.82	84.47	0.0355	29.53	217.61	0.30	0.0357
Methanol-benzene at 55°C.	5	368.37	539.97	0.0073	1193.04	671.37	0.47	0.0073
Methanol-benzene at 55°C.	9	380.38	542.49	0.0172	1204.92	709.72	0.47	0.0172
Methanol-carbon tetrachloride at 55°C.	9	401.21	571.97	0.0888	1356.85	812.98	0.47	0.0868
Methanol-carbon tetrachloride at 55°C.	6	375.79	615.30	0.0593	1545.80	835.60	0.47	0.0469
Methanol-ethanol at 760 mm. Hg.	12	-582.62	266.53	0.0416	121.25	-134.45	0.30	0.0508
Methanol-ethyl acetate at 760 mm. Hg.	17	268.04	285.01	0.0185	388.80	336.97	0.30	0.0217
Methanol-n-heptane at 760 mm. Hg.	7	592.14	559.57	0.0380	1691.48	1660.08	0.47	0.0426
Methanol-toluene at 760 mm. Hg.	6	441.34	534.35	0.0134	1128.88	855.90	0.47	0.0150
Methanol-toluene at 760 mm. Hg.	14	493.14	468.79	0.1346	863.20	1021.21	0.47	0.1351
Methanol-water at 760 mm. Hg	12	-12.53	372.55	0.0077	845.65	-223.06	0.30	0.0083
Methanol-water at 100°C.	15	-88.33	398.97	0.0538	986.76	-344.91	0.30	0.0537
Methyl acetate-benzene at 760 mm. Hg.	12	54.84	135.41	0.0266	216.89	- 0.12	0.30	0.0268

TABLE V (continued)

STANDARD DEVIATIONS OF CALCULATED ACTIVITY COEFFICIENTS WITH THE LEMF AND NRTL EQUATIONS

	DATA POINTS	LEMF EQUATION			NRTL EQUATION			
		A_{21}	A_{12}	STD. DEV.	$G_{21}-G_{11}$	$G_{12}-G_{22}$	α	STD. DEV.
Methyl acetate-chloroform at 760 mm. Hg.	15	-453.28	-132.10	0.0177	456.34	-719.80	0.30	0.0155
Methyl acetate-methanol at 50°C.	15	294.44	246.58	0.0178	295.53	431.44	0.30	0.0205
Methylethylketone-n-heptane at 760 mm. Hg.	17	280.36	412.37	0.1259	734.81	267.62	0.30	0.1300
Methylethylketone-toluene at 760 mm. Hg.	20	125.24	149.14	0.0478	189.91	121.60	0.30	0.0481
Nitroethane-toluene at 45°C.	12	148.47	266.50	0.0054	495.35	52.71	0.30	0.0081
Nitromethane-carbon tetrachloride at 45°C.	12	421.23	513.27	0.0207	1130.90	841.07	0.47	0.0205
1-Propanol-benzene at 45°C.	11	232.45	505.26	0.0232	1088.21	346.01	0.47	0.0238
1-Propanol-ethyl acetate at 60°C.	13	185.56	212.87	0.0241	285.96	201.30	0.30	0.0235
1-Propanol-water at 40°C.	12	124.59	620.76	0.0889	1735.53	-2.44	0.30	0.0890
1-Propanol-water at 60°C.	18	137.37	639.43	0.0544	1793.43	-20.00	0.30	0.0589
2-Propanol-ethyl acetate at 60°C.	19	119.49	269.28	0.0249	513.15	1.65	0.30	0.0245

SUMMARY OF RESULTS FOR BINARY MISCIBLE SYSTEMS

Table VI is a partial summary of the results obtained with the local mole fraction equations presented in this work. For comparison purposes, results obtained with the Wilson and NRTL equations are also included. The results indicate that of the modified equations, the LEMF gives the best representation of the data. Furthermore, in no case the results can be considered poor as is the case with the modified Scatchard-Hildebrand and modified NRTL equations for the systems methanol-n-heptane and acetonitrile-toluene, respectively.

Complete testing of any of these equations requires a considerable amount of effort; consequently, at this time it is convenient to choose for further study that equation with the best probability of success. The LEMF equation seems to be the candidate of choice since it gives better results for binary miscible systems, is simpler, and requires no pure component volume or energy of vaporization data for evaluation of the parameters.

A comparative study of the performance of the LEMF and NRTL equations in describing immiscible behavior and predicting multi-component phase equilibrium is the subject of the following chapters.

TABLE VI

COMPARISON OF THE LOCAL MOLE FRACTION EQUATIONS

	-- STANDARD DEVIATION --				
	MODIFIED SCATCHARD HILDEBRAND	MODIFIED NRTL	LEMF	NRTL	WILSON
Acetone-chloroform at 50°C.	0.0277	0.0281	0.0282	0.0277	0.0278
Acetone-methanol at 50°C.	0.0337	0.0447	0.0323	0.0329	0.0327
Acetone-methyl acetate at 50°C.	0.0314	0.0312	0.0314	0.0314	0.0312
Acetone-toluene at 45°C.	0.0013	0.0704	0.0024	0.0003	0.0011
Acetonitrile-toluene at 45°C.	0.0306	0.1420	0.0109	0.0221	0.0150
Carbon tetrachloride-benzene at 760 mm. Hg.	0.0040	0.0082	0.0040	0.0040	0.0040
Chloroform-methanol at 50°C.	0.0295	0.0210	0.0224	0.0210	0.0293
n-Heptane-toluene at 760 mm. Hg.	0.0403	0.0477	0.0355	0.0357	0.0357
Methanol-benzene at 55°C.	0.0483	0.0237	0.0073	0.0073	0.0076
Methanol-carbon tetrachloride at 55°C.	0.1286	0.0836	0.0593	0.0469	0.0777
Methanol-n-heptane at 760 mm. Hg.	0.1447	0.0427	0.0380	0.0426	0.0177
Methanol-toluene at 760 mm. Hg.	0.0585	0.0136	0.0134	0.0150	0.0148
Methylethylketone-toluene at 760 mm. Hg.	0.0668	0.0421	0.0478	0.0481	0.0478
Nitroethane-toluene at 45°C.	0.0110	0.0083	0.0054	0.0081	0.0063
1-Propanol-ethyl acetate at 60°C.	0.0225	0.0696	0.0241	0.0235	0.0237
1-Propanol-water at 60°C.	0.0640	0.0745	0.0544	0.0589	0.0588
2-Propanol-ethyl acetate at 60°C.	0.0236	0.0839	0.0249	0.0245	0.0247

– IV –

PARTIALLY MISCIBLE BINARY SYSTEMS

Any spontaneous mixing process carried out at constant temperature and pressure is irreversible and as such is accompanied by a decrease in free energy. Consequently the mixture will be at a state corresponding to a minimum value of the free energy of mixing G^M. Considering now a partially miscible binary system, if we plot the free energy of mixing vs. composition assuming complete miscibility, we will find that the resulting curve presents an inflexion point (Fig.5). Now, a tangent to the curve such as line AB, represents a state of lower free energy than that given by the curve, that is the free energy corresponding to a mixture of two phases of compositions X' and X'' . Therefore in this interval, the system, seeking a configuration of minimum free energy will split into two phases of compositions X' and X''.

Mathematically speaking, we would say that the condition for immiscibility is that

$$\frac{\partial^2 G^M}{\partial X^2} = 0 \qquad \text{(IV-1)}$$

for at least one value of X in the interval 0 to 1.0. Introducing the equation for G^M from Eqs. (II-31) and (III-38) we obtain

$$\frac{\partial^2}{\partial X^2}\left[\frac{G^M}{RT}\right] = \frac{\exp\ (\ 2A_{21}/RT)}{\left[X_1 + X_2 \exp\ (A_{21}/RT)\right]^2}\left[\frac{2A_{21}}{X_1 + X_2 \exp\ (A_{21}/RT)}\right] +$$

$$\frac{\exp\ (2A_{12}/RT)}{\left[X_2 + X_1 \exp\ (A_{12}/RT)\right]^2}\left[\frac{2A_{12}}{X_2 + X_1 \exp\ (A_{12}/RT)}\right] -$$

$$\frac{1}{X_1} - \frac{1}{X_2} = 0 \qquad \text{(IV-2)}$$

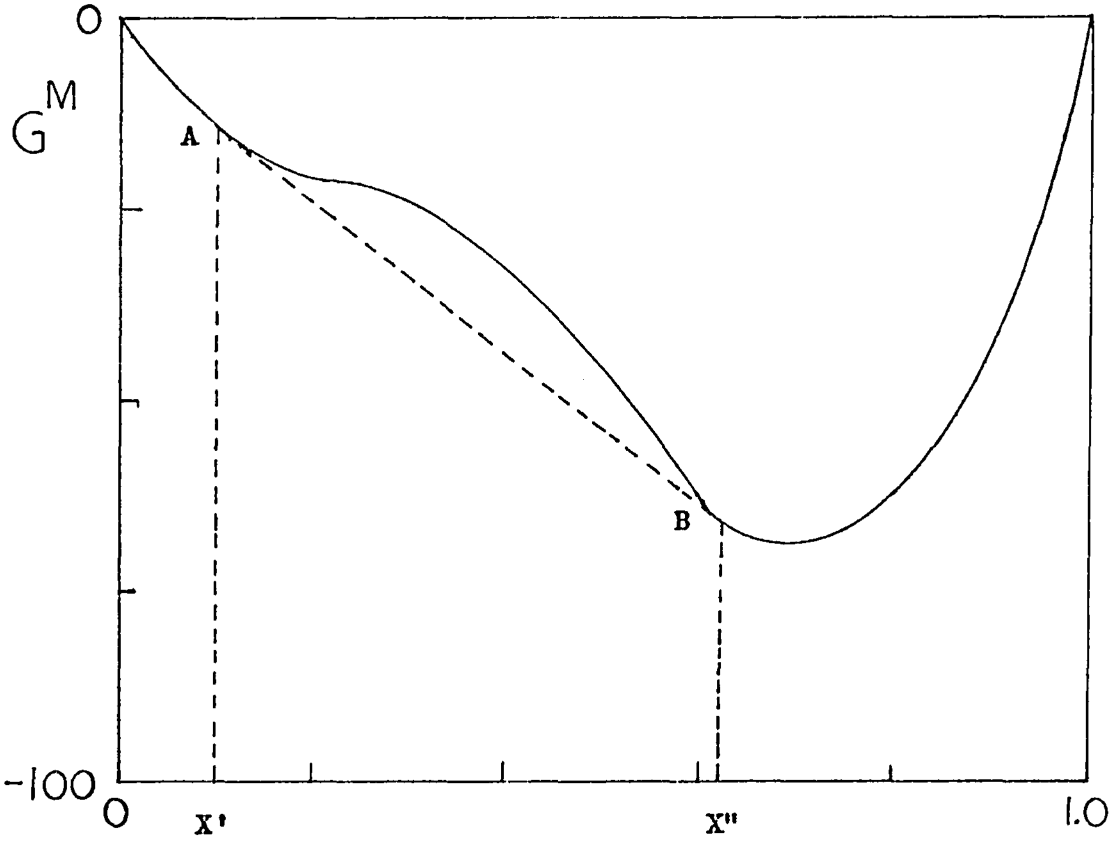


FIG. 5. FREE ENERGY OF MIXING VS. COMPOSITION FOR A PARTIALLY MISCIBLE SYSTEM.

The preceding equation can be satisfied if at least one of the constants A_{ij} is positive. What remains to be seen is if this happens in the interval 0 to 1 and what are the limits of immiscibility predicted.

In order to test the performance of the LEMF equation, several systems were chosen for study. Our purpose was first to verify if the equation would predict immiscibility from vapor-liquid equilibrium data in the miscible region and conversely to predict V.-L. equilibrium in the miscible region from mutual solubility data. A comparison with the NRTL equation was also sought.

The constants for the NRTL and LEMF equations were calculated from the available vapor-liquid equilibrium points for these systems and then were employed in calculating free energies of mixing as a function of composition. The results are presented in Figure (6) and Table VII. It can be seen that both equations predict binary immiscibility with about the same accuracy.

Turning to prediction of vapor-liquid equilibrium from mutual solubility data, the constants for the LEMF and NRTL equations were obtained from the requirements:

$$X_1' \gamma_1' = X_1'' \gamma''_1$$

$$X_2' \gamma_2' = X_2'' \gamma''_2 \qquad \text{(IV-3)}$$

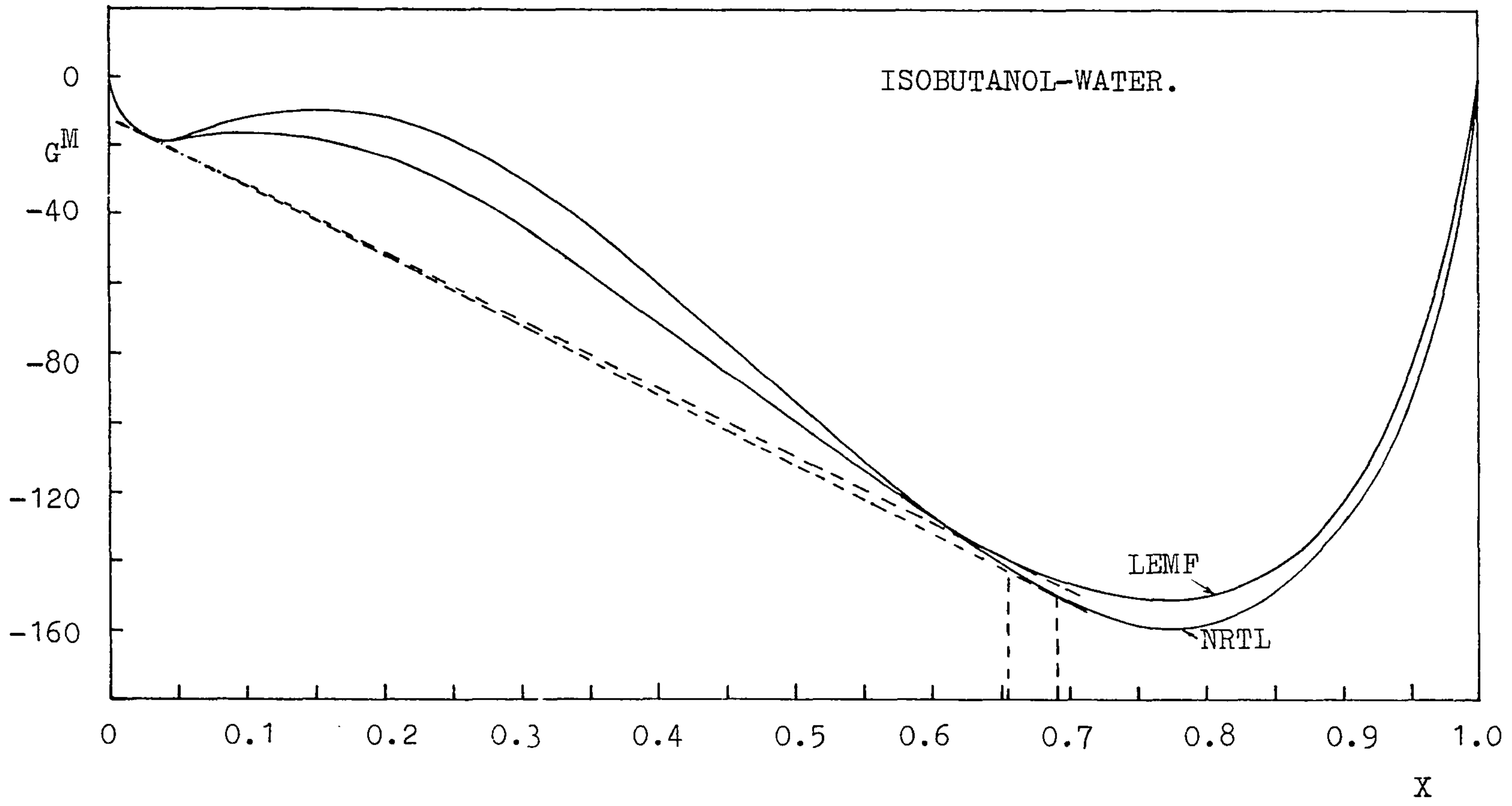


FIG. 6 PREDICTION OF LIQUID-LIQUID EQUILIBRIUM FROM VAPOR-LIQUID EQUILIBRIUM.

TABLE VII

PREDICTION OF MUTUAL SOLUBILITIES FROM VAPOR-LIQUID EQUILIBRIUM DATA.

SYSTEM	EXPERIMENTAL V.-L. EQUILIBRIUM DATA			PREDICTED MUTUAL SOLUBILITIES				EXPERIMENTAL MUTUAL SOLUBILITIES		TEMP. °C
	DATA POINTS	COMPOSITION RANGE X_1	TEMP. RANGE °C	LEMF		NRTL				
				X_1'	X_1''	X_1'	X_1''	X_1'	X_1''	
ETHYL ACETATE-WATER	3	0.94-0.976	74.1-75.8	0.05	0.68	0.35	0.72	0.014	0.768	70
n-BUTANOL-WATER	12	0.015-0.961	93.0-111.5	0.02	0.55	0.02	0.61	0.021	0.364	90
ISOBUTANOL-WATER	9	0.010-0.938	90.9-99.0	0.025	0.65	0.025	0.69	0.021	0.402	90
WATER-ANILINE	4	0.025-0.200	152-105	0.26	0.98	0.27	0.98	0.372	0.985	100
PROPYLENE OXIDE-WATER	13	0.046-0.925	50.8-34.9	0.13	0.55	0.135	0.80	0.166	0.625	36.3

Typical results are presented in Fig. (7) and Table VIII. Both equations seem to deviate most from experimental data at the extremes of the concentration range. This, however, should be expected, since any inaccuracy inherent to the equations will manifest most as we move away from the points to which the parameters were fitted. In addition, the fact that in this region experimental errors are large could contribute to the magnitude of the deviations.

With regard to temperature, any effect that it may have in the accuracy of the correlations can be disregarded, since in most cases, the temperature range considered is rather small.

It should be noted that activity coefficients obtained with the LEMF equation are closer to experimental values than those given by the NRTL equation.

PREDICTION OF VAPOR-LIQUID EQUILIBRIUM FROM MUTUAL SOLUBILITY DATA.

SYSTEM PROPYLENE OXIDE-WATER.

● EXPERIMENTAL
○ L.E.M.F. EQUATION.
▮ N.R.T.L. EQUATION.

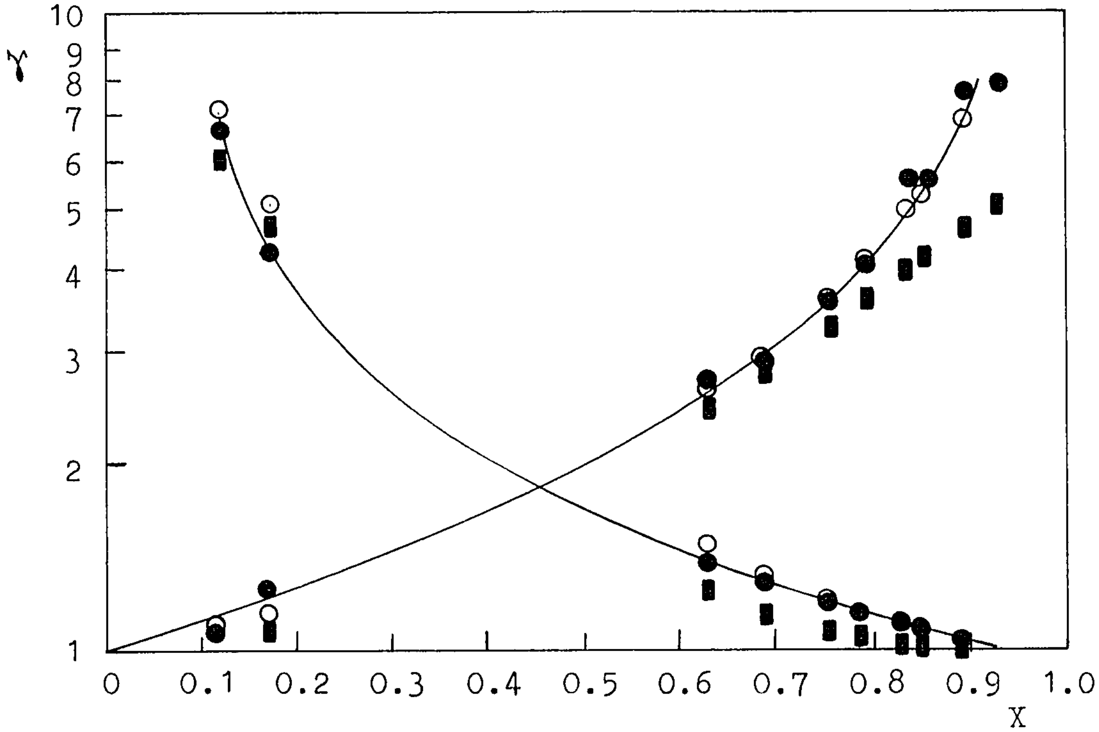


FIG. 7

TABLE VIII

PREDICTION OF V-L EQUILIBRIUM FROM MUTUAL SOLUBILITY DATA

			$\alpha = 0.2$	$\alpha = -1$		$\alpha = 0.2$	$\alpha = -1$	
	X	γ_1 EXP.	γ_1 CALC.	γ_1 CALC.	γ_2 EXP.	γ_2 CALC.	γ_2 CALC.	T
1-BUTANOL WATER	0.015	37.14	20.61	27.55	1.00	1.00	1.00	93.4
	0.020	30.69	18.23	24.56	0.99	1.00	1.00	93.0
	0.025	25.26	16.20	21.95	1.00	1.01	1.01	92.7
	0.423	1.50	0.98	1.27	1.68	1.60	1.69	92.8
	0.448	1.41	0.96	1.22	1.75	1.62	1.73	92.9
	0.494	1.30	0.95	1.16	1.85	1.65	1.81	93.4
	0.504	1.29	0.95	1.15	1.87	1.66	1.82	93.5
	0.695	1.07	0.96	1.03	2.47	1.62	2.11	96.3
	0.725	1.05	0.97	1.02	2.57	1.60	2.14	97.2
	0.743	1.03	0.97	1.02	2.63	1.59	2.16	97.9
	0.930	0.95	0.99	1.00	3.73	1.44	2.32	108.8
	0.961	0.94	0.99	1.00	4.65	1.41	2.33	111.5
ETHYL ACETATE-WATER	0.940	1.01	1.00	1.01	6.91	5.74	7.64	74.1
	0.958	1.00	1.00	1.00	8.33	5.91	8.21	74.6
	0.976	1.00	1.00	1.00	8.30	6.08	8.81	75.8
ISOBUTANOL-WATER	0.010	43.8	26.8	32.9	1.09	1.00	1.00	90.9
	0.015	38.2	23.72	29.3	1.04	1.00	1.00	90.0
	0.021	33.1	21.00	26.6	1.09	1.00	1.01	88.0
	0.371	1.78	1.14	1.39	1.60	1.60	1.61	89.2
	0.525	1.25	0.98	1.09	2.28	1.81	1.97	89.2
	0.693	1.14	0.97	1.04	2.75	1.81	2.14	90.6
	0.759	1.08	0.98	1.02	3.04	1.79	2.23	92.3
	0.906	1.03	1.00	1.00	4.65	1.68	2.37	96.8
	0.938	1.04	1.00	1.00	5.17	1.66	2.39	98.9

TABLE VIII (continued)

PREDICTION OF V-L EQUILIBRIUM FROM MUTUAL SOLUBILITY DATA

			$\alpha = 0.2$	$\alpha = -1$		$\alpha = 0.2$	$\alpha = -1$	
	X	γ_1 EXP.	$\overline{\gamma_1}$ CALC.	$\overline{\gamma_1}$ CALC.	γ_2 EXP.	$\overline{\gamma_2}$ CALC.	$\overline{\gamma_2}$ CALC.	T
PROPILENE OXIDE-WATER	0.118	6.67	6.052	7.053	1.05	1.048	1.065	38.2
	0.166	4.31	4.735	5.284	1.25	1.093	1.121	36.3
	0.625	1.37	1.258	1.386	2.67	2.431	2.490	36.3
	0.686	1.26	1.168	1.273	2.76	2.799	2.929	36.2
	0.756	1.16	1.094	1.170	3.56	3.311	3.647	36.0
	0.792	1.12	1.067	1.127	4.12	3.620	4.154	35.9
	0.831	1.07	1.043	1.087	5.47	3.996	4.867	35.6
	0.847	1.06	1.034	1.072	5.47	4.163	5.224	35.5
	0.894	1.03	1.016	1.037	7.44	4.705	6.582	35.1
	0.925	1.01	1.008	1.019	7.78	5.107	7.832	34.9
WATER-ANILINE	0.025	4.410	3.434	3.422	1.164	1.000	1.000	152
	0.059	4.739	3.323	3.507	1.192	1.000	1.002	131
	0.093	4.490	3.239	3.477	1.134	1.002	1.006	121
	0.200	3.885	3.006	3.208	0.910	1.013	1.030	105

TEMPERATURE DEPENDENCE OF PARAMETERS

Mutual solubility data at several temperatures offers a convenient way to study the temperature dependence of the parameters A_{ij} in the LEMF equation. By obtaining the parameters which satisfy Eq. (IV-3), at several temperatures, curves of A_{ij} vs. T can be constructed. Several such curves are presented in Figs. (8) through (12).

These data are well correlated by a second degree polynomial in T, as indicated by the solid line which represents the equation:

$$A_{ij} = a_{ij} + b_{ij} (T - T_1) + C_{ij} (T - T_1)^2 \qquad \text{(IV-4)}$$

where a, b and c are constants.

T = temperature of the system.

T_1 = the temperature corresponding to the first data point.

Equation (IV-4) may be useful in predicting heats of mixing with the LEMF equation. However, its use in correlating vapor-liquid equilibrium data yields little improvement over the asumption of no temperature dependence, Cukor and Prausnitz (53)

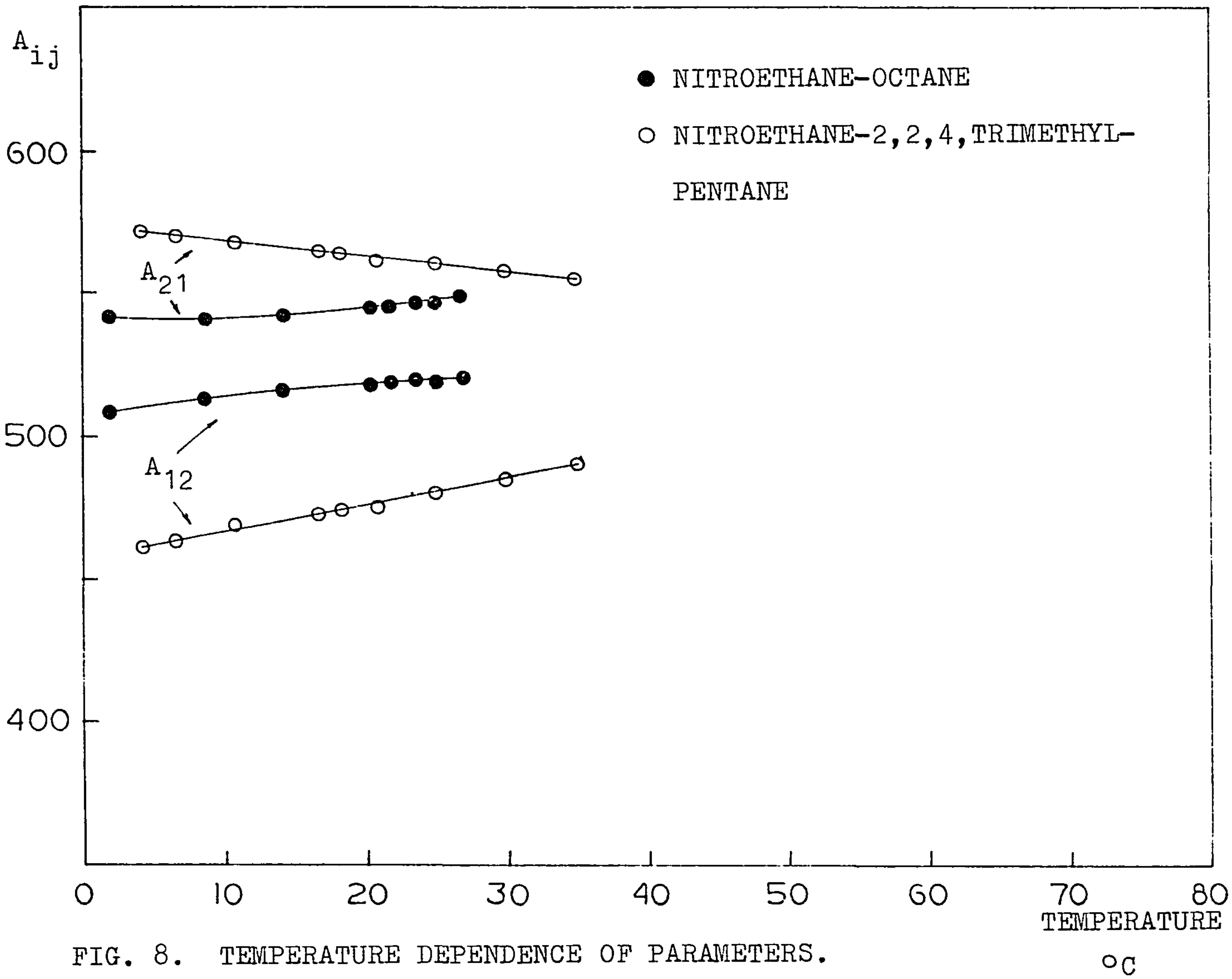


FIG. 8. TEMPERATURE DEPENDENCE OF PARAMETERS.

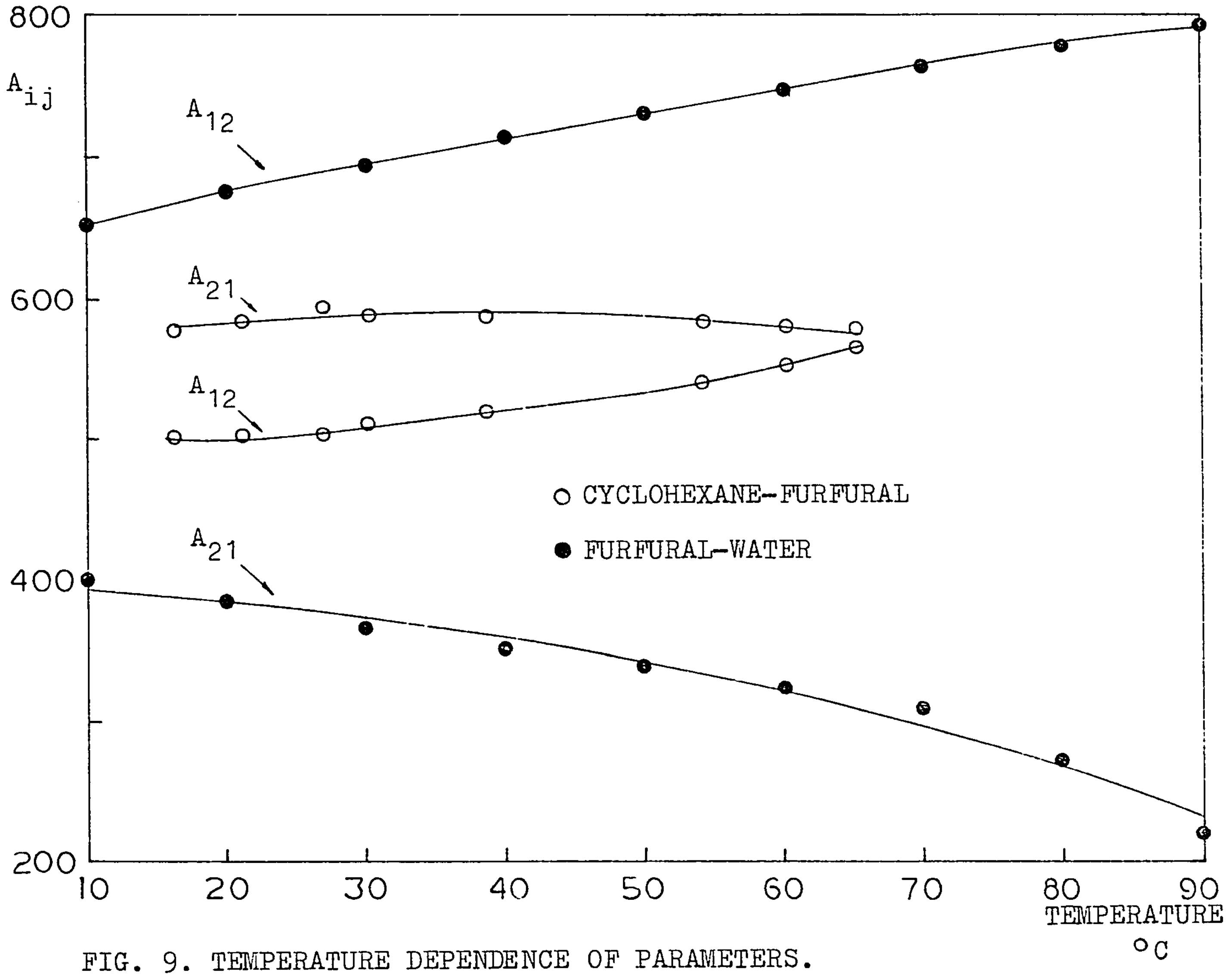


FIG. 9. TEMPERATURE DEPENDENCE OF PARAMETERS.

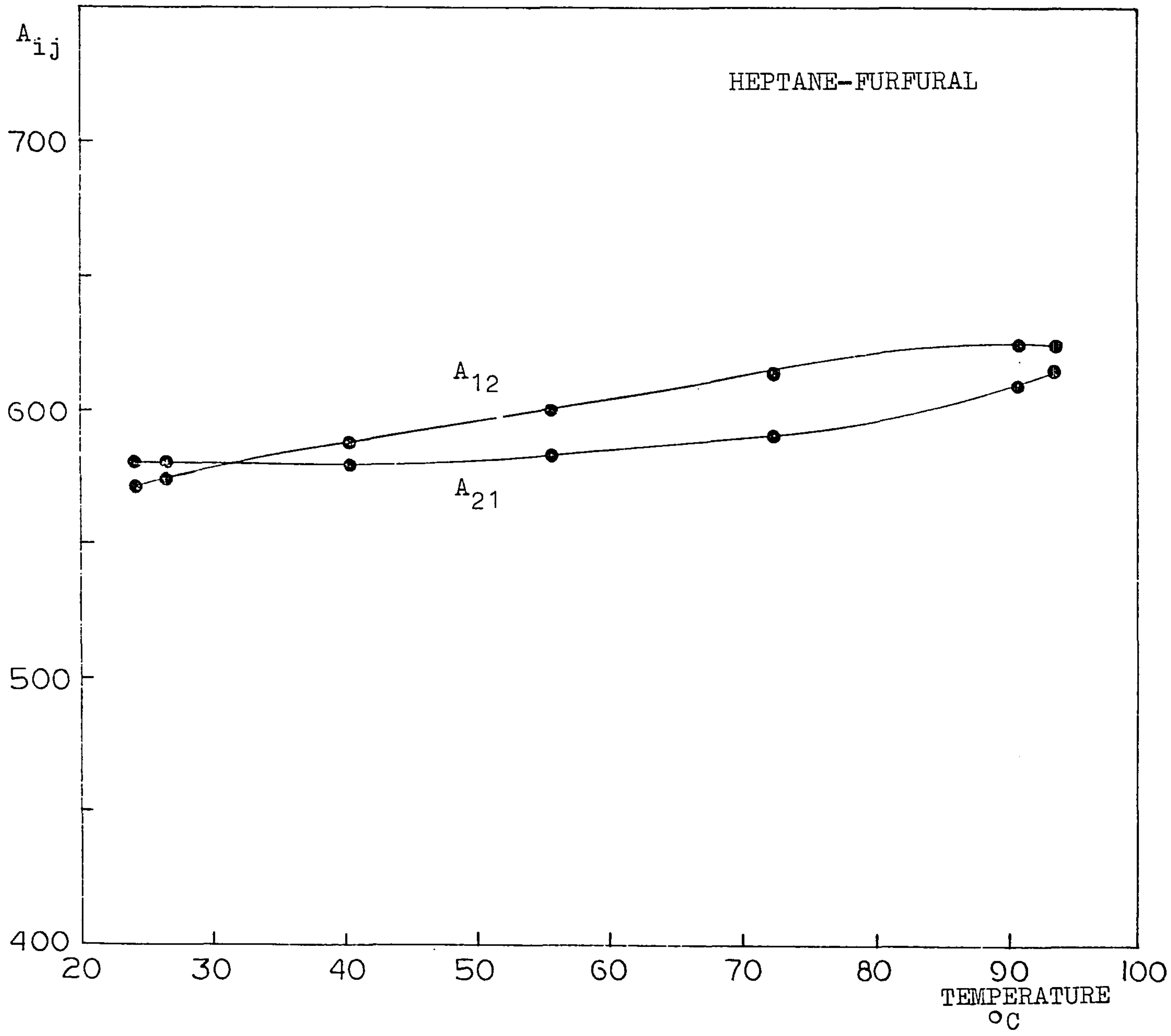


FIG. 10. TEMPERATURE DEPENDENCE OF PARAMETERS.

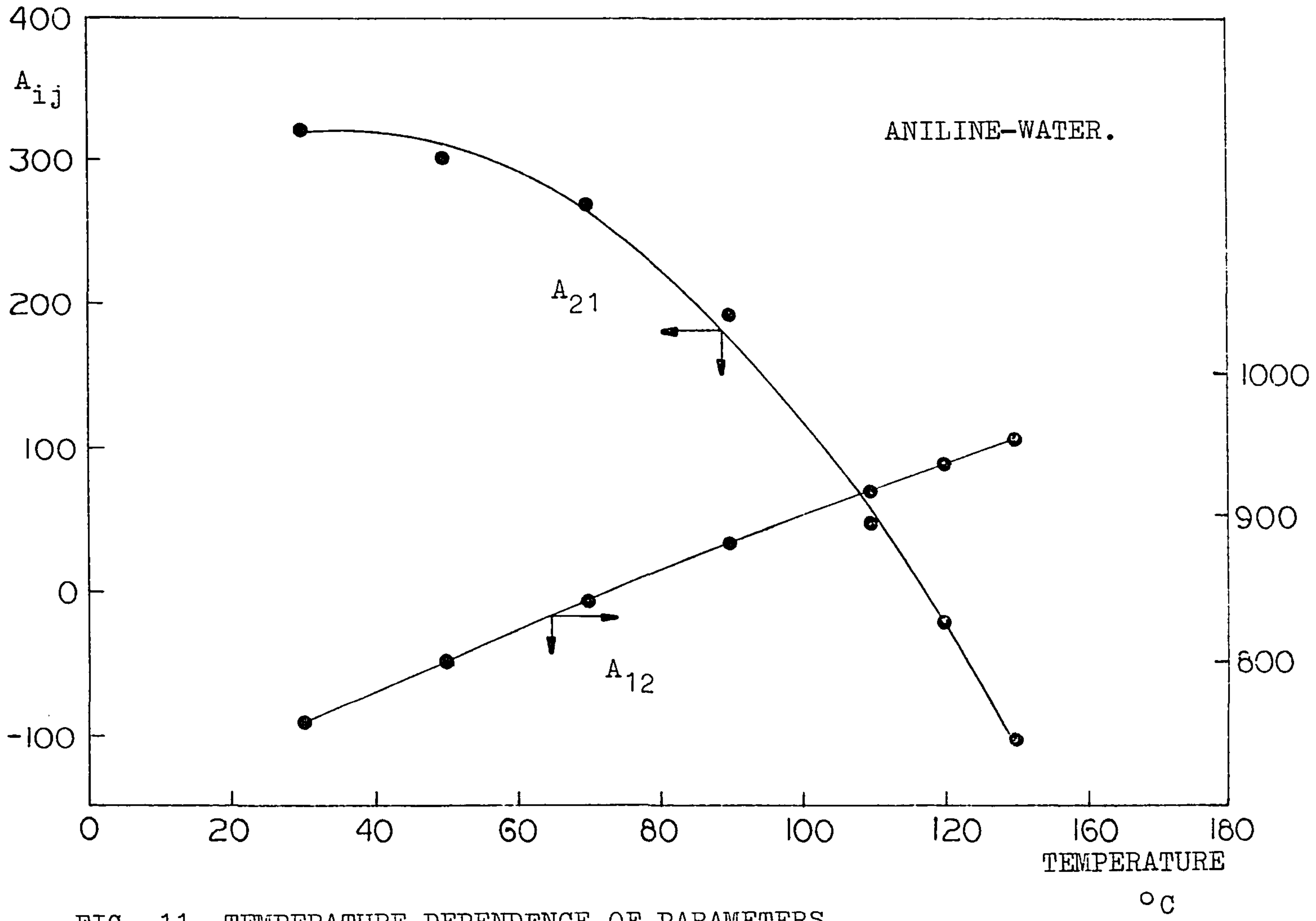


FIG. 11. TEMPERATURE DEPENDENCE OF PARAMETERS.

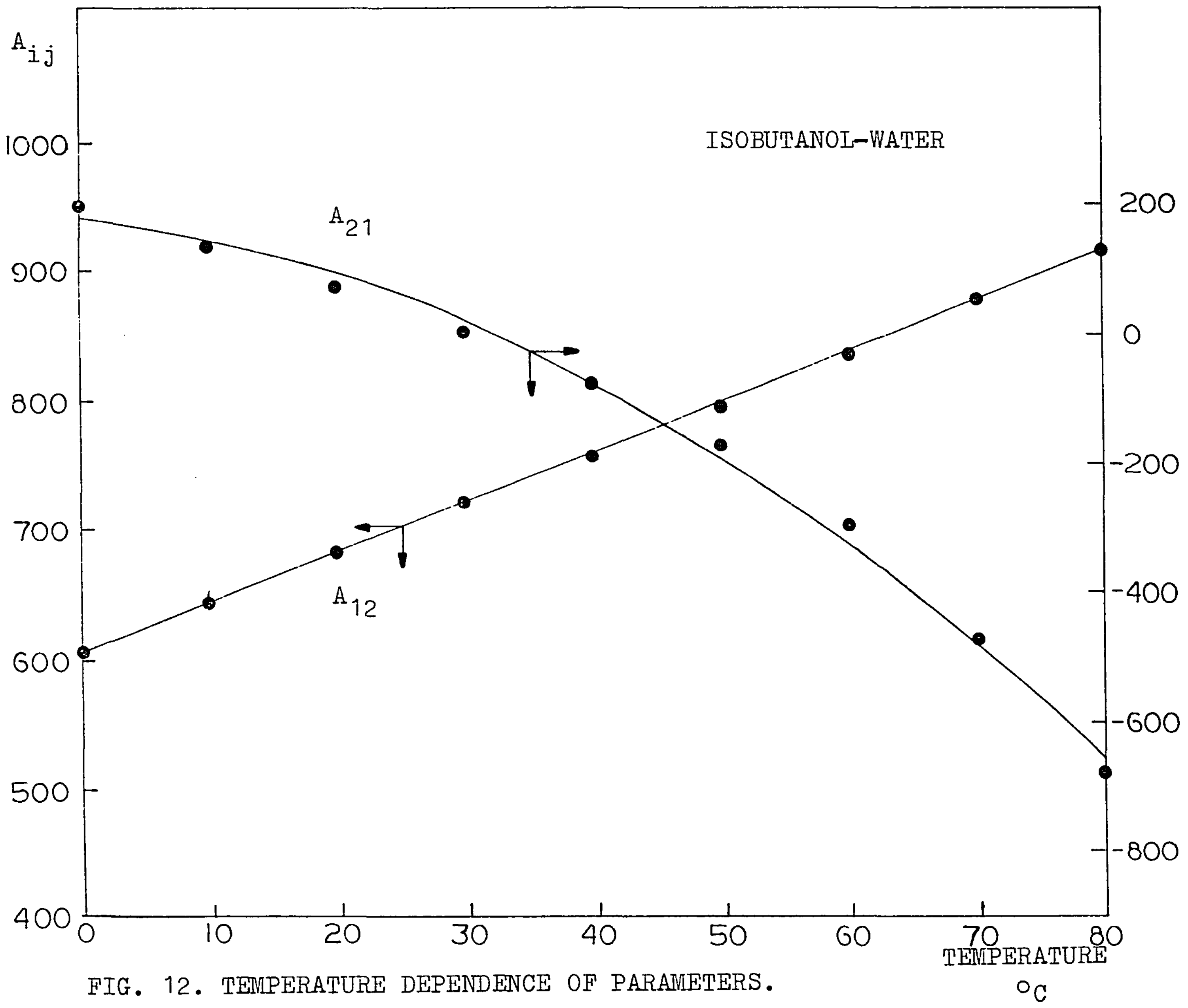


FIG. 12. TEMPERATURE DEPENDENCE OF PARAMETERS.

– V –

MULTICOMPONENT SYSTEMS

Multicomponent phase equilibrium data are necessary for several separation techniques such as distillation and extraction . In a typical situation one finds vapor-liquid or liquid-liquid equilibrium data for the binary constituents of the multicomponent system, but data on the system itself is generally unavailable and experimental determination requires considerable effort. Hence the importance of predictive techniques which with the aid of a computer may predict multicomponent equilibria from binary data alone.

Following Renon (29), we can expand the LEMF equation to multicomponent systems. The expression for the excess Gibbs energy is given by:

$$\frac{G^E}{RT} = \sum_{i=1}^{n} \frac{X_i \sum\limits_{j=1}^{n} A_{ji} \; X_j \; \exp\left(A_{ji}/RT\right)}{RT \sum\limits_{k=1}^{n} X_k \; \exp\left(A_{ki}/RT\right)} \qquad \text{(V-1)}$$

And for the activity coefficient we obtain

$$\ln \gamma_i = \frac{\sum\limits_{j=1}^{n} A_{ji} \; X_j \; \exp\left(A_{ji}/RT\right)}{RT \sum\limits_{k=1}^{n} X_k \; \exp\left(A_{ki}/RT\right)} + \sum_{j=1}^{n} \frac{X_j \; \exp\left(A_{ij}/RT\right)}{\sum\limits_{k=1}^{n} X_k \; \exp\left(A_{kj}/RT\right)}$$

$$\left[\frac{A_{ij}}{RT} - \frac{\sum\limits_{i=1}^{n} X_i \; A_{ij} \exp\left(A_{ij}/RT\right)}{RT \sum\limits_{k=1}^{n} X_k \; \exp\left(A_{kj}/RT\right)} \right] \qquad \text{(V-2)}$$

Where the parameters A_{ij} are evaluated from data on the binaries making up the multicomponent system.

TERNARY MISCIBLE SYSTEMS:

A comparison of the errors obtained in predicing vapor phase compositions with Eq. (V-2) and with the NRTL equation is presented in table IX. As can be seen both equations offer practically the same degree of accuracy.

TERNARY IMMISCIBLE SYSTEMS

The problem under consideration requires determination of the binodal curve and tielines for a three component partially miscible system. Its solution requires specification of 7 variables, 6 liquid composition variables, and the temperature. Now appliying the phase rule

$$F = n + 1 - \theta \qquad \text{(V-3)}$$

Where

F = degrees of freedom
n = number of components
θ = number of phases in the system

We find that we have two degrees of freedom, that is, two independent variables. Therefore, we can specify the temperature and one liquid composition, say (X_1'). The remaining variables are then fixed through the following equations

$$\sum_{1}^{3} X_i' = 1 \qquad \text{(V-4)}$$

$$\sum_{1}^{3} X_i'' = 1 \qquad \text{(V-5)}$$

$$X_i' \gamma_i' = X_i'' \gamma_i'' \qquad i = 1, 2, 3 \qquad \text{(V-6)}$$

TABLE IX

PREDICTION OF TERNARY VAPOR LIQUID EQUILIBRIUM

SYSTEM	DATA POINTS	AVERAGE ABSOLUTE ERROR OF PREDICTED VAPOR COMPOSITIONS					
		LEMF EQUATION			NRTL EQUATION		
Acetone-methanol-chloroform at$^\circ$50 C.	30	0.064	0.083	0.045	0.056	0.067	0.052
Acetone-methanol-water at 100°C.	46	0.016	0.024	0.011	0.019	0.025	0.012
Acetone-methyl acetate-methanol at 50°C.	35	0.006	0.009	0.013	0.006	0.010	0.012
Chloroform-methanol-ethyl acetate at 760 mm. Hg.	69	0.034	0.039	0.020	0.018	0.019	0.011
Ethanol-benzene-n-heptane at 400 mm. Hg.	50	0.034	0.019	0.017	0.022	0.010	0.014
Ethanol-ethyl acetate-water at 760 mm. Hg.	14	0.010	0.017	0.018	0.009	0.018	0.006
Methanol-carbon tetrachoride-benzene at 55°C	8	0.006	0.005	0.002	0.006	0.005	0.002
Methanol-ethanol-water at 760 mm. Hg.	19	0.020	0.015	0.030	0.021	0.016	0.032
Methanol-n-heptane-toluene at 760 mm. Hg.	8	0.012	0.009	0.004	0.012	0.008	0.004
Methyl acetate-chloroform-benzene at 760 mm. Hg.	91	0.007	0.003	0.008	0.013	0.012	0.011
Methylethylketone-n-heptane-toluene at 760 mm. Hg.	36	0.023	0.019	0.009	0.020	0.020	0.008

Equations (V-4) and (V-5) are just the conditions that in each phase the mole fractions must add to 1. Equation (V-6) represents the condition for equilibrium between phases.

A comparison of the results obtained in prediction of ternary liquid-liquid equilibrium with the LEMF and NRTL equations is presented in Figs. (13) through (19). It can be seen that the LEMF equation is in better agreement with the data than the NRTL equation with the value of α set according to the rules of Renon and Prausnitz (29).

A very important consideration in the solution of these equations is the development of a computational technique, since the trial and error solution of Eq. (V-6) subject to the constraints (V-4) and (V-5), with the activity coefficient given by Eq. (V-2) is an almost impossible task due to the complexity of the equations.

Three different computational techniques are considered in this work.

1 - The Tangent Method
2 - The LSQ2 Method
3 - The Newton Raphson Method

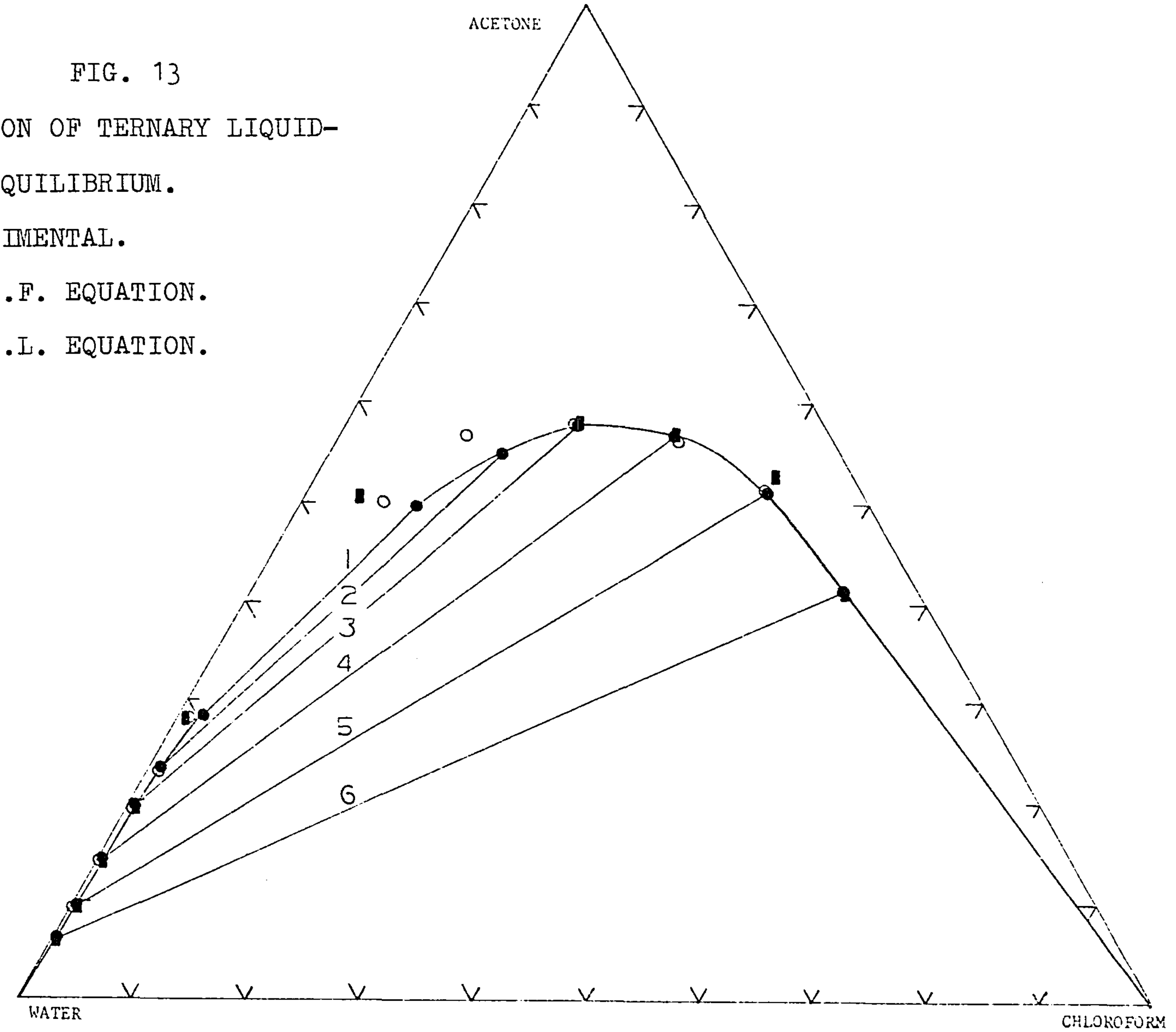


FIG. 13

PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIUM.

- ● EXPERIMENTAL.
- ○ L.E.M.F. EQUATION.
- ■ N.R.T.L. EQUATION.

T = 25 C

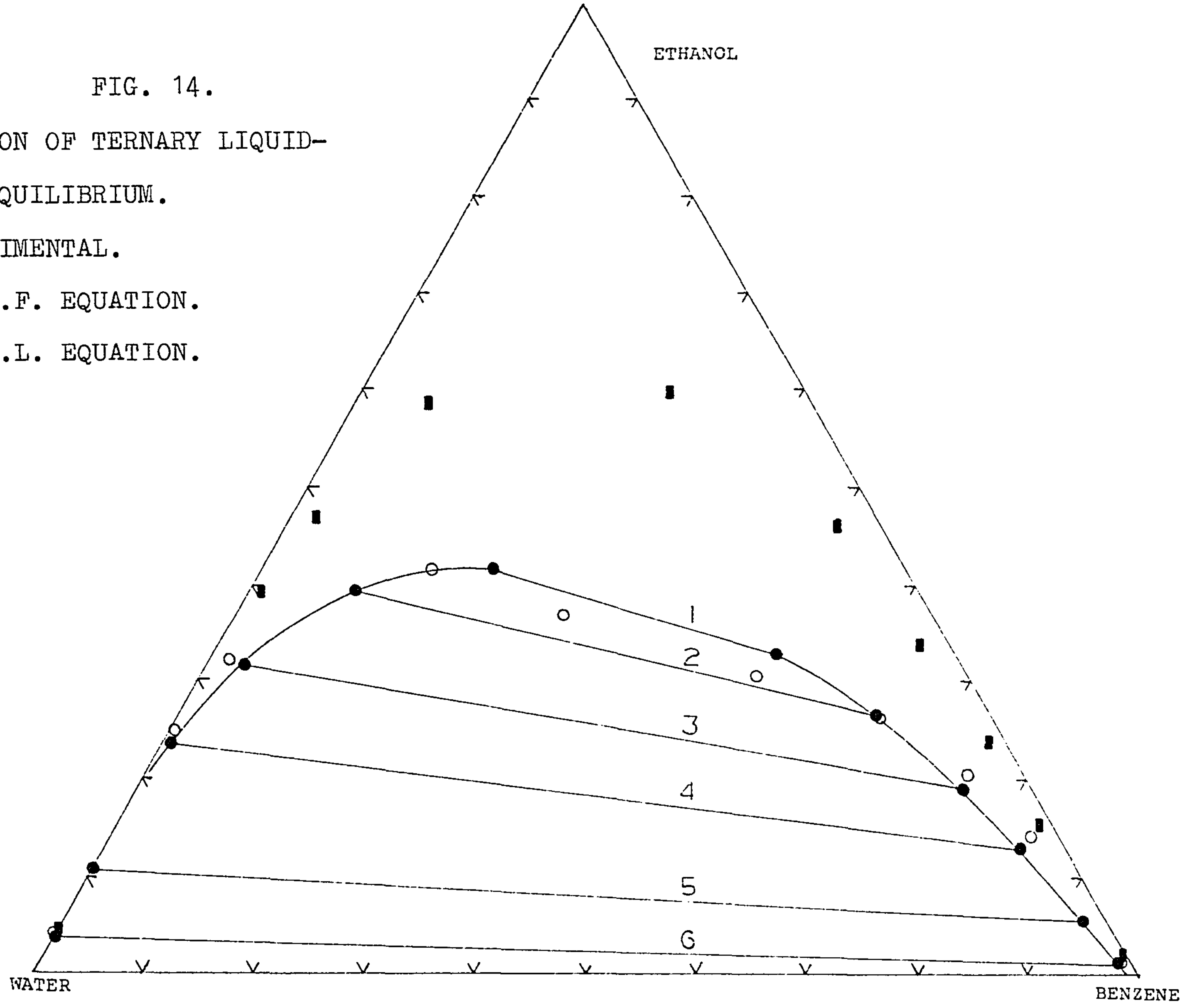


FIG. 14.

PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIUM.

● EXPERIMENTAL.

○ L.E.M.F. EQUATION.

■ N.R.T.L. EQUATION.

T = 25°C

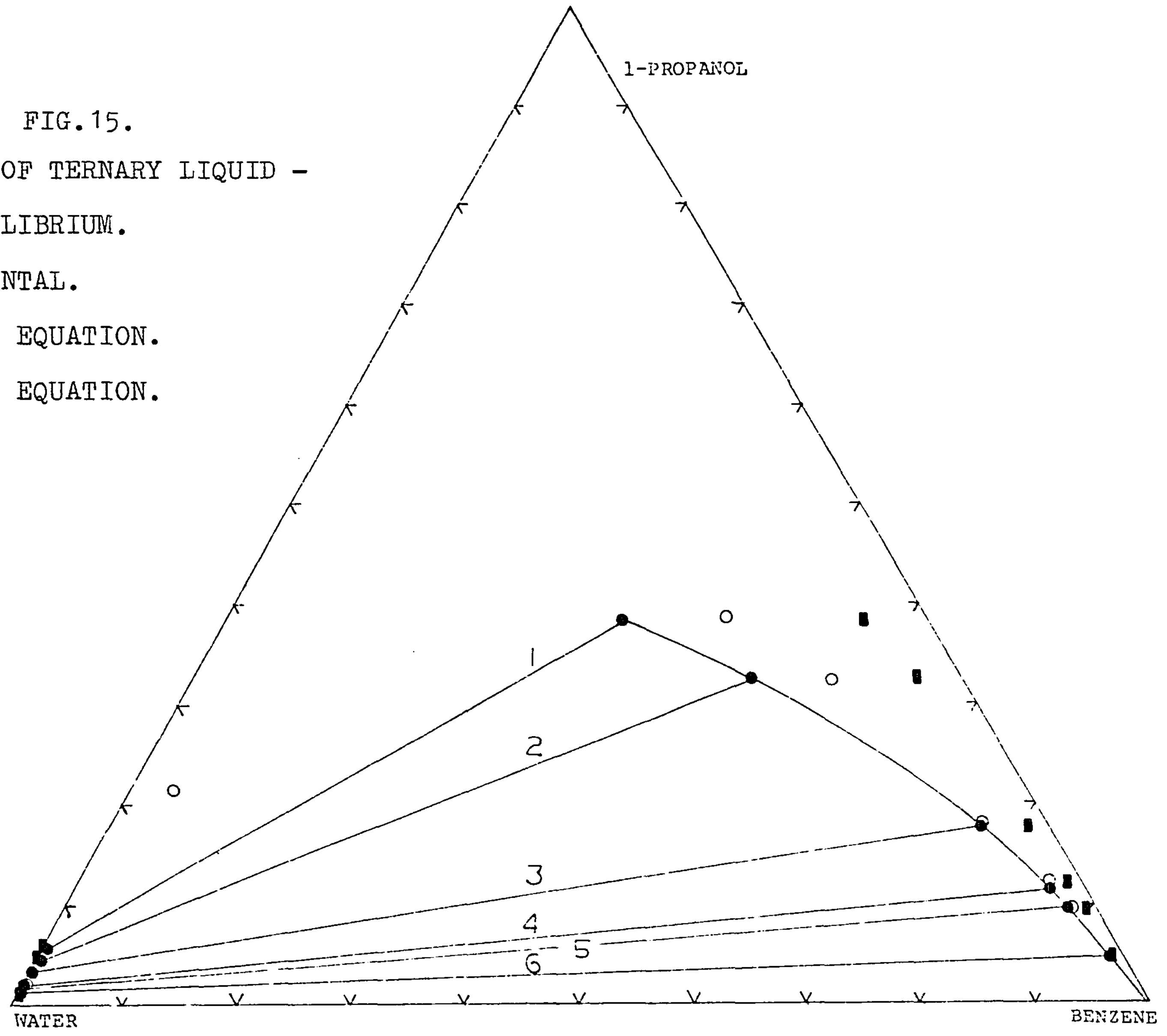


FIG.15.

PREDICTION OF TERNARY LIQUID - LIQUID EQUILIBRIUM.

- ● EXPERIMENTAL.
- ○ L.E.M.F. EQUATION.
- ■ N.R.T.L. EQUATION.

T = 37.7°C

FIG. 16.

PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIUM.

● EXPERIMENTAL.

○ L.E.M.F. EQUATION.

▮ N.R.T.L. EQUATION.

T = 30°C

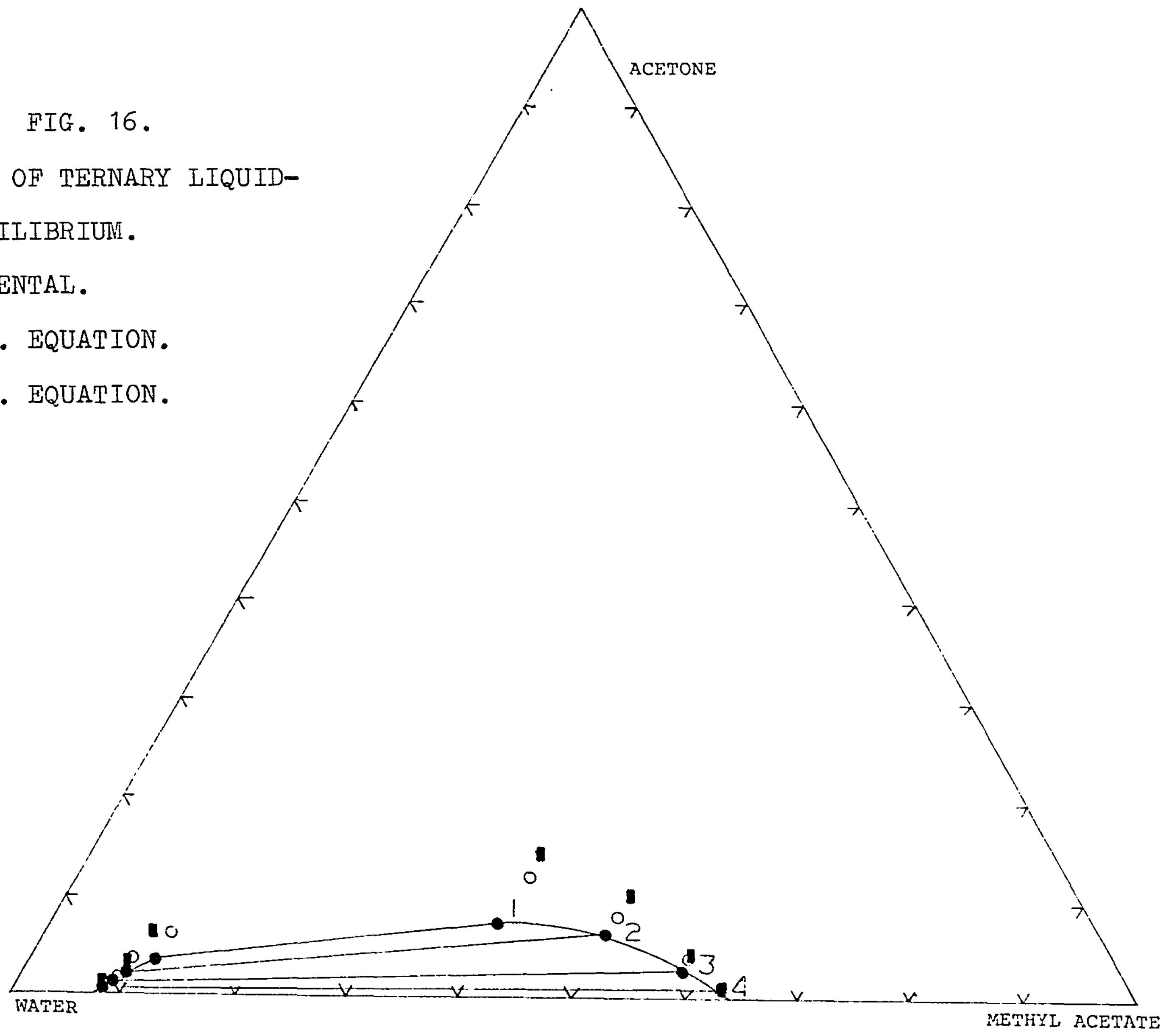


FIG. 17.

PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIUM.

● EXPERIMENTAL.

○ L.E.M.F. EQUATION.

▮ N.R.T.L. EQUATION.

T = 70°C

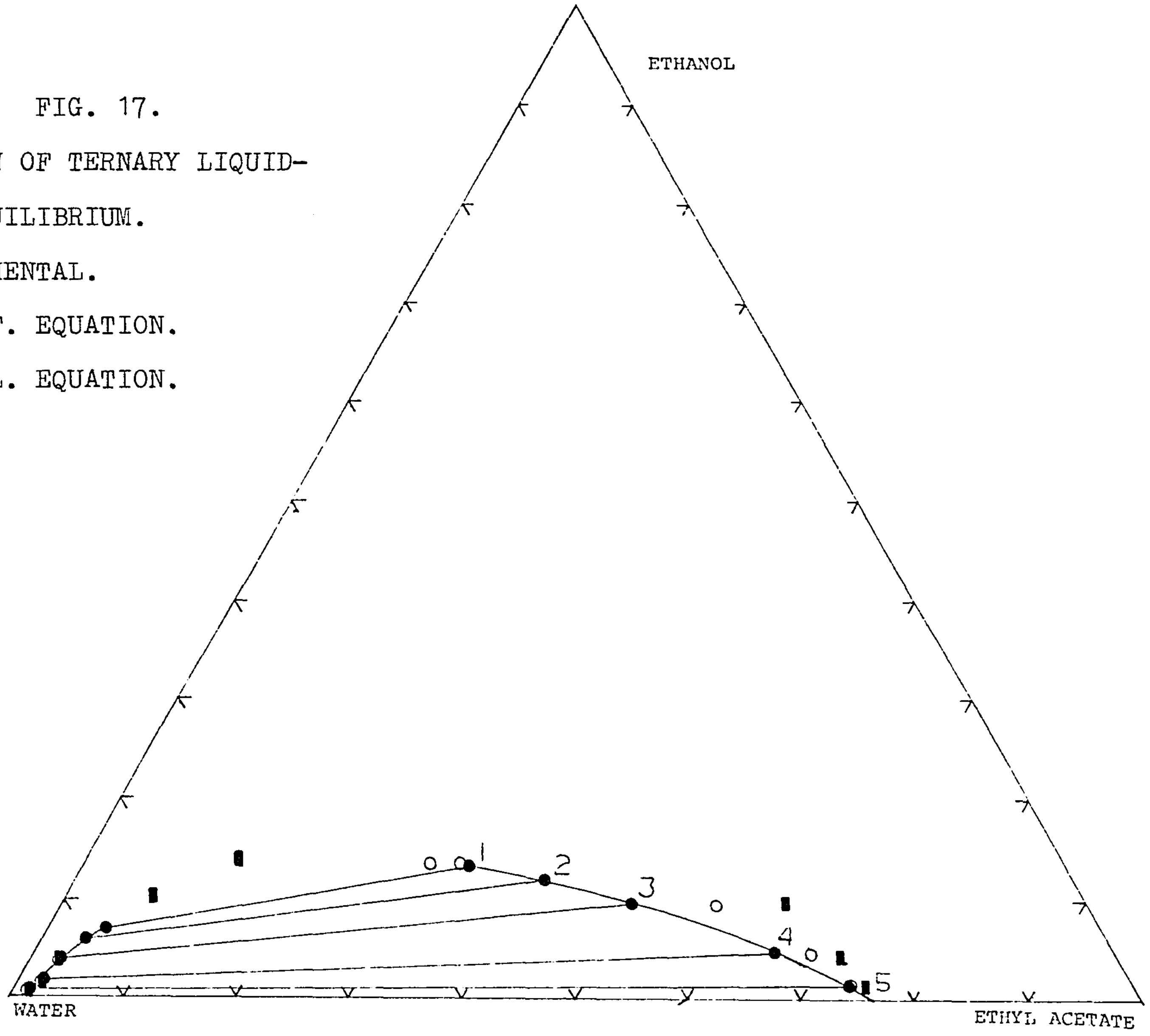
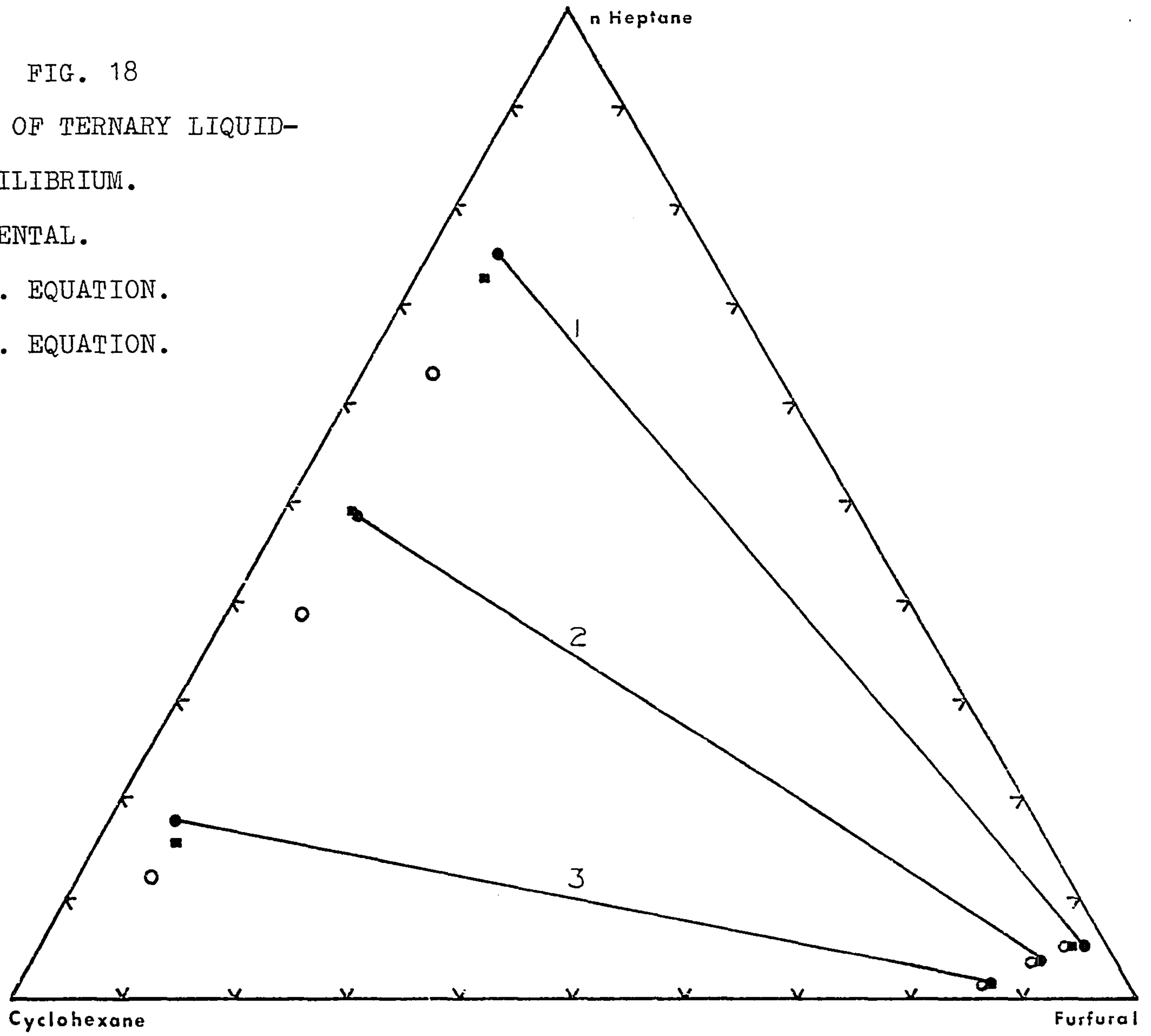


FIG. 18

PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIUM.

- ● EXPERIMENTAL.
- ○ L.E.M.F. EQUATION.
- ■ N.R.T.L. EQUATION.

T = 30°C



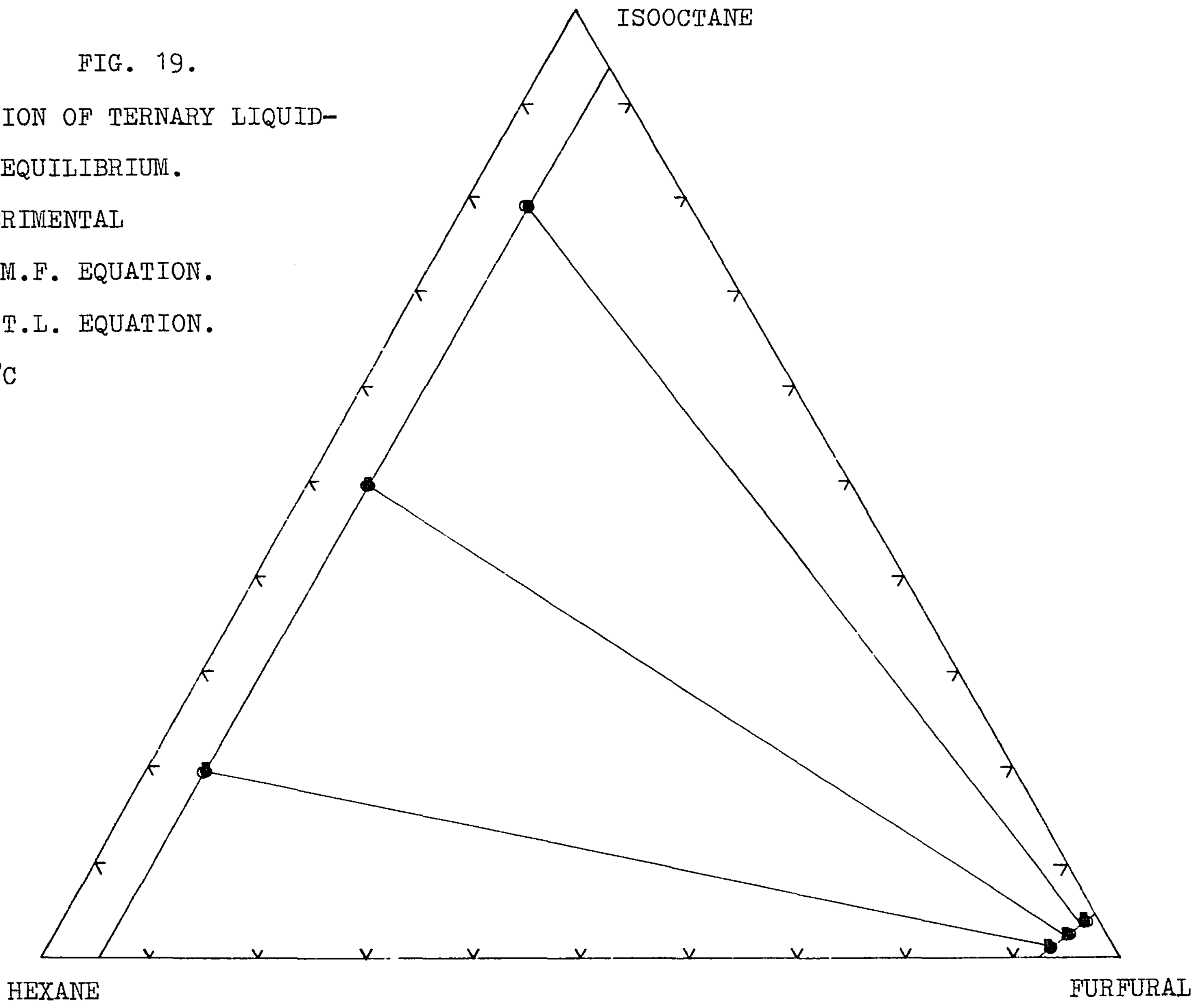


FIG. 19.

PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIUM.

- ● EXPERIMENTAL
- ○ L.E.M.F. EQUATION.
- ■ N.R.T.L. EQUATION.

T = 30°C

1. The Tangent Method

In chapter IV we saw how a tangent to the free energy of mixing vs. composition curve gives the immiscibility limits for a partially miscible binary system. A similar reasoning would lead us to expect the same phenomena in a partially miscible ternary system. In this case however, we have two independent overall compositions, X_1 and X_2, therefore when plotting G^M vs. X_1 we must specify how X_2 is to be constrained. Considering that compositions in equilibrium must lie on a tieline, we can restrict ourselves to compositions along a straight line of slope M which, for the moment, we assume corresponds to a tieline of the system. This would leave only one overall independent composition and will allow us to plot G^M vs X_1. Next the points of tangency are found and from these the corresponding equilibrium compositions X_1', X_1'', X_2' X_2'' and X_3' X_3''. If these compositions satisfy the condition of equilibrium then our arbitary line corresponds to a tieline of the system. Otherwise a new line must be chosen and the process repeated.

At this point it is convenient to define a function that gives the magnitude of the error resulting from applying the condition of equilibrium to compositions other than those at equilibrium.

$$E = \sum_{1}^{3} \left|\left(X_1' \, Y_1' - X_1'' \, Y_1''\right)\right| \qquad (V-7)$$

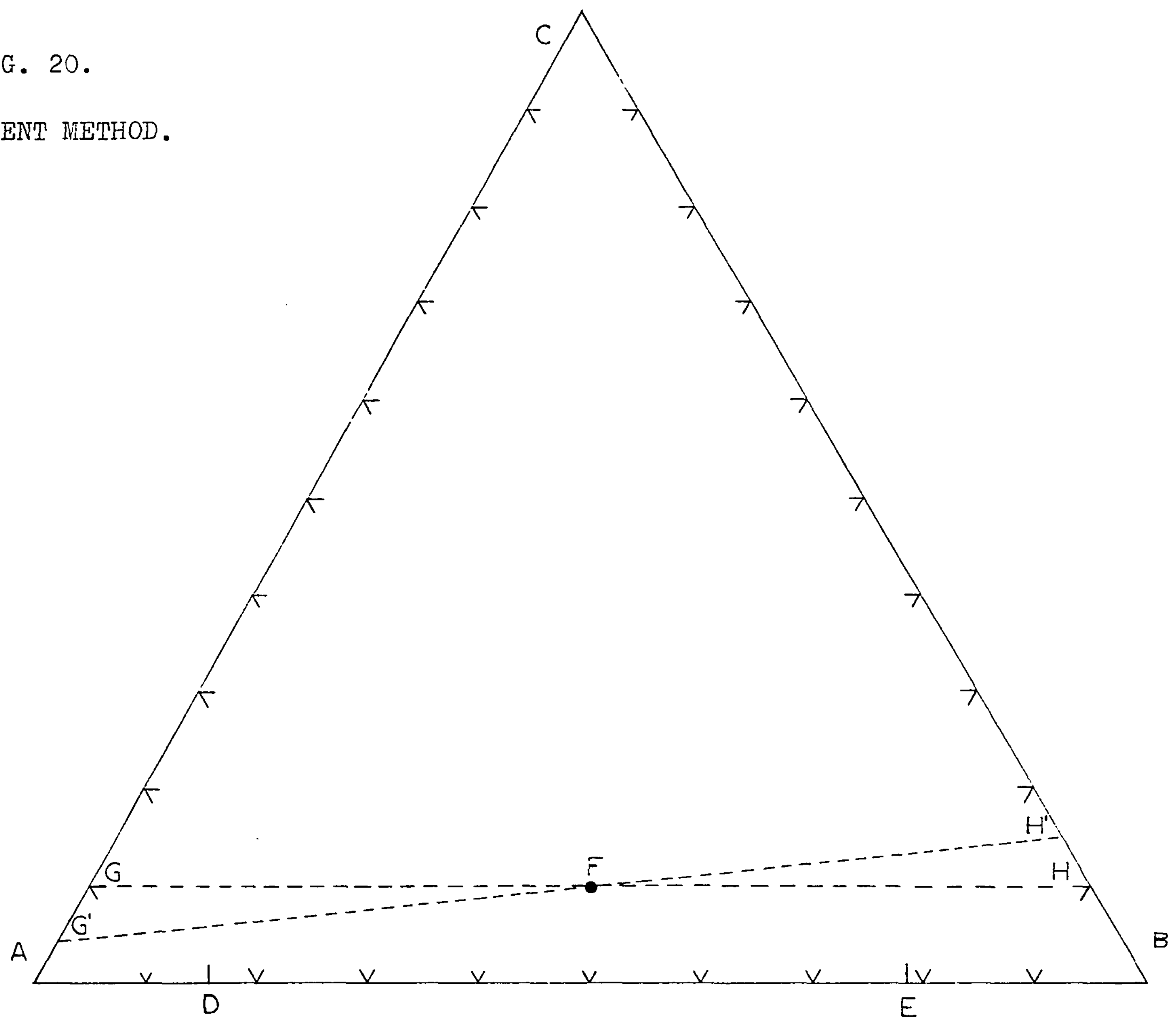
For compositions in equilibrium, the expression inside the parenthesis vanishes and therefore the error E is zero.

Perhaps this could be understood better by referring to Fig **20** **Let us** assume that we have a ternary mixture of A, B and C, where the binary A–B is partially miscible. The solubility limits of this binary are known and are given by points D and E. Now although we do not know the shape of the binodal curve, we can safely assume that a point such as F will be well inside the insoluble region. Now we draw our first tieline (GH) through F which we assume as a first guess has a zero slope, and plot G^M vs. X_1 the total mole fraction of component 1, Fig.(21). Since the point we are considering lie in the tieline, fixing X_1 automatically fixes X_2 and X_3. Now the tangent line NO gives the equilibrium compsotions X_1' and X_1'' and since we are still constrained to compositions along the tieline, we automatically obtain the compositions X_2' X_3' and X_2'' and X_3''. Those are the compositions that we use to calculate the error as per equation (V–7). If the error is zero then these are equilibrium compositions, if not, we change the slope of the tieline to obtain a new tieline $G' - H'$, the process being repeated until a zero error is obtained.

Using this technique we were successful in predicting tielines for the systems Ethanol-Ethylacetate-Water and Acetone-Methylacetate-Water. However, the method failed to find tielines for the system. n-Heptane, Cyclohexane, Furfural. Possibly this failure was due to the computer program rather than the concept itself, however this technique was abandoned in favor of the LSQ2 method which on the surface at least appears to be much simpler.

FIG. 20.

THE TANGENT METHOD.



THE TANGENT METHOD.

FREE ENERGY OF MIXING VS. COMPOSITION FOR A PARTIALLY MISCIBLE SYSTEM.

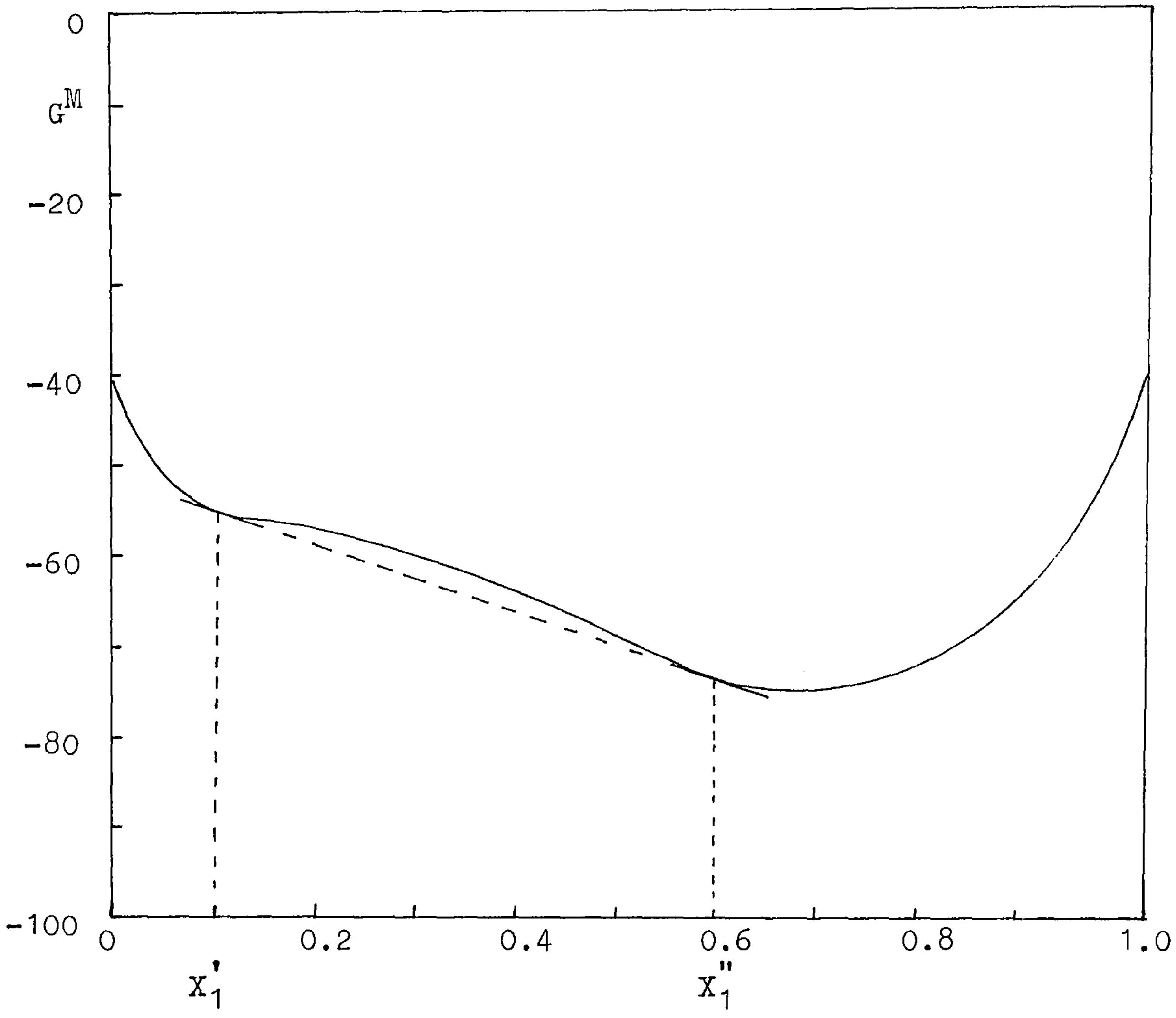


Fig. 21

2. The LSQ2 Method

The concept behind this method is very simple. As we saw, according to the phase rule we have two degrees of freedom. Therefore we can set the temperature and one composition say X_1' , guess the other compositions, i.e., X_2', X_1'' and X_2'' and calculate the error of our guess according to equation (V–7).

In theory at least we could keep guessing until a zero error is obtained. But then, why not use a computer program such as LSQ2 which is designed to search for the minimum of a function of several independent variables. If we define our function as that given by equation (V–7) and consider as independent variables the compositions X_2', X_1'' and X_2'', LSQ2 should be able to find a set of compositions such that the error E equals zero. A program written for this purpose gave the results presented in Figs. VI through X. The program used consists of a calling program which reads the binary parameters, the temperature of the system, the arbitrary composition X_1' and initial guesses for the remaining compositions X_2', X_1'' and X_2''. Then calls LSQ2, which tests the validity of these guesses by calling FN, a subroutine that calculates ternary activity coefficients and the errors resulting from applying the condition of equilibrium according to equation (V–7). According to the magnitude of this error, LSQ2 calculates a new set of compositions and calls FN again. The cycle is repeated until the resulting error falls below a predetermined limit or until a specific number of iterations have been performed. Since the set of compositions thus obtained satisfy the condition of equilibrium they must represent phases in equilibrium. However in some cases results are obtained that do not correspond to compositions in equilibrium. At present we have no explanation for this except to say that perhaps equation (V–7) represents a necessary but not sufficient condition of equilibrium.

It is also possible to obtain the trivial solutions $X_1' = X_1''$, $X_2' = X_2''$ and $X_3' = X_3''$. Two different meaning are associated with this result. It could be that the point in question is outside the immiscible region or it could be due to the particular path followed by the program while searching for the unkown compositions. In any case, when either of these difficulties was found, a minor change such as a new set of starting values or the use of a different increment was all that was required to obtain the desired results.

3. THE NEWTON RAPHSON METHOD

In addition to the techniques described above, there is also that described by Renon (27). In this case, the unkown compositions are found through an iterative Newton method. During the course of our work, we had the opportunity to use this technique with good results for the systems Ethanol-Ethyl acetate-Water and Acetone-Methyl acetate-Water. The program, however, failed to yield results for the other five systems. It is most probable that by proper adjustment of the starting values in Renon's program we could have obtained good results. However, considering that the desired results had already been obtained with the LSQ2 method, further work on this subject was discontinued.

– VI –

PARAMETER OPTIMIZATION

As previously mentioned, the parameters for the NRTL and LEMF equations are obtained by using a non linear least square program (LSQ2). This program works by changing a set of initial values in a preset manner according to the error obtained in each new iteration. During the course of our work it was noticed that occassionally different sets of parameters were obtained for the same system. A closer look at this phemomena revealed that for some systems, the parameters obtained depended on the set of initial values chosen. In order to obtain a better understanding of this behavior, so that the best initial values could be consistently chosen, the parameters of a few systems were recomputed starting with 121 different sets of initial values. This lead to the finding that for some systems, as much as 4 or 5 different sets of parameters can be obtained from starting values in the range –2000 to +2000. It also became evident that for the majority of systems a 0-0 set of initial values gives the best set of parameters. Actually this is the same as saying that we start with the assumption that the mixture behaves ideally. The program then will presumably zero in a pair of parameters which corrects for deviations from ideality. In Fig. (22) through (27) some of the results obtained are presented in graphical form. It can be seen that the surface of initial values is divided into regions, from which different sets of parameters are obtained. It must be noted that some sets of starting values cause LSQ2 to diverge, that is to yield parameters resulting in large standard deviations. In other cases, although acceptable standard deviations are obtained the corresponding parameters seem erroneous since their values are one order of magnitude higher than expected.

The picture emerging from this study is that a three dimensional plot of the std. deviation of calculated activity coefficients vs. the value of the parameters results in a surface containing several valleys or minimas. Therefore the parameters found by LSQ2 depend on the path followed while searching for the minimum std. deviation, which in turn depends on the starting values.

For the remaining systems,the parameters were recomputed from 9 different sets of initial values covering the range between -1200 to 1200 in intervals of 1200. Out of a total of 40 systems, 11 were found to have multiple sets of parameters. A listing of these systems with the corresponding sets of parameters and standard deviations is presented in Table X.

The fact that different sets of parameters give a good correlation of the binary data, with either the LEMF or NRTL equation, poses a new question. Namely which set of binary parameters should be used for prediction of multicomponent equilibria; should we look for the best set of parameters or can we safely assume that a 0-0 set of initial values, which usually yieds the best set of parameters, is satisfactory, even when better fits are possible from other sets of initial values.

In order to answer this question, vapor liquid equilibrium data for several ternary systems was predicted from several sets of binary parameters. The results are presented in Tables XI and XII.

It can be seen that in the majority of cases, the errors obtained with either set of parameters are within 10% of each other. For the LEMF equation, however, the 0-0 set of initial values seem to give slightly better results. That is better predictions were obtained in 4 out of the 6 cases studied.

Throughout this chapter standard deviations are defined as per Eq. (III-7).

INITIAL VALUES AND PARAMETERS FOR THE N.R.T.L. EQUATION.
CHLOROFORM-BENZENE at 760 mm. Hg.

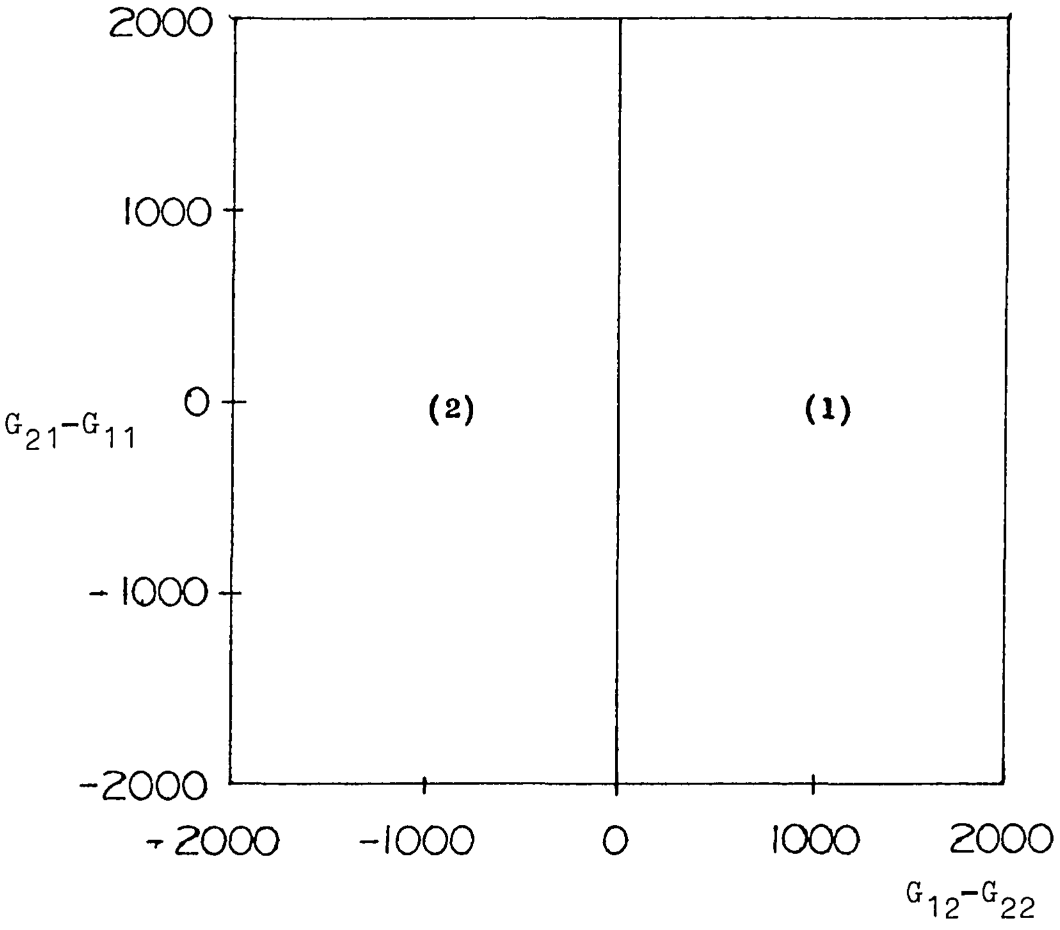


FIG. 22

(1) STD. DEV. = 0.0248
$G_{21} - G_{11}$ = - 166
$G_{12} - G_{22}$ = 26

(2) STD. DEV. = 0.0264
$G_{21} - G_{11}$ = 845
$G_{12} - G_{22}$ = - 723

INITIAL VALUES AND PARAMETERS FOR THE N.R.T.L. EQUATION.

CHLOROFORM-ETHYL ACETATE at 760 mm. Hg.

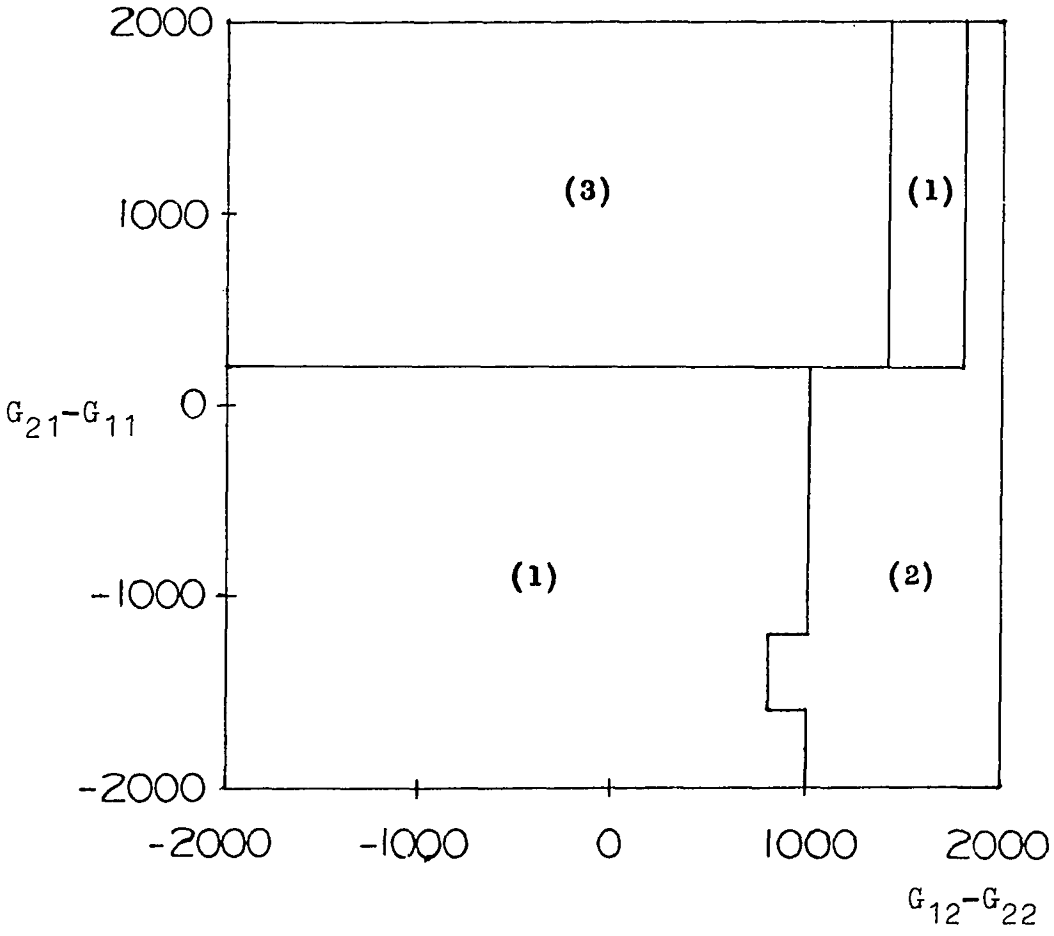


FIG. 23

(1) STD. DEV. = 0.0070

$G_{21} - G_{11}$ = - 817

$G_{12} - G_{22}$ = 452

(2) STD. DEV. = 0.0082

$G_{21} - G_{11}$ = -1161

$G_{12} - G_{22}$ = 1205

(3) STD. DEV. = 0.0262

$G_{21} - G_{11}$ = 2234

$G_{12} - G_{22}$ = -1371

INITIAL VALUES AND PARAMETERS FOR THE N.R.T.L. EQUATION.

METHYL ACETATE-CHLOROFORM at 760 mm. Hg.

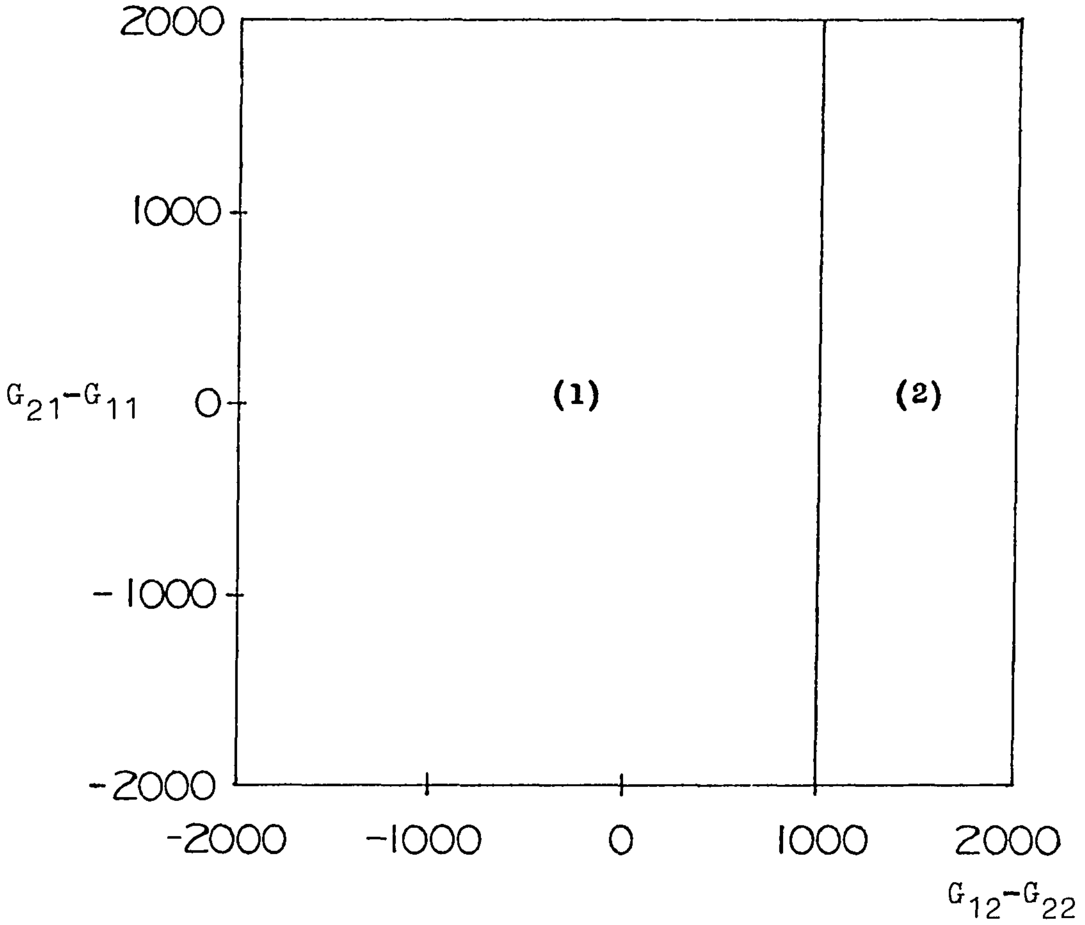


FIG. 24

(1) STD. DEV. = 0.0102

$G_{21} - G_{11} = 446$

$G_{12} - G_{22} = -714$

(2) STD. DEV. = 0.0188

$G_{21} - G_{11} = -1247$

$G_{12} - G_{22} = 2033$

INITIAL VALUES AND PARAMETERS FOR THE L.E.M.F. EQUATION.
CHLOROFORM-BENZENE at 760 mm. Hg.

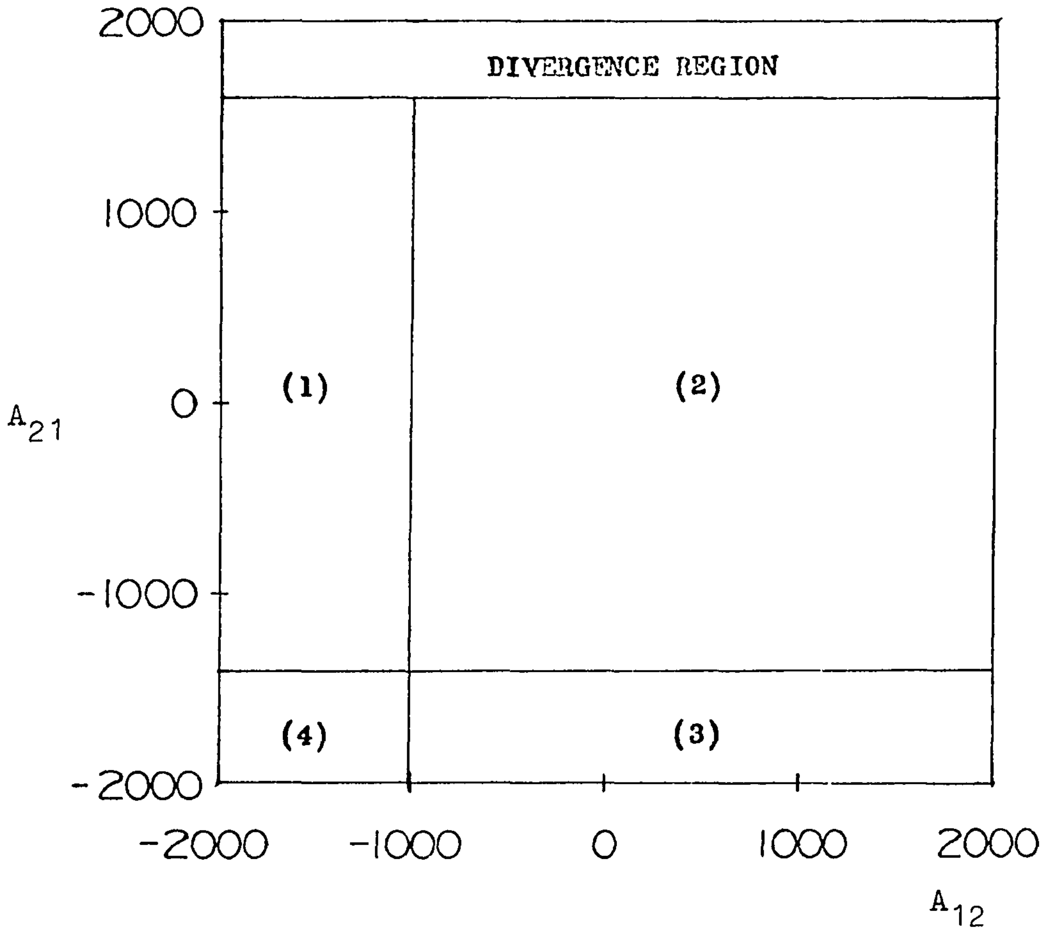


FIG. 25

(1) **STD. DEV. = 0.0146**
A_{21} = - 112
A_{12} = -3166

(2) **STD. DEV. = 0.0246**
A_{21} = - 33
A_{12} = - 126

(3) **STD. DEV. = 0.0248**
A_{21} = -16351
A_{12} = - 168

(4) **STD. DEV. = 0.0338**
A_{21} = - 3460
A_{12} = - 2433

INITIAL VALUES AND PARAMETERS FOR THE L.E.M.F. EQUATION.

CHLOROFORM-ETHYL ACETATE at 760 mm. Hg.

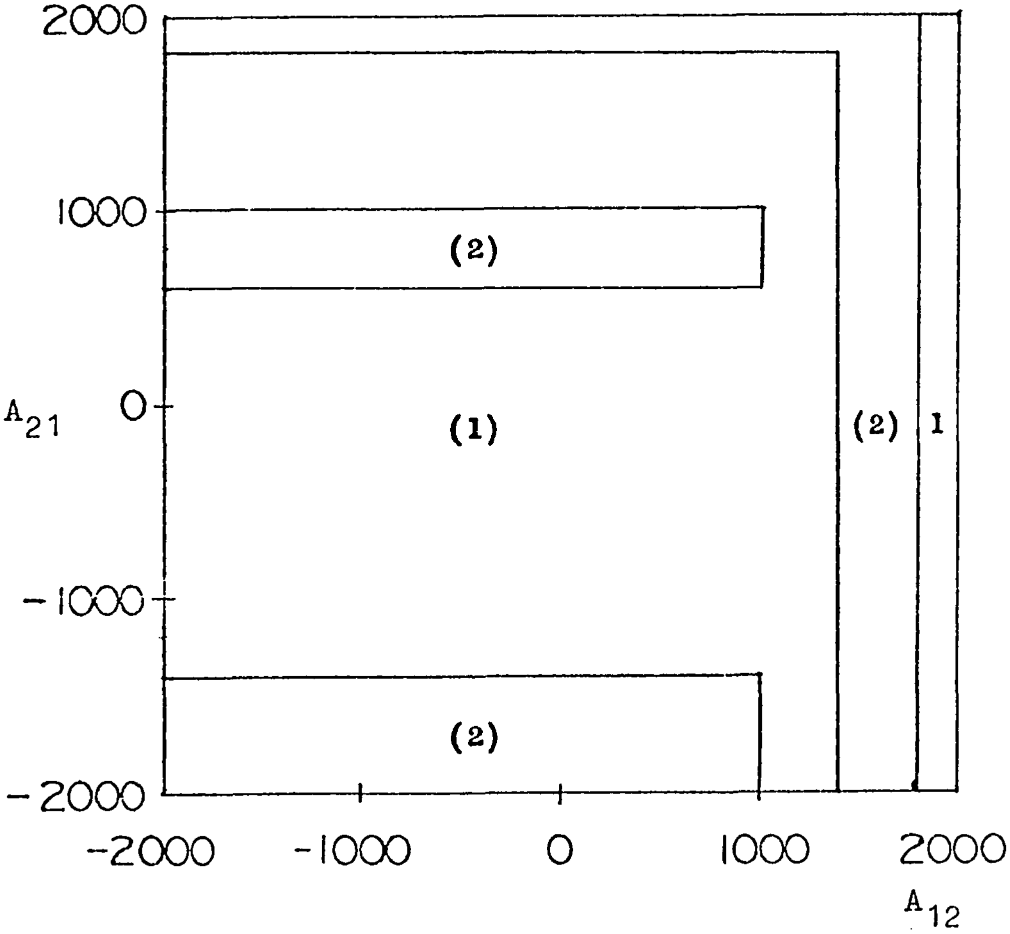


FIG. 26

(1) STD. DEV. = 0.0093

A_{21} = - 228

A_{12} = - 630

(2) STD. DEV. = 0.0478

A_{21} = -2299

A_{12} = - 830

INITIAL VALUES AND PARAMETERS FOR THE L.E.M.F. EQUATION.

METHYL ACETATE-CHLOROFORM at 760 mm. Hg.

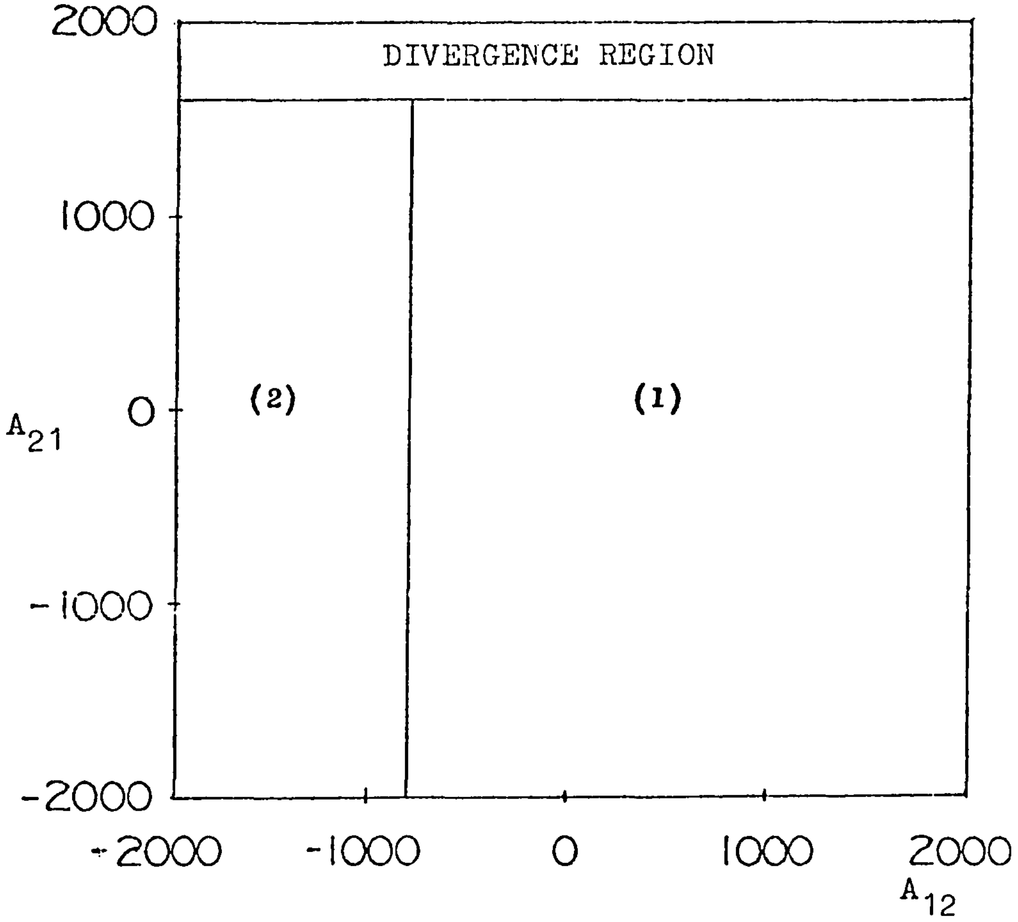


FIG. 27

(1) STD. DEV. = 0.0116

A_{21} = - 455

A_{12} = - 133

(2) STD. DEV. = 0.0265

A_{21} = - 624

A_{12} = -2892

TABLE X

SETS OF BINARY PARAMETERS FOR THE LEMF AND NRTL EQUATIONS

SYSTEM	LEMF EQUATION			NRTL EQUATION			
	A_{21}	A_{12}	STD. DEV.	$G_{21}-G_{11}$	$G_{12}-G_{22}$	α	STD. DEV.
Acetone-methyl acetate at 50°C.	308.75	-434	0.0383	486	-322	0.3	0.0361
	-187	211	0.0362				
	-5157	81	0.0373				
Acetone-chloroform at 50°C.	-188.4	-463	0.0366	-1221	1899	0.3	0.0237
	-422	-214	0.0198	101	-505	0.3	0.0194
Acetone-methanol at 50°C.	508	-809	0.0584	251	133	0.3	0.430
	141	182	0.0421				
	-17979	307	0.0571				
Acetone-water at 100°C.	279	619	0.0941	1507	156	0.3	0.1171
	223	629	0.1502				
Benzene-n-heptane at 400 Mm.Hg.	500	-678	0.0087	-263	705	0.3	0.0026
	286	- 30	0.0038				
Carbon tetrachloride-benzene at 760 Mm.Hg.	30	42	0.0041	63	12	0.3	0.0041
	285	-358	0.0044				
	-6844	70	0.0042				
Chloroform-methanol at 50°C.	555	35	0.0339	-172	1514	0.3	0.0315
	737	-1280	0.0370				
Methanol-water at 760 Mm.Hg.	- 9	371	0.0090	-835	-216	0.3	0.0099
	-17383	365	0.0094				
Methanol-ethanol at 760 Mm.Hg.	19	-22	0.0228	601	-478	0.3	0.0218
	142	-186	0.0227	-255	285	0.3	0.0227
	-3893	-16816	0.0156				
	-3650	15	0.0136				
Methyl acetate-methanol at 50°C.	649	-1266	0.2540	287	449	0.3	0.0464
	298	245	0.0415				
	493	-2817	0.2707				
n-Heptane-toluene at 760 Mm.Hg.	472	-529	0.0524	-314	712	0.3	0.0515
	290	- 73	0.0510				

TABLE XI

PREDICTION OF TERNARY VAPOR LIQUID EQUILIBRIUM
WITH THE LEMF EQUATION FROM DIFFERENT SETS OF BINARY PARAMETERS

SYSTEM	MATRIX OF PARAMETERS A_{ij}*			AVERAGE ABSOLUTE ERROR Y_1	Y_2	Y_3
Acetone-methanol-chloroform at 50°C. starting values = 0-0	0.0	182.2	-213.8	0.064	0.085	0.046
	141.0	0.0	555.5			
	-422.1	35.0	0.0			
Acetone-methanol-chloroform at 50°C. starting values ≠ 0-0	0.0	-809.0	-463.0	0.072	0.095	0.044
	508.0	0.0	737.0			
	-188.4	-1280.0	0.0			
Acetone-methanol-water at 100°C. starting values = 0-0	0.0	-400.9	619.5	0.018	0.025	0.011
	506.4	0.0	412.7			
	278.5	-109.1	0.0			
Acetone-methanol-water at 100°C. starting values ≠ 0-0	0.0	-400.9	629.0	0.021	0.028	0.011
	506.4	0.0	412.7			
	223.0	-109.1	0.0			
Acetone-methyl acetate-methanol at 50°C. starting values = 0-0	0.0	210.0	182.2	0.006	0.009	0.012
	-185.2	0.0	245.3			
	141.0	297.8	0.0			
Acetone-methyl acetate-methanol at 50°C. starting values = 0-0	0.0	-434.0	-809.0	0.008	0.021	0.025
	308.1	0.0	-1266.0			
	508.0	649.0	0.0			

* i = row
j = column

TABLE XI (continued)

PREDICTION OF TENARY VAPOR LIQUID EQUILIBRIUM
WITH THE LEMF EQUATION FROM DIFFERENT SETS OF BINARY PARAMETERS

SYSTEM	MATRIX OF PARAMETERS A_{ij}*			AVERAGE ABSOLUTE ERROR		
				Y_1	Y_2	Y_3
Ethanol-benzene-n-heptane at 400 mm. Hg. starting values = 0-0	0.0	505.6	576.1			
	334.9	0.0	-54.4	0.029	0.017	0.014
	506.9	298.3	0.0			
Ethanol-benzene-n-heptane at 400 mm. Hg. starting values ≠ 0-0	0.0	505.6	576.1			
	334.9	0.0	-677.0	0.018	0.010	0.013
	506.9	499.0	0.0			
Methanol-carbon tetrachloride-benzene at 55°C. starting values = 0-0	0.0	627.6	541.8			
	313.2	0.0	235.4	0.007	0.006	0.005
	384.0	-220.4	0.0			
Methanol-carbon tetrachloride-benzene at 55°C. starting values ≠ 0-0	0.0	627.6	543.6			
	313.2	0.0	-358.0	0.008	0.006	0.003
	358.2	285.0	0.0			
Methyl acetate-chloroform-benzene at 760 mm. Hg. starting values = 0-0	0.0	-133.4	114.06			
	-455.2	0.0	-125.9	0.008	0.004	0.008
	80.0	-33.4	0.0			
Methyl acetate-chloroform-benzene at 760 mm. Hg. starting values ≠ 0-0	0.0	-133.4	-820.4			
	-455.2	0.0	-3166.2	0.008	0.006	0.007
	444.2	-112.1	0.0			

---

* i = row
j = column

TABLE XII

PREDICTION OF TERNARY VAPOR-LIQUID EQUILIBRIUM WITH THE NRTL EQUATION FROM DIFFERENT SETS OF BINARY PARAMETERS

SYSTEM	MATRIX OF PARAMETERS A_{ij}*			AVERAGE ABSOLUTE ERROR Y_1	Y_2	Y_3
Acetone-methanol-chloroform at 50°C. starting values = 0-0	0.0	132.4	-505.2	0.056	0.067	0.052
	250.7	0.0	-171.8			
	101.3	1514.1	0.0			
Acetone-methanol-chloroform at 50°C. starting values ≠ 0-0	0.0	132.4	1899.0	0.056	0.048	0.065
	250.7	0.0	-171.8			
	-1221.0	1514.1	0.0			
Methanol-ethanol-water at 760 mm. Hg. starting values = 0-0	0.0	-61.3	-216.3	0.021	0.016	0.031
	56.3	0.0	-175.4			
	834.9	1391.2	0.0			
Methanol-ethanol-water at 760 mm. Hg. starting values ≠ 0-0	0.0	285.0	-216.3	0.020	0.015	0.030
	-255.0	0.0	-175.4			
	834.9	1391.2	0.0			
Methyl acetate-chloroform-benzene at 760 mm. Hg. starting values = 0-0	0.0	-714.4	63.3	0.007	0.003	0.007
	445.8	0.0	25.2			
	151.35	-165.5	0.0			
Methyl acetate-chloroform-benzene at 760 mm. Hg. starting values ≠ 0-0	0.0	-714.4	63.3	0.014	0.013	0.012
	445.8	0.0	-723.2			
	151.3	845.1	0.0			

---

*i = row
j = column

CONCLUSIONS

It can be concluded, from this work, that the substitution $\alpha = -1$, in the NRTL equation, leads to an improved expression for the excess free energy of mixing. The new expression or LEMF equation correlates and predicts miscible data with an accuracy equal to that obtained with the NRTL equation, even though it contains one parameter less. Furthermore, for immiscible systems, the LEMF equation predicts data with better accuracy than the NRTL equation.

Our results indicate that little improvement in accuracy can be obtained, over the LEMF equation, by fitting α to binary data. Fitting α to multicomponent data may yield a better correlation for the system under study. In this case, however, α becomes a multicomponent parameter and the equation a correlating tool. Under such conditions the equation is not used to its fullest potential. That is, the most important feature of an equation is its ability to predict data from a minimum of experimental points. Therefore the need for a minimum of experimental parameters in the equation.

In this respect the LEMF equation is superior to the NRTL equation since it can predict miscible and immiscible behavior with equal or better accuracy than the NRTL equation with the value of α set according to the rules of Renon and Prausnitz.

Compared to the Wilson equation, the LEMF equation has the advantage of being able to describe immiscible behavior which the former does not. As for miscible systems, both equations offer practically the same degree of accuracy.

APPENDIX A

COMPUTATIONAL METHODS

The computer programs used during the course of our work are presented in appendix B. Here we present a brief description of the programs, their purpose and use.

1. PROGRAM ATHENE

This program is used for the calculation of binary activity coefficients and for the prediction of ternary vapor-liquid equilibrium. The CALLING PROGRAM and subroutine TERGAM which calculates ternary activity coefficients using the NRTL and LEMF equations were developed during the course of our work. All other subroutines used were previously developed by Prausnitz et. al., (25) and were adopted with minor modifications. The program consists of the following subroutines.

SUBROUTINE BUBLE P

This subroutine calculates vapor phase compositions and total pressure from liquid phase compositions and temperature data. Essentially the program begins by setting the total pressure P and the fugacity coefficient in the vapor phase equal to 1. Then in statement 520 the temperature, liquid phase compositions and experimental vapor phase compositions, if available, are read in. Vapor phase compositions are read only for calculating the error of the predictions. The subroutine then calls subroutines VIRIAL, RSTATE and TERGAM. This provides the program with the reference-state properties of the pure liquids at the temperature in question and with the multicomponent activity coefficients.

The program then enters an iteration loop and calculates the vapor phase fugacity $\hat{f}_i$, for the first time, as follows

$$\hat{f}_i^{\,v} = x_i \gamma_i^{(o)} P^s \, e^{\left[\frac{B_{ii}P^s + V^L(P-P^s)}{RT}\right]} \quad (1)$$

where γ_i the multicomponent activity coefficient is calculated by subroutine TERGAM. Vapor phase compositions and the total pressure are calculated as follows

$$Y_i = \frac{\hat{f}_i^{\,v}}{P\,\phi_i^V} \quad (2)$$

$$P = \sum_i^n \frac{\hat{f}_i^{\,v}}{\phi_i^V} \quad (3)$$

The program then checks the new estimated pressure against the previous value POLD. If this difference falls below a preset tolerance the programs checks if $\sum_i^n y_i =$ SUMY = 1. If a value of 1 for SUMY is obtained the results are printed and the program goes on to calculate the next point.

Had the program found the difference between P and P OLD above the allowed tolerance it would have called subroutine PHIMIX for the 1st time to evaluate the vapor phase fugacity coefficients at the new pressure. The program will then begin a new iteration by calculating $\hat{f}_i$.

Had the program found that SUMY ≠ 1 it would have called PHIMIX to recalculate Y and P only. The output of this subroutine gives for each point the pressure, temperature, liquid phase compositions, experimental vapor phase compositions, calculated vapor phase composition, error of prediction and the activity coefficient of each component. At the end the program prints out the average absolute error of the predictions for each component.

SUBROUTINE GAMMA 4

This subroutine evaluates binary activity coefficients for the liquid phase from X–Y, temperature and pressure data. Basically Eq. II-76 is used for this purpose. This subroutine calls subroutines VIRIAL, RSTATE and PHIMIX and reads the following data: NPOINT = number of points in the system. If NPOINT = 0 the subroutine will not be executed and control will return to the calling program; NPUNCH = 01 if punched output is desired otherwise use 00; NPC = 01 if compositions are in mole %. If in mole fractions use 00; SYS = name of system; X = liquid phase compositions; Y = vapor phase composition and PT = total pressure.

On output the program gives the pressure, temperature, liquid phase composition, vapor phase composition and the activity coefficient for each binary component.

SUBROUTINE INPUT

This subroutine is used to read pure component properties. In addition the constants for the equation

$$V^L = C_1 + C_2T + C_3T^2 \tag{4}$$

giving liquid molar volumes in function of temperature and the critical temperature, pressure and volume of the binary mixture are calculated. The first card read by this subroutine sets the value of some control parameters as follows: NCOMP = number of components; NLIGHT = number of components to be treated in the unsymetric convention; NACTCO = number of parameters per pair of components. Next the following pure component properties are read for each component. Critical temperature, pressure and volume; OMEGA, the accentric factor as per Eq. II-78; OMEGAH the accentric factor of the polar component's homorph; DIPOLE the dipole moment; ETA the vapor phase association constant and the identification of the component. Then, three temperatures and three volumes are read in to calculate the constants in e.q. (4) and finally the constants (CPSAT) for the vapor pressure equation.

$$\ln P = C_1 + \frac{C_2}{C_3 + T} + C_4 T + C_5 T^2 + C_6 \ln T \qquad (5)$$

are read in.

There is no output from this subroutine. All information is transmitted to other subroutines through common statements.

SUBROUTINE PHIMIX

This subroutine calculates the vapor phase fugacity coefficients from the VIRIAL equation of state (II-39) truncated after the second VIRIAL coefficient.

$$\frac{PV}{RT} = 1 + \frac{B}{V} \qquad (6)$$

This is a quadratic equation in the molar volume V and its solution may yield imaginary roots. When this situation is found the program reverts to the less desirable pressure series.

$$\frac{PV}{RT} = 1 + \frac{BP}{RT} \tag{7}$$

which always yields a solution for V.

The argument MARK is used to signal the program when the pressure series must be used.

When the volumes series is used, the fugacity coefficient is given by

$$\ln \phi_i = \frac{2}{V_m} \sum_{j=1}^{n} Y_j B_{ij} - \ln Z_m \tag{8}$$

If the pressure series is used instead, the expression for the fugacity coefficient is given by

$$\ln \phi_i = \left[2 \sum_{j=1}^{n} Y_j B_{ij} - B_m \right] \frac{P}{RT} \tag{9}$$

Since the fugacity coefficient is a function of temperature pressure and composition, it must be recalculated everytime any of this variables change. As a result this subroutine is the most often recalled subroutine in the program.

SUBROUTINE RSTATE

This subroutine calculates the liquid reference state fugacity $f_i^{\circ(P^\circ)}$ and partial molal volumes $\overset{L}{V_i}$ of each component. For subcritical components the program calculates the fugacity of the saturated liquid corrected to zero pressure. For supercritical components, if the reduced temperature is not much greater than 1, the component is treated as a hypothetical liquid or pseudo condensable component, the reference fugacity is found by extrapolation and the partial molal volume is an estimated partial molal volume at infinite dilution. If the reduced temperature is much higher than 1, the component is treated as a non condensable gas and the reference fugacity is given by Henry's constant for the component in a chosen reference solvent. The partial molal volumes are obtained from experimental data at infinite dilution.

SUBROUTINE TERGAM

This subroutine calculates multicomponent activity coefficient from the binary parameters according to Eq. (V-2).

SUBROUTINE VIRIAL

This subroutine calculates the VIRIAL coefficients B_{ij} for all possible pairs of pure components.

PROGRAM JACKIE

This program is used to calculate binary parameters for the expressions for the activity coefficients. The program consists of a CALLING PROGRAM and several subroutines.

CALLING PROGRAM

The calling program reads the data, sets the value for the arguments in LSQ2 and prints the results. The program begins by setting the value of switch, an integer variable used to select one of the several equations studied, then it reads SYS; the name of system; REF; the literature reference; ALFA12; the value of ALPHA in the NRTL equation; N; the number of data points; T; the temperature if the data is isothermal otherwise use T = –500.0; NLOG = 00 if activity coefficients are reported as such, if reported as the log use NLOG = 01. If the data is isobaric the program now reads the temperature corresponding to each data point and then continues by reading X_i = the mole fraction of component 1; G1OBS and G2OBS, the activity coefficients of components 1 and 2; CODE = 01 or 02 according to the data available for evaluation of molar volumes and energies of vaporization. If for the pure components there is data on the molar volumes at three different temperatures and the constants for the vapor pressure equation are known then use code = 02 and the program will read this data and call subroutines VOLINT and DELTAU for evaluation of molar volumes and energies of vaporization. If this data is not available then use code = 01 and the program will read VA and VB, the molar volumes at a given temperature; FL1 and FL2 the nonplar solubility parameters and TAOU1 and TAOU2 the polar solubility parameters. Then the energy of vaporization is calculated as follows

$$\Delta U_1 = V_1 \left[(FL1)^2 + (TAOUI)^2 \right] \qquad (10)$$

The program then continues by setting the initial values for the parameters in the equation for the activity coefficients XT (1) and XT (2), and by defining other arguments of LSQ2 (see subroutine LSQ2).

On output the program prints the name of the system, the reference, the best set of parameters. the Std. Deviation of calculated activity coefficients, and tabulates the mole fraction, the temperature, the observed and calculated activity coefficients and the % error for each point.

SUBROUTINE VOLINT (TEMP, VOL, T. VA, VB)

This subroutine is called by subroutine FN whenever necessary to calculate liquid molar volumes in function of temperature according to the following equation

$$V = a + bT + cT^2 \tag{11}$$

where

$$c = \frac{(T_3-T_1)(V_2^L-V_1^L)-(V_3^L-V_1^L)(T_2-T_1)}{(T_2^2-T_1^2)(T_3-T_1) - (T_3^2-T_1^2)(T_2-T_1)}$$

$$b = \frac{(V_2^L-V_1^L) - c(T_2^2 - T_1^2)}{T_2 - T_1}$$

$$a = V_1^L - bT_1 - cT_1^2$$

A compilation of molar volumes vs. temperature can be found in Ref. (25).

SUBROUTINE DELTAU (T, C, G11, G22)

This subroutine calculates pure component energies of vaporization from the constants for the vapor pressure equation as follows

From thermodynamics we have for the energy of vaporization.

$$\Delta U = \Delta H - \Delta PV \qquad (12)$$

And since liquid molar volumes are small compared to vapor molar volumes we can write

$$\Delta U = \Delta H - RT \qquad (13)$$

Now the Classious Clapeyron equation is given by

$$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2} \qquad (14)$$

And combining (13) and (14)

$$\Delta U = RT^2 \frac{d\ln P}{dT} - RT \qquad (15)$$

If we now introduce the vapor pressure equation

$$\ln P = C_1 + \frac{C_2}{C_3 + T} + C_4T + C_5T^2 + C_6\ln T \qquad (16)$$

into equation (15) we obtain

$$\Delta U = RT^2 \left[\frac{-C_2}{(C_3 + T)^2} + C_4 + \frac{C_6 - 1}{T} + 2C_5T \right] \qquad (17)$$

which is the equation used in the program. Subroutine DELTAU is called by subroutine FN whenever required.

SUBROUTINE FN (YY,XT)

This subroutine calculates activity coefficients and the std. deviation when called by LSQ2 to test a new set of parameters. Then according to the std. deviation obtained, LSQ2 calculates a new set of parameters and calls FN again. The cycle is repeated until the error falls below a predetermined level or until a specific number of iterations have been performed.

SUBROUTINE LSQ2 (52)

This subroutine, in general, minimizes a function of several independent variables. In our case the function to be minimized is the std. deviation of calculated activity coefficients and the independent variables are the parameters in the equation for the activity coefficients. This subroutine calls subroutine FN which is the one containing the equation under consideration. Subroutine FN calculates the activity coefficients, the error of the calculated activity coefficient and the std. deviation. From the new value for the std. deviation thus obtained, LSQ2 calculates a new value for the parameters. As previously mentioned the cycle is repeated until the std. deviation falls below a stablished limit or until the specified number of iterations have been performed. This subroutine contains the following arguments which must be specified by the calling program.

XT, a vector containing values of the independent variable, in this particular case the parameters of the equation for the activity coefficients. Initial values for these parameters must be provided by the calling program. Our experience indicates that for the LEMF or NRTL equations. initial values of XT (1) = 0 and XT (2) = 0 are the best choice. On output from LSQ2, XT contains the set of parameters which best fits the data.

X, a storage matrix containing values of the independent variable.

DX, an scaler increment applicable to each independent variable.

Y, a vector of M1 components containing values of the dependent variable, the std. deviation in the present case. On exit from LSQ2, Y (1) is the standard deviation corresponding to the best value of XT.

M, the number of independent variables, that is the number of parameters to be determined.

M1 = M + 1

M3 = M + 3

L, the maximum number of iterations.

E, the allowable error.

PROGRAM OTILIA

This program is used for the prediction of activity coefficients from binary solubility data. In this case the criteria of equilibrium is used to calculate the best value of the parameters in the equation for activity coefficients. In other words the function to be minimized is

$$Z = (X_1'\gamma_1' - X_1''\gamma_1'')^2 + (X_2'\gamma_2' - X_2''\gamma_2'')^2 \tag{18}$$

Which follows from the consideration that at equilibrium we must have

$$\begin{aligned} X_1'\gamma_1' &= X_1''\gamma_1'' \\ X_2'\gamma_2' &= X_2''\gamma_2'' \end{aligned} \tag{19}$$

Therefore we take as parameters for the equation the set which satisfies Eq. (19)

Except for the above, this program is very similar to "JACKIE" and deserves no further consideration.

PROGRAM LLEQUM

This program is used for the prediction of ternary liquid-liquid equilibrium from knowledge of the binary parameters. The program consists of a calling program and several subroutines as follows.

CALLING PROGRAM

The calling program reads the data i.e. SYS, the name of the system; COM, any appropriate comments; NCOMP, the number of components, CATCO, the binary parameters; ALFA, the value of ALPHA in the NRTL equation, for the LEMF equation this value is -1; T, the temperature of the system; X11, a chosen liquid composition and X12, X21 and X22, initial guesses for the remaining independent compositions of the phases in equilibrium. On output the program prints the compositions which best fits the condition of equilibrium.

SUBROUTINE FN (YY,XT)

In this case subroutine FN calculates ternary activity coefficients from the binary parameters and calculates the error corresponding to the predicted compositions as follows

$$Y = \sum_{i}^{n} |(x_i' \gamma_i' - x_i'' \gamma_i'')| \qquad (20)$$

This error is returned to LSQ2 which finds new values for the compositions X12, X21 and X22 and calls FN again. The cycle is repeated until Y equals zero or falls below a predetermined limit.

Those compositions satisfying E q. (20), since they satisfy the condition of equilibrium must correspond to the phases in equilibrium. If any of the compositions calculated by LSQ2 falls outside the range $0 \leqslant X \leqslant 1$, FN returns a large error, thus forcing LSQ2 to stay within the range 0 to 1.

SUBROUTINE LSQ2

This subroutine is the same as that used in program JACKIE except that here we have three independent variables instead of two, i.e., the compositions X_{12}, X_{21} and X_{22}.

APPENDIX B

COMPUTER PROGRAM LISTINGS

```
      PROGRAM ATHENE
C
C   THIS PROGRAM CALCULATES BINARY GAMMAS AND PREDICTS
C   TERNARY GAMMAS FROM BINARY PARAMETERS
C
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9)
C
      COMMON/GIJS/G12S,G23S,G31S,ALFA,G21S,G32S,G13S
C
C
      COMMON/COMWIL/G11,G22,G12SUB,STEP,VA,VB,X2(30),Y2(30),COM(25),G12,
     1SYS(25),N,NUM,LL,NSYST,SALFA,NCODE,G21
C
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),G(9),NPOINT,NSS,TEMP,GT(9,9)
C
C
      COMMON/NPTTRN/NTPOIN
C
C
   15 FORMAT(1H1,/////)
   16 FORMAT(1H0,T20,'  MATRIX OF PARAMETERS FOR THE NRTL EQ.')
   17 FORMAT(1H0,T20,3F15.2)
   18 FORMAT(1H0,T20,'  MATRIX OF ALPHA VALUES FOR THE NRTL EQ.')
   19 FORMAT(20A4)
   20 FORMAT(1H0,T10,20A4)
   21 FORMAT(8F10.3)
   22 FORMAT(3I2)
   24 FORMAT('0',T10,'G12 =',F10.3,T35,'G23 =',F10.3,T60,'G31 =',F10.3)
   25 FORMAT(F10.2)
  140 FORMAT(9I2)
  141 FORMAT(10F8.3)
C
C
C  NSYST = # OF BINARY SYSTEMS
C  NCOMP = NSYST FOR PREDICTION OF V-L EQUILIBRIUM. FOR EVALUATION OF
C  GAMMAS ONLY, USE 01
C  NGAMMA = 00 FOR PREDICTION OF V-L EQUILIBRIUM. FOR EVALUATION OF
C  GAMMAS USE 01
C
      DO 200 ISYS = 1,9
      READ(97,19)(SYS(I),I=1,20)
      READ(97,19)(COM(I),I=1,20)
      READ(97,25) T
      READ 22, NSYST,NCOMP,NGAMMA
      READ 140, (MM(I),I = 1,NSYST)
C  READ BINARY PARAMETRS IN MATRIX FORM
C  FIRST SUBSCRIPT INDICATES ROW SECOND SUBSCRIPT INDICATES COLUMN
      DO 50 I = 1,NCOMP
```

```
   50 READ 21,(GT(I,J),J = 1,NCOMP)
C  READ ALFA VALUES IN MATRIX FORM
C  FOR THE LEMF EQUATION ALFA = -1.0
      DO 51 I = 1,NCOMP
   51 READ 21,(ALFA(I,J),J = 1,NCOMP)
      DO 52 I = 1,NCOMP
   52 GT(I,I) = 0.0
      IF(T .GT. -273.) GO TO 150
      NN = MM(1)
      DO 149 I = 1,NSYST
      READ 141,(TEMP(I,J),J = 1,NN)
      DO 148 J = 1,NN
  148 TEMP(I,J) = TEMP(I,J) + 273.2
  149 NN = MM(I+1)
      GO TO 153
  150 NN = MM(1)
      DO 152 I = 1,NSYST
      DO 151 J = 1,NN
      TEMP(I,J) = T
  151 TEMP(I,J) = TEMP(I,J) + 273.2
  152 NN = MM(I+1)
  153 CONTINUE
C
C  CALCULATION OF BINARY GAMMAS
C
      NCODE = 0
      DO 100 NS=1,NSYST
      NSS = NS
      CALL INPUT
      CALL GAMMA4
      IF(NPOINT)100,100,120
  120 CONTINUE
      DO 5 I=1,NPOINT
      X2(I)=1.-X1(I)
      Y2(I)=1.-Y1(I)
    5 CONTINUE
  100 CONTINUE
      IF(NGAMMA .EQ. 1)GO TO 200
C
C  PREDICTION OF MULTICOMPONENT GAMMAS AND VAPOR PHASE COMPOSITIONS
C
      CALL INPUT
      PRINT 15
      PRINT 20,(COM(I),I = 1,20)
      PRINT 20,(SYS(I),I=1,20)
      PRINT 16
      PRINT 17,((GT(I,J),J=1,NCOMP),I=1,NCOMP)
      PRINT 18
      PRINT 17,((ALFA(I,J),J=1,NCOMP),I=1,NCOMP)
      CALL BUBLP
```

```
  101   200   CONTINUE
  102         STOP
  103         END
```

```
      SUBROUTINE BUBLP
C
      DIMENSION ERROR(9),DELTA(9),YEXP(9)
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9)
C
      COMMON/XBUB/XT(15)
C
C
      COMMON/G4OLD/
     1 NCOMP,NLIGHT,NACTCO,TCRIT(4,4),PCRIT(4,4),VCRIT(4)  ,OMEGA(4),
     2 IDENT(4,2),PSAT(4),GAMMA(6),X(12),Y(12),SUMX,SUMY,P,TOLD,PHI(12),
     3 B(4,4),BMIX,ZMIX,F(12),FREFER(12),NREFER(12),OMEGAH(10),DIPOLE(10
     4),ETA(4),NCRIT
C
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),G(9),NPOINT,NSS,TEMP,GT(9,9)
C
      COMMON/GAMTRN/GAMT(15)
C
      COMMON/CPSAT/CPSAT(10,6)
C
C
      COMMON/NPTTRN/NTPOIN
      COMMON/PHIBUB/ VMIX
C
C
C
C     MAIN PROGRAM FOR CALCULATION OF PRESSURE AND VAPOR COMPOSITION
C     FROM LIQUID COMPOSITION AND TEMPERATURE DATA
C
C
C
C     GUESS INITIAL PRESSURE  FOR FIRST ITERATION
C
 6960 FORMAT('0',T60,' ENTER BUBLP  ')
      MPOINT = 0
      DO 2 I = 1,NCOMP
      ERROR(I) = 0.0
    2 CONTINUE
      PRINT 1002
      P = 1.0
  500 CONTINUE
      DO 510 I = 1,NCOMP
      PHI(I) = 1.0
  510 CONTINUE
  520 READ 910, T,X(1),X(2),YEXP(1),YEXP(2)
      T = 273.2 + T
      X(3) = 1.0 - X(1) - X(2)
      YEXP(3) = 1.0 - YEXP(1) - YEXP(2)
```

```
      MPOINT = MPOINT + 1
 6902 CONTINUE
      DO 6901 I=1,NCOMP
      XT(I)=X(I)
 6901 CONTINUE
      IF  (T)        660, 500, 530
  530 RT = 82.057 * T
      MARK = -1
      CALL VIRIAL
      CALL RSTATE
      CALL TERGAM
      TOLO = T
C
C     BEGIN AN ITERATIVE PROCEDURE TO FIND A PRESSURE AND THE
C     CORRESPONDING VAPOR PHASE FUGACITY COEFFICIENTS
C
  540 DO 550 I = 1, NCOMP
      F(I) = X(I) * GAMT  (I) * FREFER(I) * EXP (VLIQ(I) * P / RT)
  550 CONTINUE
  560 SUMY = 0.0
      SUMP = 0.0
      DO 570 I = 1,NCOMP
      Y(I) = F(I) / (P * PHI(I))
      SUMY = SUMY + Y(I)
      SUMP = SUMP + F(I) / PHI(I)
  570 CONTINUE
C
C     CHECK TO SEE IF PRESSURE IS CONSTANT
C
      POLD = P
      P = SUMP
      IF (ABS ((POLD - P) / P ) - 1.0E-5) 585, 585, 580
  580 CALL PHIMIX (MARK)
      IF (VMIX) 610, 610, 540
C
C     CHECK TO SEE WHETHER SUMY IS UNITY
C
  585 IF (ABS (SUMY - 1.0) - 1.0E-5) 610,610,590
  590 CALL PHIMIX (MARK)
      IF (VMIX) 610, 610, 560
  610 CONTINUE
      IF(MARK)521,521,655
  521 CONTINUE
      DO 1 I = 1,NCOMP
      DELTA(I) = YEXP(I) - Y(I)
    1 CONTINUE
      DO 10 I = 1,NCOMP
      ERROR(I) = ABS(DELTA(I)) + ERROR(I)
   10 CONTINUE
      PRINT 1003,P,T,(I,X(I),YEXP(I),Y(I),DELTA(I),GAMT(I),I = 1,1)
```

```
      PRINT 1006,    (I,X(I),YEXP(I),Y(I),DELTA(I),GAMT(I),I = 2,NCOMP)
      PRINT 1004
      GO TO 520
   26 FORMAT(1H1,T10,'T E R N A R Y  D A T A ',  ////)
   27 FORMAT(1H0,T10,'X =',F10.3,  5X,'Y =',F10.3, 5X,'P =',F10.3)
  655 PRINT 923
      GO TO 520
  910 FORMAT(F8.4,2F8.5,8X,6F8.5)
  923 FORMAT (1H0,T10,'VOLUME SERIES VIRIAL EQUATION HAS IMAGINARY SOLUT
     1IONS -- PRESSURE SERIES USED FOR FINAL CALCULATION',//)
 1000 FORMAT('1',T4,'PRESSURE',T20,'SUMY',T25,'COMPONENT',T41,'X',
     1 T54,'Y',T65,'F',T75,'FREFER',T89,'GAMMA',T99,'VLIQ',T112,'B',T125
     2 ,'PHI',//)
 1001 FORMAT('0',T4,F10.8,F10.4,8X,I2,8F12.5)
 1002 FORMAT(1H1,24X,'P',13X,'T',8X,'COMP',7X,'X',8X,'YEXP',6X,'YCAL',
     15X,'DELTA',10X,'GAMMA')
 1003 FORMAT(1H0,18X,F10.5,F15.5,5X,I2,2X,4F10.5,F15.5)
 1004 FORMAT(1H0)
 1005 FORMAT(1H0,T20,'AVERAGE ABSOLUTE ERROR FOR COMP',I2,'=',
     1F10.5,/,(50X,I2,'=',F10.5,/))
 1006 FORMAT(1H0,48X,I2,2X,4F10.5,F15.5)
  660 CONTINUE
      DO 12 I = 1,NCOMP
      ERROR(I) = ERROR(I)/MPOINT
   12 CONTINUE
      PRINT 1005,(I,ERROR(I),I = 1,NCOMP)
69601 FORMAT('0',T60,' LEAVE BUBLP  ')
      RETURN
      END
```

```
      SUBROUTINE GAMMA4
C
C
C  THIS ROUTINE EVALUATES BINARY GAMMAS FROM X-Y-P-T DATA
C  VAPOR PHASE CORRECTIONS ARE MADE BY THE PRAUSNITZ METHOD
C
C
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9),SYS(20)
C
      COMMON/G4OLD/
     1 NCOMP,NLIGHT,NACTCO,TCRIT(4,4),PCRIT(4,4),VCRIT(4)   ,OMEGA(4),
     2 IDENT(4,2),PSAT(4),GAMMA(6),X(12),Y(12),SUMX,SUMY,P,TOLD,PHI(12),
     3 B(4,4),BMIX,ZMIX,F(12),FREFER(12),NREFER(12),OMEGAH(10),DIPOLE(10
     4),ETA(4),NCRIT
C
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),G(9),NPOINT,NSS,TEMP,GT(9,9)
C
C
      COMMON/CPSAT/CPSAT(10,6)
C
C
  450 FORMAT(F6.4,2F6.3)
  500 FORMAT(20A4)
  501 FORMAT(1H0,T20,20A4)
  502 FORMAT(1H0,11X,'P',12X,'T',14X,'X',14X,'Y',12X,'GAMMA1',9X,
     1'GAMMA2')
  503 FORMAT(1H0,F15.5,F12.2,4F15.4)
  910 FORMAT (10F8.4)
 6901 FORMAT(3I2)
 6903 FORMAT('1',T50,'RESULTS FROM GAMMA 4',////)
 6904 FORMAT(1H0,T10,6(F10.4,10X))
 6960 FORMAT('0',T60,' ENTER GAMMA4 ')
      SUMY=1.0
      SUMX=1.0
      R= 82.057
C
C  NPOINT = # OF POINTS IN SYSTEM
C  NPUNCH = 01 IF PUNCHED OUTPUT IS DESIRED. OTHERWISE USE 00
C  NPC = 01 IF COMPOSITIONS ARE IN MOLE %. IF IN MOLE FRACTIONS USE 00
C
      READ 6901,NPOINT,NPUNCH,NPC
      IF(NPOINT)600,600,120
  120 CONTINUE
      READ 500, (SYS(I),I = 1,20)
      PRINT 6903
      PRINT 501,(SYS(J),J = 1,20)
      PRINT 502
      DO 6902 I=1,NPOINT
```

```
      T = TEMP(NSS,I)
      TOLD=T
      READ 910, X(1),Y(1),PT(1)
      IF(NPC .EQ. 1)X(1) = X(1)/100.
      IF(NPC .EQ. 1)Y(1) = Y(1)/100.
      X(2)=1.-X(1)
      Y(2)=1.-Y(1)
      PT(1) = PT(1)/760.
      P=PT(1)
      CALL VIRIAL
      CALL RSTATE
      MARK=-1
C    BEGIN AN ITERATION TO FIND VAPOR PHASE FUGACITY COEFFICENTS
  560 CALL PHIMIX (MARK)
      DO 6905 JD=1,2
             GG=PT(1 )*Y(JD)*PHI(JD)/(X(JD)*FREFER(JD)*EXP(VLIQ(JD)*PT
     1(1 )/(R*T)))
      GAMMA(JD)=GG
 6905 CONTINUE
      PRINT 503, PT(1),T,X(1),Y(1),GAMMA(1),GAMMA(2)
      IF(NPUNCH .EQ. 1)PUNCH 450,X(1),GAMMA(1),GAMMA(2)
      X1(I)=X(1)
      Y1(I)=Y(1)
      PT(I)=PT(1)
      G1OBS(I)=GAMMA(1)
      G2OBS(I)=GAMMA(2)
 6902 CONTINUE
  600 CONTINUE
69601 FORMAT('0',T60,' LEAVE GAMMA4 ')
      RETURN
      END
```

```
      SUBROUTINE INPUT
C
C  SUBROUTINE TO READ IN ALL PURE COMPONENT DATA
C
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9)
C
      COMMON/NCOMP/NCOMP2
C
C
      COMMON/CPSAT/CPSAT(10,6)
C
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),G(9),NPOINT,NSS,TEMP,GT(9,9)
C
C
      COMMON/G4OLD/
     1 NCOMP,NLIGHT,NACTCO,TCRIT(4,4),PCRIT(4,4),VCRIT(4)  ,OMEGA(4),
     2 IDENT(4,2),PSAT(4),GAMMA(6),X(12),Y(12),SUMX,SUMY,P,TOLD,PHI(12),
     3 B(4,4),BMIX,ZMIX,F(12),FREFER(12),NREFER(12),OMEGAH(10),DIPOLE(10
     4),ETA(4),NCRIT
C
C
6960  FORMAT('0',T60,' ENTER INPUT  ')
C   NCOMP=2   NLIGHT=0   NACTCO=2
      READ 902, NCOMP, NLIGHT, NACTCO
C
C
      N1 = NLIGHT + 1
      NCOMP1 = NCOMP - 1
      NCOMP2=NCOMP
C
C
      DO 90 I=1,NCOMP
     0READ 903,TCRIT(I,I),PCRIT(I,I),VCRIT(I),OMEGA(I),OMEGAH(I),DIPOLE
     1(I), ETA(I), IDENT(I,1), IDENT(I,2)
      IF(DIPOLE(I)) 33, 33, 36
   33 OMEGAH(I) = OMEGA(I)
   36 READ 904,T1,V1,T2,V2,T3,V3
      READ 904, (CPSAT(I,J), J=1,6)
   39 IF(T3) 40,40,70
   40 CVLIQ(I,3)=0.0
      IF(T2) 50,50,60
   50 CVLIQ(I,2)=0.0
      CVLIQ(I,1)=V1
      GO TO 90
   60 CVLIQ(I,2)=(V2-V1)/(T2-T1)
      CVLIQ(I,1)=V1-CVLIQ(I,2)*T1
      GO TO 90
   700CVLIQ(I,3) = ((T3-T1) * (V2-V1) - (V3-V1) * (T2-T1)) / ((T
```

```
     12**2 - T1**2) * (T3-T1) - (T3**2-T1**2) * (T2-T1))
      CVLIQ(I,2)=((V2-V1)-CVLIQ(I,3)*(T2**2-T1**2))/(T2-T1)
      CVLIQ(I,1)=V1-CVLIQ(I,2)*T1-CVLIQ(I,3)*T1**2
   90 CONTINUE
      PRINT 904,(( CVLIQ(I,K),K = 1,3),I = 1,2)
C
C     CALCULATE CRITICAL PROPERTIES FOR BINARY INTERACTIONS
C
      DO 110 I=1,NCOMP1
      DO 100 J=I,NCOMP
      TCRIT(I,J) = SQRT (TCRIT(I,I) * TCRIT(J,J))
     OPCRIT(I,J) = 4.0 * TCRIT(I,J) * (PCRIT(I,I) * VCRIT(I) / TCRIT(I,I
     1) + PCRIT(J,J) * VCRIT(J) / TCRIT(J,J)) / (VCRIT(I)**0.33333333 +
     2 VCRIT(J)**0.33333333)**3
      TCRIT(J,I)=TCRIT(I,J)
      PCRIT(J,I)=PCRIT(I,J)
  100 CONTINUE
  110 CONTINUE
  901 FORMAT (12A3)
  902 FORMAT (3I4)
  903 FORMAT(7F8.4, 16X, 2A4)
  904 FORMAT(F12.6,F12.5,4F12.6)
  905 FORMAT (8F8.4)
69601 FORMAT('0',T60,' LEAVE INPUT  ')
      RETURN
      END
```

FORTRAN IV030 SOURCE PROGRAM PHIMIX SUBROUTINE

```
      SUBROUTINE PHIMIX (MARK)
C
C     SUBROUTINE FOR CALCULATION OF VAPOR PHASE FUGACITY COEFFICENTS
C
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9)
C
      COMMON/CPSAT/CPSAT(10,6)
C
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),G(9),NPOINT,NSS,TEMP,GT(9,9)
C
C
      COMMON/G4OLD/
     1 NCOMP,NLIGHT,NACTCO,TCRIT(4,4),PCRIT(4,4),VCRIT(4)  ,OMEGA(4),
     2 IDENT(4,2),PSAT(4),GAMMA(6),X(12),Y(12),SUMX,SUMY,P,TOLD,PHI(12),
     3 B(4,4),BMIX,ZMIX,F(12),FREFER(12),NREFER(12),OMEGAH(10),DIPOLE(10
     4 ),ETA(4),NCRIT
C
      COMMON/PHIBUB/ VMIX
C
C  CALCULATE MOLAR VOLUME OF THE VAPOR
 6960 FORMAT('0',T60,' ENTER PHIMIX ')
      PORT=P/(82.057*T)
      BMIX=0.0
      DO 15 I=1,NCOMP
      DO 10 J=1,NCOMP
      BMIX=BMIX+Y(I)*Y(J)*B(I,J)
   10 CONTINUE
   15 CONTINUE
      BMIX=BMIX /SUMY**2
      IF (MARK) 20,20,22
   20 SQARG=0.25 + BMIX*PORT
C  IF BMIX*P/RT IS MORE NEGATIVE THAN 0.25, THE PRESSURE SERIES VIRIAL
C  EQ. MUST BE USED, THE ARGUMENT MARK IS USED TO COMUNICATE THIS
C  TO THE MAIN PROGRAM
      IF (SQARG) 22,25,25
   22 VMIX=BMIX +1. /PORT
      ZMIX=PORT*VMIX
      DO 24 I=1,NCOMP
      SUMB=0.0
      DO 23 J=1,NCOMP
      SUMB =SUMB +Y(J)*B(I,J)
   23 CONTINUE
       SUMB=SUMB / SUMY
      PHI(I)=EXP ((2.0*SUMB-BMIX)*PORT)
   24 CONTINUE
      MARK=MARK+1
      RETURN
   25 VMIX=(0.5+SQRT (SQARG))/PORT
```

```
      ZMIX=PORT*VMIX
C  CALCULATIUN OF FUGACITY COEFFICIENTS
      DO 40 I=1,NCOMP
      SUMB=0.0
      DO 30 J=1,NCOMP
      SUMB=SUMB + Y(J)*B(I,J)
   30 CONTINUE
      SUMB=SUMB /SUMY
      PHI(I)=EXP (2.0*SUMB/VMIX)/ZMIX
   40 CONTINUE
69601 FORMAT('0',T60,' LEAVE PHIMIX ')
       RETURN
      END
```

FORTRAN IV G 30 SOURCE PROGRAM

```
      SUBROUTINE RSTATE
C
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9)
C
      COMMON/CPSAT/CPSAT(10,6)
C
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),G(9),NPOINT,NSS,TEMP,GT(9,9)
C
C
      COMMON/G4OLD/
     1 NCOMP,NLIGHT,NACTCO,TCRIT(4,4),PCRIT(4,4),VCRIT(4)   ,OMEGA(4),
     2 IDENT(4,2),PSAT(4),GAMMA(6),X(12),Y(12),SUMX,SUMY,P,TOLD,PHI(12),
     3 B(4,4),BMIX,ZMIX,F(12),FREFER(12),NREFER(12),OMEGAH(10),DIPOLE(10
     4 ),ETA(4),NCRIT
C
C
C
C
C
      N1=NLIGHT + 1
  290 RT = 82.057 * T
C
C     CALCULATE THE REFERENCE FUGACITY AND LIQUID VOLUME OF ALL COMPONENTS
C     BELOW THEIR CRITICAL POINT,
C
      NCRIT=NLIGHT
      DO 380 J=N1, NCOMP
      TR=T /TCRIT(J,J)
      W= OMEGA(J)
      IF (TR-1.0) 295, 295, 370
  295 IF (CPSAT(J,1)) 300,310, 300
  3000PSAT(J) = EXP  (CPSAT(J,1) + CPSAT(J,2) / (CPSAT(J,3) + T) + CPSAT
     1(J,4) * T + CPSAT(J,5) * T**2 + CPSAT(J,6) * LOG (T))
      GO TO 320
  310 PSAT(J)=PCRIT(J,J)*VAPRES(TR,W)
  320 IF (TR-0.56) 330, 330, 340
  330 PHIS = EXP  (B(J,J) * PSAT(J) / RT)
      GO TO 360
  340 PHIS=EXP(PHIS0F(TR)+W*PHIS1F(TR))
  360 VLIQ(J) = CVLIQ(J,1) + CVLIQ(J,2) * T + CVLIQ(J,3) * T**2
      FREFER(J) = PSAT(J) * PHIS * EXP ( -VLIQ(J) * PSAT(J) / RT)
   20 FORMAT('0',T20,'FROM RSTATE',/,'0' ,T10,'PSAT',F20.5,T60,'FRER',
     1F20.5,////)
      GO TO 380
  370 NCRIT=J
  380 CONTINUE
  430 CONTINUE
69601 FORMAT('0',T60,' LEAVE RSTATE ')
```

```
 503 6960  FORMAT('0',T60,' ENTER RSTATE ')
 504       RETURN
 505       END
```

```
      SUBROUTINE TERGAM
C
C  THIS SUBROUTINE PREDICTS TERNARY GAMMAS FROM BINARY PARAMETERS USING
C  THE NRTL EQUATION
C
C      THIS ROUTINE EVALUATES TERNARY GAMMAS USING BINARY CONSTANTS
C      FROM THE NRTL EQUATION.
C
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9)
      DIMENSION TADU(3,3),G(3,3),A(3),B(3),C(3),
     1D(3),CC(3),AA(3),BB(3),GLC(3)
C
      COMMON/GIJS/G12S,G23S,G31S,ALFA,G21S,G32S,G13S
C
C
      COMMON/CPSAT/CPSAT(10,6)
C
C
      COMMON/NCOMP/NCOMP
C
C
      COMMON/COMWIL/G11,G22,G12SUB,STEP,VA,VB,X2(30),Y2(30),COM(25),G12,
     1SYS(25),N,NUM,LL,NSYST,SALFA,NCODE,G21
C
      COMMON/GAMTRN/GAMT(15)
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),GG(9),NPOINT,NSS,TEMP,GT(9,9)
C
C
      COMMON/XBUB/XT(15)
C
C
C
C
 03   FORMAT('0',T20,'FROM TERGAM** GAMT(',I2,')  =',F10.4)
      GMIX = 0.0
      RT=1.987*T
      DO 298 I = 1,NCOMP
      DO 298 J = 1,NCOMP
      ALFA(J,J) = 0.
      ALFA(J,I) = ALFA(I,J)
      TAOU(J,I) = (GT(J,I) - GT(I,I))/RT
      G(J,I) = EXP(-ALFA(J,I)*TAOU(J,I))
 298  CONTINUE
      DO 302 I = 1,NCOMP
      CC(I) = 0
      A(I) = 0.
      B(I) = 0.
      DO 301 J = 1,NCOMP
```

```
       C(J) = 0
       D(J) = 0
       DO 300 K = 1,NCOMP
       IF(J ,GE. 2) GO TO 299
       A(I) = A(I) + TAOU(K,I)*G(K,I)*XT(K)
       B(I) = B(I) + G(K,I)*XT(K)
   299 C(J) = C(J) +XT(K)*TAOU(K,J)*G(K,J)
       D(J) = D(J) + G(K,J)*XT(K)
   300 CONTINUE
       AA(I) = A(I)/B(I)
       BB(J) = C(J)/D(J)
       CC(I) = CC(I) +((XT(J)*G(I,J))/D(J))*(TAOU(I,J) - BB(J))
   301 CONTINUE
       GLC(I) = AA(I) + CC(I)
       GAMT(I) = EXP(GLC(I))
       GMIX = GMIX + RT*(XT(I)*ALOG(XT(I)*GAMT(I)) )
   302 CONTINUE
     5 FORMAT(1H0,T20, ' FREE ENERGY OF MIXING = ',F10.3)
 69601 FORMAT('0',T60,' LEAVE TERGAM ')
  6960 FORMAT('0',T60,' ENTER TERGAM ')
       RETURN
       END
```

```
      SUBROUTINE VIRIAL
C
      DIMENSION TEMP(9,30),MM(9),ALFA(9,9)
C
      COMMON/CPSAT/CPSAT(10,6)
C
C
      COMMON/G4TRAN/T,VLIQ(10),CVLIQ(4,4),X1(30),Y1(30),PT(30),
     1  G1OBS(30),G2OBS(30),G(9),NPOINT,NSS,TEMP,GT(9,9)
C
C
      COMMON/G4OLD/
     1 NCOMP,NLIGHT,NACTCO,TCRIT(4,4),PCRIT(4,4),VCRIT(4)  ,OMEGA(4),
     2 IDENT(4,2),PSAT(4),GAMMA(6),X(12),Y(12),SUMX,SUMY,P,TOLD,PHI(12),
     3 B(4,4),BMIX,ZMIX,F(12),FREFER(12),NREFER(12),OMEGAH(10),DIPOLE(10
     4),ETA(4),NCRIT
C
C
      DIMENSION P2VPF(10,10)
C
C
C     SUBROUTINE FOR THE CALCULATION OF SECOND VIRIAL COEFFICIENTS
C
C
 6960 FORMAT('0',T60,' ENTER VIRIAL ')
      DO 202 I=1,NCOMP
      DO 201 J=1,NCOMP
      TR=T/TCRIT(I,J)
      W=(OMEGAH(I) + OMEGAH(J)) / 2.0
C
C     CALCULATE NONPOLAR SECOND VIRIAL COEFFICIENT FROM
C     CORRELATION OF PITZER AND CURL
C
     OSECVIR = (0.1445 - (0.330 + (0.1385 + 0.0121 / TR) / TR) / TR + W
     1* (0.073 + (0.46 - (0.50 +(0.097 + 0.0073 / TR**5)/TR) /TR) /TR))
C
C  ADD POLAR CONTRIBUTIONS  AT REDUCED TEMPERATURES BELOW 0.95 WHEN
C  REDUCED DIPOLE MOMENT RD IS LARGER THAN 4.0
C
      IF(DIPOLE(I)*DIPOLE(J)) 200,200,100
  100 IF(0.95-TR) 200,200,125
  125 CONTINUE
      RD=100000.*DIPOLE(I)*DIPOLE(J)*PCRIT(I,J)/(TCRIT(I, J)**2)
      IF(RD-4.0) 200,200,135
  135 P2VPF(I,J)=-5.237220+LOG (RD) *(5.665807+LOG(RD)*(-2.133816 +
     1 LOG(RD)*.2525373)) + (5.769770 + LOG(RD)*(-6.181427 + LOG(RD)*
     2 (2.283270 - LOG(RD)*.2649074))) / TR
      SECVIR=SECVIR+P2VPF(I,J)
C
C  ADD CONTRIBUTION FOR MOLECULAR ASSOCIATION
```

```
 C
   150 IF(ETA(I)+ETA(J)) 200,200,175
   175 SECVIR=SECVIR-0.5*(ETA(I)+ETA(J))*EXP(6.6*(0.7-TR))
   200 B(I,J) = SECVIR * 82.057 * TCRIT(I,J) / PCRIT(I,J)
       B(J,I)=B(I,J)
   201 CONTINUE
   202 CONTINUE
 69601 FORMAT('0',T60,' LEAVE VIRIAL ')
       RETURN
       END
```

```
FORTRAN IV030 SOURCE PROGRAM  VAPRES   FUNCTION

  638        FUNCTION VAPRES(TR,OMEGA)
  639        VAPRES=EXP(2.3025*((((-0.3456/TR+1.454)/TR-4.318)/TR+3.209)+OMEGA*
  640       1 (((0.3981/TR-2.524)/TR+2.008)/TR+0.1175)))
  641        RETURN
  642        END
```

```
      FUNCTION FSATOF(TR)
      FSATOF      = (-1.1970522/TR - 1.3785023)/TR + 2.0048841
      RETURN
      END
```

```
FORTRAN IV030 SOURCE PROGRAM  FSAT1F   FUNCTION

          FUNCTION FSAT1F(TR)
          FSAT1F=(-2.7741817/TR+1.5454928)/TR+1.3057555
          RETURN
          END
```

```
FORTRAN IV030 SOURCE PROGRAM  PHISOF   FUNCTION

      FUNCTION PHISOF(TR)
      PHISOF      = (( 0.57335015/TR -3.076574)/TR + 5.6085595)/TR
     1  -3.5021358
      RETURN
      END
```

```
FORTRAN IV030 SOURCE PROGRAM  PHIS1F   FUNCTION

      FUNCTION PHIS1F(TR)
      PHIS1F     = ((((((((((( 0.012089114/TR - 0.015172164)/TR
     1 -0.068603516)/TR +0.024364816)/TR + 0.14936906)/TR + 0.1892703
     2 7)/TR - 0.12147436)/TR -0.1066573)/TR -1.1662283)/TR
     3  +0.12666184)/TR +0.3166137)/TR +4.3538729)/TR -3.7694018
      RETURN
      END
```

FORTRAN IV030 SOURCE PROGRAM

```
      PROGRAM JACKIE
C
C   THIS PROGRAM CALCULATES BINARY PARAMETERS FOR
C   THE NRTL AND LEMF EQUATIONS
C
      INTEGER SWITCH,CODE
C
      DIMENSION  GECAL(20),GEOBS(20),GMCAL(20),GMOBS(20),G1LC(20),
     1G1CAL(20),G2LC(20),G2CAL(20),TS(20),ERROR1(20),ERROR2(20),
     2XT(2),X(2,5),Y(3),JJ(3),A(3,3),TEMP(3,2),VOL(3,2),C(4,2),
     3REF(20),SYS(20),Y1(20)
C
      COMMON T,VA,VB,X1(20),X2(20),G1OBS(20),G2OBS(20),N,SWITCH,
     1G1MCAL(20),G2MCAL(20),G11,G22,ALFA12,TS,II,ALFA21
     2,GMCAL,GMOBS,ERROR1,ERROR2,TEMP,VOL,C
C
    7 FORMAT(I2)
    8 FORMAT(3F8.4)
    9 FORMAT(4F18.10)
   10 FORMAT(F4.2,I2,F7.2,I2)
   11 FORMAT(F6.4,2F6.3,F6.4)
   12 FORMAT(1H0,////,12X,'A21ST = ',F7.1,10X,'A12ST = ',F7.1)
   13 FORMAT(10F6.2)
   15 FORMAT(6F7.3)
   19 FORMAT(20A4)
   21 FORMAT(1H ,11X,20A4)
  165 FORMAT(1H0,////,14X,'X',5X,'TEMP',7X,'G1OBS',6X,'G1CAL',2X,
     1'%ERROR',6X,'G2OBS',6X,'G2CAL',2X,'%ERROR',/)
  166 FORMAT(9X,F8.4,F8.2,2F11.4,F8.2,2F11.4,F8.2)
  167 FORMAT(1H ,11X,'PEFFERENCE, ',20A4)
  201 FORMAT(1H ,11X,I2,' DATA POINTS')
  202 FORMAT(1H ,11X,'A21 = ',F9.2,10X,'A12 = ',F9.2)
  203 FORMAT(1H1,//////////////,12X,'ORIGINAL NRTL EQUATION')
  204 FORMAT(1H ,11X,'STD. DEV. OF CALCULATED GAMMAS = ',F8.4)
  205 FORMAT(1H1,//////////////,12X,'LEMF EQUATION ')
  206 FORMAT(1H ,11X,'ALFA21 = ',F6.3,10X,'ALFA12 = ',F6.3)
C
C  ALFA12 = NONRANDOMNESS PARAMETER IN THE NRTL EQUATION
C  N = NUMBER OF DATA POINTS
C  T = TEMPERATURE FOR ISOTHERMAL DATA. FOR ISOBARIC DATA USE -500.0
C  TS = TEMPERATURE FOR EACH DATA POINT IN AN ISOBARIC SYSTEM
C  NLOG = 01 TO READ LOG 10 GAMMA DATA
C  NLOG = 00 TO READ GAMMA DATA
C
     DO 6969 II = 1,70
     READ  19,(SYS(I),I=1,20)
     READ 19, (REF(I),I = 1,20)
     READ 10,ALFA12,N,T,NLOG
     IF(T .GT. -273) GO TO 37
     READ 13,(TS(K),K=1,N)
```

```
      GO TO 39
  37  DO 38 K = 1,N
  38  TS(K) = T
  39  CONTINUE
C
C  READ LIQUID COMPOSITIONS AND EXPERIMENTAL GAMMAS
C
      DO 40 L=1,N
      READ 11, X1(L),G1OBS(L),G2OBS(L),Y1(L)
      IF(NLOG .EQ. 1)G1OBS(L) = 10.**G1OBS(L)
      IF(NLOG .EQ. 1)G2OBS(L) = 10.**G2OBS(L)
      X2(L) =1.- X1(L)
   40 CONTINUE
      READ 7,CODE
      GO TO (35,36),CODE
  35  CONTINUE
      READ 15,VA,VB,FL1,FL2,TAOU1,TAOU2
      G11 = VA * (FL1**2 + TAOU1**2)
      G22 = VB * (FL2**2 +TAOU2**2)
      GO TO 41
  36  CONTINUE
      READ 8,TEMP
      READ 8,VOL
      READ 9,C
  41  CONTINUE
      V1 = VA
      V2 = VB
      SWITCH = 2
  28  CONTINUE
      GSAVE=G12
      DO 219 I = 1,2
      DO 219 J = 1,5
      X(I,J) = 0.
  219 CONTINUE
      XT(1) = 0.0
      XT(2) = 0.0
      A21ST = XT(1)
      A12ST = XT(2)
      M = 2
      M1 = M + 1
      M3 = M + 3
      DX = 10.0
      L = 500
      E = 0.01
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
      CONTINUE
      IF(ALFA12 .GT. 0.0 .AND. ALFA12 .LT.0.5)GO TO 150
      PRINT 205
      GO TO 151
  150 PRINT 203
```

```
  151 CONTINUE
      PRINT 21,(SYS(I),I=1,20)
      PRINT 167, (REF(I),I = 1,20)
      PRINT 12, A21ST,A12ST
      PRINT 202, XT(1),XT(2)
      PRINT 206, ALFA21,ALFA12
      PRINT 201,N
      PRINT 204, Y(1)
 161  PRINT 165
      PRINT 166, (X1(K),TS(K),G1OBS(K),G1MCAL(K),ERROR1(K),G2OBS(K),
     1G2MCAL(K),ERROR2(K),K = 1,N)
  225 CONTINUE
  500 CONTINUE
      SWITCH = SWITCH + 1
      GO TO(28,28,28,6969),SWITCH
 6969 CONTINUE
      STOP
      END
```

FORTRAN IV030 SOURCE PROGRAM FN   SUBROUTINE

```
      SUBROUTINE FN(YY,XT)
       INTEGER SWITCH
C
      DIMENSION  GECAL(20),GEOBS(20),GMCAL(20),GMOBS(20),G1LC(20),
     1G1CAL(20),G2LC(20),G2CAL(20),TS(20),ERROR1(20),ERROR2(20),XT(2)
     2,TEMP(3,2),VOL(3,2),C(4,2)
C
      COMMON T,VA,VB,X1(20),X2(20),G1OBS(20),G2OBS(20),N,SWITCH,
     1G1MCAL(20),G2MCAL(20),G11,G22,ALFA12,TS,II,ALFA21
     2,GMCAL,GMOBS,ERROR1,ERROR2,TEMP,VOL,C
C
      YS = 0.
      IF(SWITCH .EQ. 3)ALFA12 = -1.0
      IF(SWITCH .EQ. 4)ALFA12 = 1.0
      ALFA21 = ALFA12
      IF(SWITCH .EQ. 5)ALFA12 = -1.0
      IF(SWITCH .EQ. 5)ALFA21 = 1.0
C
C  CALCULATION OF ACTIVITY COEFFICIENTS WITH THE NRTL
C  AND LEMF EQUATIONS
C
      DO 20 K = 1,N
      T = TS(K)
      U1 = XT(1)
      U2 = XT(2)
      EXP1 = U1/(1.987*(273.2 + T))
      EXP2 = U2/(1.987*(273.2 + T))
       A= EXP1*EXP(-EXP1*ALFA21)/((X1(K)  +X2(K)*EXP(-EXP1*ALFA21))**2)
       B= EXP2*EXP(-EXP2*ALFA12)/((X2(K) + X1(K)*EXP(-EXP2*ALFA12))**2)
       G1LC(K) = (X2(K)**2)*( A*EXP(-EXP1*ALFA21) + B)
       G2LC(K) = (X1(K)**2)*(B*EXP(-EXP2*ALFA12) + A)
       G1CAL(K) = EXP(G1LC(K))
       G2CAL(K) = EXP(G2LC(K))
      ERROR1(K) = (G1CAL(K) - G1OBS(K))*100/G1OBS(K)
      ERROR2(K) = (G2CAL(K) - G2OBS(K))*100/G2OBS(K)
      Y = ((G1CAL(K)-G1OBS(K))/G1OBS(K))**2+((G2CAL(K)-G2OBS(K))/G2OBS(K
     1))**2
       YS =YS + Y
       Z = 2*N
      G1MCAL(K) = G1CAL(K)
      G2MCAL(K) = G2CAL(K)
   20 CONTINUE
      STDEV = SQRT(YS/(Z-1.))
      YY = STDEV
   10 CONTINUE
      RETURN
      END
```

FORTRAN IV030 SOURCE PROGRAM   VOLINT   SUBROUTINE

```
      SUBROUTINE VOLINT(TEMP,VOL,T,VA,VB)
C
C  THIS SUBROUTINE CALCULATES MOLAR VOLUMES AS A FUNCTION
C  OF TEMPERATURE
C
      DIMENSION TEMP(3,2), VOL(3,2)
      DO 10 J = 1,2
      D = ((TEMP(3,J) - TEMP(1,J))*(VOL(2,J)-VOL(1,J)) -
     1(VOL(3,J)-VOL(1,J))*(TEMP(2,J)-TEMP(1,J)))/
     2  ((TEMP(2,J)**2 -TEMP(1,J)**2)*(TEMP(3,J)-TEMP(1,J)) -
     3(TEMP(3,J)**2-TEMP(1,J)**2)*(TEMP(2,J) - TEMP(1,J)))
      B=((VOL(2,J)-VOL(1,J))-D*(TEMP(2,J)**2-TEMP(1,J)**2))/
     1 (TEMP(2,J)-TEMP(1,J))
      A= VOL(1,J) - B*TEMP(1,J) - D*(TEMP(1,J)**2)
      V=A+B*(273.2+T)+D*((273.2+T)**2)
      GO TO (1,2),J
    1 VA = V
      GO TO 10
    2 VB = V
   10 CONTINUE
      RETURN
      END
```

FORTRAN IV030 SOURCE PROGRAM DELTAU   SUBROUTINE

```
      SUBROUTINE DELTAU(T,C,G11,G22)
C
C  THIS SUBROUTINE CALCULATES ENERGIES OF VAPORIZATION
C
      DIMENSION TEMP(3,2), VOL(3,2)
      DIMENSION C(4,2)
      DO 20 J= 1,2
      G = (1.987*(( 273.2+T)**2))*( -C(1,J)/((C(2,J) + 273.2 + T)**2)
     1 + C(3,J) + C(4,J)/(273.2 + T) - 1./(273.2 + T))
      GO TO(11,12),J
 11   G11 = G
      GO TO 20
 12   G22 = G
 20   CONTINUE
      RETURN
      END
```

```
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
      DIMENSION XT(2),X(2,5),Y(3),JJ(3),A(3,3)
   10 L1C = 0
      IF(L.LE.0) GO TO 50
      IHC = M1+1
      EN = M
      L1 = L
      EN = EN*1.5
      L = -L
      L2 = (3*M)/2+5
      K3 = 2
      IF(M.GE.3) K3=3
      K4 = K3-1
      G = K3*2
      G = 1.0/G
      DO 100 I=1,M
  100 X(I,1) = XT(I)
      CALL FN(Y(1),XT)
      DO 106 J=2,M1
      XT(J-1) = XT(J-1)+DX
      DO 104 I=1,M
  104 X(I,J) = XT(I)
      CALL FN(Y(J),XT)
      XT(J-1) = X(J-1,1)
  106 CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
  108 L1C = L1C +1
      IF(L1C.GE.L1) GO TO 400
   50 YL = 1.0E38
      YH = -YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH)GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
 1091 IF(Y(J).LT.Y2) GO TO 109
      Y2 = Y(J)
      I2 = J
  109 IF(Y(J).GT.YL) GO TO 1101
      Y3 = YL
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
```

```
1101 IF(Y(J).GT.Y3) GO TO 110
     Y3 = Y(J)
     I3 = J
110  CONTINUE
     L2C = L2C+1
     IF(L2C.LT.L2) GO TO 111
     L2C = 0
     JJ(1) = IL
     JJ(2) = I2
     JJ(3) = I3
     DO 60 K1=1,K3
     J1 = JJ(K1)
     DO 60 K2=K1,K3
     J2 = JJ(K2)
     S = 0.0
     DO 55 I=1,M
55   S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
60   A(K1,K2) = S
     D = A(1,1)*A(2,2)-A(1,2)**2
     GO TO(62,61),K4
61   D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)
     D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
 62  IF(D .EQ. 0.0)GO TO 65
     IF(D .LE. 0.)D = ABS(D)
     D = (D/4.0)**G
     IF(D.LT.E) GO TO 65
     FLG = 1.0
     GO TO 111
65   IF(FLG.LT.0.0) GO TO 400
     FLG = -1.0
111  DO 115 I=1,M
     XT(I) = 0.0
     DO 112 J=1,M1
     IF(J.NE.IH) XT(I) = XT(I)+X(I,J)
112  CONTINUE
115  XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
121  CALL FN(YT,XT)
     IF(YT.GE.Y2) GO TO 167
     IHC = M1+1
     IF(YT.GE.YL) GO TO 140
     YTT = YT
     DO 135 I=1,M
135  XT(I) = 1.5*XT(I)-0.5*X(I,IH)
     CALL FN(YT,XT)
     IF(YT.LE.YL ) GO TO 140
     DO 138 I=1,M
138  X(I,IH) = (2.0*XT(I)+X(I,IH))/3.0
     Y(IH) = YTT
     GO TO 108
140  DO 142 I=1,M
```

```
  142 X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
  167 IHC = IHC-1
      IF(IHC.EQ.0) GO TO 300
      IF(YT.GE.YH) GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
  168 X(I,IH) = XS
  173 DO 174 I=1,M
  174 XT(I)    = 0.75*X(I,IH)+0.25*XT(I)
      CALL FN(YT,XT)
      IF(YT.GT.YH) GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
  175 X(I,IH) = XT(I)
      GO TO 108
  180 DO 185 J=1,M1
      IF(J.EQ.IL) GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J)+X(I,IL))/2.0
  182 X(I,J) = XT(I)
      CALL FN(Y(J),XT)
  185 CONTINUE
      GO TO 108
  300 IHC = 2*M1
      IF(M.GE.3) GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH)-X(I,IL)
      X(I,M+3) = X(I,IH)-X(I,I3)
  302 S = S+X(I,M+2)**2
  303 S = SQRT(S)
      IF(S .EQ. 0.0)GO TO 500
      GO TO 304
  500 XT(1) = XT(1) + 1000.
      XT(2) = XT(2) + 1000.
      PRINT 501,XT(1),XT(2)
  501 FORMAT(1H0,T10,' LSQ2 RESTARTED,XT(1) = ',F10.2,T10,' XT(2) = ',
     1F10.2)
      GO TO 10
  304 U = -X(2,M+2)/S
      X(2,M+2) = X(1,M+2)/S
      X(1,M+2) = U
      S = X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
  305 X(I,M+2) = X(I,M+2)*S
  306 DO 307 I=1,M
  307 XT(I) = X(I,IH)+X(I,M+2)
```

```
      CALL FN(YT,XT)
      DO 309 I=1,M
  309 XT(I) = X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT) GO TO 320
      DO 311 I=1,M
  311 XT(I) = X(I,IH)+X(I,M+2)
      YTT = YT
  320 Y(IH) = YTT
      DO 321 I=1,M
  321 X(I,IH) = XT(I)
      GO TO 108
  350 DO 352 I=1,M
      XT(I) = X(I,IH) - X(I,IL)
      X(I,M+2) = X(I,IH) - X(I,I2)
  352 X(I,M+3) = X(I,IH) - X(I,I3)
      S = 0.0
      S1 = 0.0
      DO 355 I=1,M
      S = S+XT(I)**2
  355 S1 = S1+X(I,M+3)**2
      S  = SQRT(S )
      S1 = SQRT(S1)
      S2 = 0.0
      DO 357 I=1,M
      XT(I) = XT(I)/S
      S2 = S2+XT(I)*X(I,M+2)
  357 X(I,M+3) = X(I,M+3)/S1
      DO 360 I=1,M
  360 X(I,M+2) = X(I,M+2)-XT(I)*S2
      S1 = 0.0
      DO 362 I=1,M
  362 S1 = S1+X(I,M+2)**2
      S1 = SQRT(S1)
      DO 365 I=1,M
  365 X(I,M+2) = X(I,M+2)/S1
      S1 = 0.0
      S2 = 0.0
      DO 367 I=1,M
      S1 = S1+XT(I)*X(I,M+3)
  367 S2 = S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
  370 X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
  400 S = Y(1)
      Y(1) = Y(IL)
      Y(IL) = S
      DO 402 I=1,M
      XT(I) = X(I,IL)
      X(I,IL) = X(I,1)
```

```
 404  402  X(I,1) = XT(I)
 405       RETURN
 406       END
```

FORTRAN IV030 SOURCE PROGRAM

```
      PROGRAM OTILIA
C
C   THIS PROGRAM CALCULATES THE PARAMETERS FOR THE NRTL AND LEMF
C   EQUATIONS FROM MUTUAL SOLUBILITY DATA
C
      INTEGER SWITCH
      REAL MW1,MW2
      DIMENSION XT(2),X(2,5),Y(3),JJ(3),A(3,3)
      DIMENSION G1LC(20),G1CAL(20),G2LC(20),G2CAL(20),TS(20)
      DIMENSION REF(20)  ,SYS(20 )
      COMMON T,TS,VA,VB,X1(20),X2(20),G1OBS(20),G2OBS(20),N,SWITCH,
     1G1MCAL(20),G2MCAL(20),ALFA12,II
    7 FORMAT(I2)
   10 FORMAT(F4.2,I2,F7.2,I2)
   11 FORMAT(F12.10)
   12 FORMAT(1H0,////,12X,'A21ST = ',F7.1,10X,'A12ST = ',F7.1)
   13 FORMAT(10F6.2)
   15 FORMAT(6F7.3)
   19 FORMAT(20A4)
   21 FORMAT(1H ,11X,20A4)
  165 FORMAT(1H0,////,14X,'X',5X,'TEMP',7X,'G1CAL',6X,'G2CAL ')
  166 FORMAT(9X,F8.4,F8.2,2F11.4)
  167 FORMAT(1H ,11X,'REFFERENCE, ',20A4)
  200 FORMAT(1H1,//////////////,12X,'ORIGINAL NRTL EQUATION')
  201 FORMAT(1H ,11X,I2,' DATA POINTS')
  202 FORMAT(1H ,11X,'A21 = ',F9.2,10X,'A12 = ',F9.2)
  203 FORMAT(1H1,//////////////,12X,'LEMF EQUATION ')
  204 FORMAT(1H ,11X,'STD. DEV. OF CALCULATED GAMMAS = ',F8.4)
  206 FORMAT(1H ,11X,'ALFA21 = ',F6.3,10X,'ALFA12 = ',F6.3)
C
C   ALFA12 = NONRANDOMNESS PARAMETER IN THE NRTL EQUATION
C   N = 02
C   T = TEMPERATURE OF THE SYSTEM
C   MW1 AND MW2 = MOLECULAR WEIGHTS. IF SOLUBILITY DATA IS GIVEN
C   IN MOLE FRACTIONS USE 1.0
C
      DO 6970 II = 1,50
      SWITCH = 1
      READ  19,(SYS(I),I=1,20)
      READ 19,(REF(I),I=1,20)
      READ 10,ALFA12,N,T
      READ 15,MW1,MW2
   37 DO 38 K = 1,N
   38 TS(K) = T
   39 CONTINUE
      DO 40 L=1,N
      READ 11,X1(L)
      X2(L) =1.- X1(L)
      X1(L) = X1(L)/MW1
      X2(L) = X2(L)/MW2
```

FORTRAN IV030 SOURCE PROGRAM OTILIA PROGRAM

```
      X1(L) = X1(L)/(X1(L)+X2(L))
      X2(L) = 1.0 - X1(L)
   40 CONTINUE
   28 CONTINUE
      XT(1) = 0.0
      XT(2) = 0.0
      A21ST = XT(1)
      A12ST = XT(2)
      M = 2
      M1 = M + 1
      M3 = M + 3
      DX = 100.
      L = 500
      E = 0.05
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
  220 CONTINUE
      IF(SWITCH .EQ. 1)PRINT 200
      IF(SWITCH .EQ. 2)PRINT 203
      PRINT 21,(SYS(I),I=1,20)
      PRINT 167, (REF(I),I =1,20)
      PRINT 12,A21ST,A12ST
      PRINT 202, XT(1),XT(2)
      PRINT 206, ALFA21, ALFA12
      PRINT 201,N
      PRINT 204,Y(1)
  161 PRINT 165
      PRINT 166,(X1(K),TS(K),G1MCAL(K),G2MCAL(K),K = 1,N)
      CALL FMIX(XT,ALFA12,SYS)
  225 CONTINUE
 6969 CONTINUE
      SWITCH = SWITCH + 1
      GO TO(28,28,6970),SWITCH
 6970 CONTINUE
      STOP
      END
```

```
      SUBROUTINE FN(YY,XT)
       INTEGER SWITCH
      DIMENSION GMCAL(20)
      DIMENSION ACT1(2,20),ACT2(2,20)
      DIMENSION XT(2)
      DIMENSION G1LC(20),G1CAL(20),G2LC(20),G2CAL(20),TS(20)
      COMMON T,TS,VA,VB,X1(20),X2(20),G1OBS(20),G2OBS(20),N,SWITCH,
     1G1MCAL(20),G2MCAL(20),ALFA12,II
      U1 = XT(1)
      U2 = XT(2)
      YS = 0.
    1 CONTINUE
C
C    THIS SUBROUTINE CALCULATES PARAMETERS FOR THE NRTL AND LEMF
C    EQUATIONS FROM MUTUAL SOLUBILITY DATA
C
      IF(SWITCH .EQ. 2)ALFA12 = -1.0
      DO 3 K=1,N
      T = TS(K)
      RT = 1.987*(273.2 + T)
      EXP1 = U1/(1.987*(273.2 + T))
      EXP2 = U2/(1.987*(273.2 + T))
       A= EXP1*EXP(-EXP1*ALFA12)/((X1(K)  +X2(K)*EXP(-EXP1*ALFA12))**2)
       B= EXP2*EXP(-EXP2*ALFA12)/((X2(K) + X1(K)*EXP(-EXP2*ALFA12))**2)
       G1LC(K) = (X2(K)**2)*( A*EXP(-EXP1*ALFA12) + B)
       G1CAL(K) = EXP(G1LC(K))
       G2LC(K) = (X1(K)**2)*(B*EXP(-EXP2*ALFA12) + A)
       G2CAL(K) = EXP(G2LC(K))
      G1MCAL(K) = G1CAL(K)
      G2MCAL(K) = G2CAL(K)
      ACT1(K,II) = X1(K)*G1CAL(K)
      ACT2(K,II) = X2(K)*G2CAL(K)
      GMCAL(K) = X1(K)*ALOG(ACT1(K,II)) + X2(K)*ALOG(ACT2(K,II))
      GMCAL(K) = GMCAL(K)*RT
      IF(GMCAL(K) .LT. 0.0)GO TO 3
      G1MCAL(K) = 0.0
      G2MCAL(K) = 0.0
      YY = GMCAL(K) + 50.
      GO TO 10
    3 CONTINUE
      Z = (ACT1(1,II)-ACT1(2,II))**2 + (ACT2(1,II)-ACT2(2,II))**2
      Z = SQRT(Z/2)
      YY = Z
   10 CONTINUE
      RETURN
      END
```

FORTRAN IV030 SOURCE PROGRAM LSQ2   SUBROUTINE

```
     SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
     DIMENSION XT(2),X(2,5),Y(3),JJ(3),A(3,3)
10   L1C = 0
     IF(L.LE.0) GO TO 50
     IHC = M1+1
     EN = M
     EN = EN*1.5
     L1 = L
     L = -L
     L2 = (3*M)/2+5
     K3 = 2
     IF(M.GE.3) K3=3
     K4 = K3-1
     G = K3*2
     G = 1.0/G
     DO 100 I=1,M
100  X(I,1) = XT(I)
     CALL FN(Y(1),XT)
     DO 106 J=2,M1
     XT(J-1) = XT(J-1)+DX
     DO 104 I=1,M
104  X(I,J) = XT(I)
     CALL FN(Y(J),XT)
     XT(J-1) = X(J-1,1)
106  CONTINUE
     L2C = 0
     FLG = 1.0
     GO TO 50
108  L1C = L1C +1
     IF(L1C.GE.L1) GO TO 400
50   YL = 1.0E38
     YH = -YL
     Y2 = YH
     Y3 = YL
     DO 110 J=1,M1
     IF(Y(J).LT.YH) GO TO 1091
     Y2 = YH
     I2 = IH
     YH = Y(J)
     IH = J
     GO TO 109
1091 IF(Y(J).LT.Y2) GO TO 109
     Y2 = Y(J)
     I2 = J
109  IF(Y(J).GT.YL) GO TO 1101
     Y3 = YL
     I3 = IL
     IL = J
     YL = Y(J)
     GO TO 110
```

```
1101  IF(Y(J).GT.Y3) GO TO 110
      Y3 = Y(J)
      I3 = J
110   CONTINUE
      L2C = L2C+1
      IF(L2C.LT.L2) GO TO 111
      L2C = 0
      JJ(1) = IL
      JJ(2) = I2
      JJ(3) = I3
      DO 60 K1=1,K3
      J1 = JJ(K1)
      DO 60 K2=K1,K3
      J2 = JJ(K2)
      S = 0.0
      DO 55 I=1,M
55    S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
60    A(K1,K2) = S
      D = A(1,1)*A(2,2)-A(1,2)**2
      GO TO(62,61),K4
61    D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)
      D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
62    IF(D .EQ. 0.0)GO TO 65
      IF(D .LE. 0.0)D = ABS(D)
      D = (D/4.0)**G
      IF(D.LT.E) GO TO 65
      FLG = 1.0
      GO TO 111
65    IF(FLG.LT.0.0) GO TO 400
      FLG = -1.0
111   DO 115 I=1,M
      XT(I) = 0.0
      DO 112 J=1,M1
      IF(J.NE.IH) XT(I) = XT(I)+X(I,J)
112   CONTINUE
115   XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
121   CALL FN(YT,XT)
      IF(YT.GE.Y2) GO TO 167
      IHC = M1+1
      IF(YT.GE.YL) GO TO 140
      YTT = YT
      DO 135 I=1,M
135   XT(I) = 1.5*XT(I)-0.5*X(I,IH)
      CALL FN(YT,XT)
      IF(YT.LE.YL ) GO TO 140
      DO 138 I=1,M
138   X(I,IH) = (2.0*XT(I)+X(I,IH))/3.0
      Y(IH) = YTT
      GO TO 108
140   DO 142 I=1,M
```

```
 142  X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
 167  IHC = IHC-1
      IF(IHC.EQ.0) GO TO 300
      IF(YT.GE.YH) GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
 168  X(I,IH) = XS
 173  DO 174 I=1,M
 174  XT(I)   = 0.75*X(I,IH)+0.25*XT(I)
      CALL FN(YT,XT)
      IF(YT.GT.YH) GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
 175  X(I,IH) = XT(I)
      GO TO 106
 180  DO 185 J=1,M1
      IF(J.EQ.IL) GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J)+X(I,IL))/2.0
 182  X(I,J) = XT(I)
      CALL FN(Y(J),XT)
 185  CONTINUE
      GO TO 108
 300  IHC = 2*M1
      IF(M.GE.3) GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH)-X(I,IL)
      X(I,M+3) = X(I,IH)-X(I,I3)
 302  S = S+X(I,M+2)**2
      IF(S .EQ. 0.0)GO TO 500
      GO TO 303
 500  XT(1) = XT(1) + 1000.
      XT(2) = XT(2) + 1000.
      PRINT 501, XT(1),XT(2)
 501  FORMAT(1H0,T10,'  LSQ2 RESTARTED,XT(1) = ',F10.2,T10,' XT(2) = ',
     1F10.2)
      GO TO 10
 303  S = SQRT(S)
      U = -X(2,M+2)/S
      X(2,M+2) = X(1,M+2)/S
      X(1,M+2) = U
      S = X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
 305  X(I,M+2) = X(I,M+2)*S
 306  DO 307 I=1,M
 307  XT(I) = X(I,IH)+X(I,M+2)
```

```
      CALL FN(YT,XT)
      DO 309 I=1,M
309   XT(I) = X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT) GO TO 320
      DO 311 I=1,M
311   XT(I) = X(I,IH)+X(I,M+2)
      YTT = YT
320   Y(IH) = YTT
      DO 321 I=1,M
321   X(I,IH) = XT(I)
      GO TO 108
350   DO 352 I=1,M
      XT(I) = X(I,IH) - X(I,IL)
      X(I,M+2) = X(I,IH) - X(I,I2)
352   X(I,M+3) = X(I,IH) - X(I,I3)
      S = 0.0
      S1 = 0.0
      DO 355 I=1,M
      S = S+XT(I)**2
355   S1 = S1+X(I,M+3)**2
      S = SQRT(S)
      S1 = SQRT(S1)
      S2 = 0.0
      DO 357 I=1,M
      XT(I) = XT(I)/S
      S2 = S2+XT(I)*X(I,M+2)
357   X(I,M+3) = X(I,M+3)/S1
      DO 360 I=1,M
360   X(I,M+2) = X(I,M+2)-XT(I)*S2
      S1 = 0.0
      DO 362 I=1,M
362   S1 = S1+X(I,M+2)**2
      S1 = SQRT(S1)
      DO 365 I=1,M
365   X(I,M+2) = X(I,M+2)/S1
      S1 = 0.0
      S2 = 0.0
      DO 367 I=1,M
      S1 = S1+XT(I)*X(I,M+3)
367   S2 = S2+X(I,M+2)*X(I,M+3)
      DO 370 I=1,M
370   X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
      GO TO 306
400   S = Y(1)
      Y(1) = Y(IL)
      Y(IL) = S
      DO 402 I=1,M
      XT(I) = X(I,IL)
      X(I,IL) = X(I,1)
```

```
  332  402  X(I,1) = XT(I)
  333       RETURN
  334       END
```

```
        SUBROUTINE FMIX(XT,ALFA12,SYS)
C
C  THIS SUBROUTINE CALCULATES FREE ENERGIES OF MIXING USING THE
C  NRTL AND LEMF EQUATIONS
C
         INTEGER SWITCH
        DIMENSION ACT1(20,20),ACT2(20,20)
        DIMENSION X1(20),X2(20),COM(25),SYS(20)
        DIMENSION XT(2),A21(20),A12(20)
        DIMENSION G1LC(20),G1CAL(20),G2LC(20),G2CAL(20),TS(20)
        DIMENSION GECAL(20),GEOBS(20),GMCAL(20),GMOBS(20),SLOPEM(20)
   21   FORMAT(1HO,/,T20,'SYSTEM =    ',20A4,//)
   30   FORMAT(2F10.5)
   40   FORMAT(I2,6F12.6)
   166  FORMAT(5X,7F12.6)
   167  FORMAT(1HO,11X,'X1',10X,'G1CAL',7X,'G2CAL',7X,'GMCAL',7X,
       1'T',11X,'A21',9X,'A12')
   200  FORMAT(1HO,T10,'A1 = ',F15.6,'B1 = ',F15.6,'C1 = ',F15.6,
       1/,T10,'A2 = ',F15.6,'B2 = ',F15.6,'C2 = ',F15.6)
   201  FORMAT(1HO,/,T20,I2,'DATA SETS')
   202  FORMAT(1HO,////,T20,'  A21 = ',F10.2,'     A12 = ',F10.2)
   203  FORMAT(1H1,/////,T20,'             LEMF EQUATION.  ALFA12 = -1')
   204  FORMAT(1H1,/////,T20,'  ORIGINAL NRTL EQ., ALFA12 = ',F6.3)
C
C
        II = 1
        IF(ALFA12 .EQ. -1.0)GO TO 33
        READ 40,N,A1,B1,C1,A2,B2,C2
        IF(N .EQ. 0)GO TO 35
        DO 36 K = 1,N
        READ 30,X1(K),T
        T = 273.2 + T
   36   TS(K) = T
   33   CONTINUE
        IF(N .EQ. 0)GO TO 35
   34   CONTINUE
        DO 20 K = 1,N
        T = TS(K)
        RT = 1.987*T
        IF(A1 .NE. 0.0)XT(1) = A1 + B1*(T-TS(1)) + C1*(T-TS(1))**2
        A21(K) = XT(1)
        IF(A2 .NE. 0.0)XT(2) = A2 + B2*(T-TS(1)) + C2*(T-TS(1))**2
        A12(K) = XT(2)
        EXP1 = XT(1)/RT
        EXP2 = XT(2)/RT
        X2(K) = 1.0 - X1(K)
         A= EXP1*EXP(-EXP1*ALFA12)/((X1(K)  +X2(K)*EXP(-EXP1*ALFA12))**2)
         B= EXP2*EXP(-EXP2*ALFA12)/((X2(K) + X1(K)*EXP(-EXP2*ALFA12))**2)
         G1LC(K) = (X2(K)**2)*( A*EXP(-EXP1*ALFA12) + 3)
         G2LC(K) = (X1(K)**2)*(B*EXP(-EXP2*ALFA12) + A)
```

```
            G1CAL(K) = EXP(G1LC(K))
            G2CAL(K) = EXP(G2LC(K))
          ACT1(K,II) = X1(K)*G1CAL(K)
          ACT2(K,II) = X2(K)*G2CAL(K)
          GMCAL(K) = X1(K)*ALOG(ACT1(K,II)) + X2(K)*ALOG(ACT2(K,II))
          GMCAL(K) = GMCAL(K)*RT
    20    CONTINUE
          IF(ALFA12 .EQ. -1.0)GO TO 2
    1     PRINT 204,ALFA12
          GO TO 3
    2     PRINT 203
          GO TO 3
    3     CONTINUE
          PRINT 21 ,(SYS(I),I = 1,20)
          PRINT 201,N
          IF(A1 .NE. 0.0)PRINT 200,A1,B1,C1,A2,B2,C2
          PRINT 167
          PRINT 166,(X1(K),G1CAL(K),G2CAL(K),GMCAL(K),TS(K),A21(K),A12(K),
         1K = 1,N)
    35    CONTINUE
          RETURN
          END
```

FORTRAN IVO30 SOURCE PROGRAM

```
      PROGRAM LLEQUM
C
C  THIS PROGRAM CALCULATES TERNARY LIQUID LIQUID EQUILIBRIUM
C  COMPOSITIONS FROM BINARY DATA USING THE NRTL AND LEMF EQUATIONS
C
      DIMENSION CACTCO(3,3),ALFA(3,3),SYS(20),COM(20)
      DIMENSION XT(3),X(3,6),Y(4),JJ(3),A(3,3)
      COMMON T,X11,X12,X21,X22,X31,X32,CACTCO,ALFA,NCOMP,YY
    1 FORMAT(8F10.5)
    2 FORMAT(I2)
    3 FORMAT(1H0,/////,T20,' PREDICTED TIE LINE DATA')
    4 FORMAT(1H0,T20,' X11 = ',F6.4,' X12 = ',F6.4,' X21 = ',F6.4,
     1' X22 = ',F6.4,' X31 = ',F6.4,' X32 = ',F6.4,' ERROR = ',F10.6)
    5 FORMAT(1H0,T20,'  ERROR = ',F8.4)
    6 FORMAT(20A4)
    7 FORMAT(1H0,////,T10,20A4)
    8 FORMAT(1H1,////,T10,20A4)
    9 FORMAT(1H0,T10,' DX = ',F10.8)
  501 FORMAT(1H0,T10,' LSQ2 RESTARTED, XT(1),XT(2),XT(3) = ',3F10.5)
      DO 450 NT = 1,15
      READ 6 ,(SYS(I),I = 1,20)
      READ 6,(COM(I),I = 1,20)
      READ 2,NCOMP
      PRINT 8,(COM(I),I = 1,20)
      PRINT 7,(SYS(I),I = 1,20)
      PRINT 3
      DO 20 I = 1,NCOMP
C
C  READ BINARY PARAMETERS IN MATRIX FORM, FIRST
C  SUBSCRIPT INDICATES ROW SECOND SUBSCRIPT INDICATES COLUMN
C
   20 READ 1,(CACTCO(I,J),J = 1,NCOMP)
      DO 21 I = 1,NCOMP
C
C  READ ALFA VALUES IN MATIX FORM.  FOR THE LEMF
C  EQUATION ALFA = -1.0
C
   21 READ 1,(ALFA(I,J),J=1,NCOMP)
      DO 22 I = 1,NCOMP
      CACTCO(I,I) = 0.0
   22 CONTINUE
   23 CONTINUE
      K = 0
      I = 0
C
C  READ THE TEMPERATURE OF THE SYSTEM AND INITIAL GUESSES
C  FOR THE COMPOSITIONS IN EQUILIBRIUM, FIRST SUBSCRIPT
C  INDICATES COMPONENT SECOND SUBSCRIPT INDICATES PHASE
C
      READ1,T,X11,X12,X21,X22
```

FORTRAN IVO30 SOURCE PROGRAM LLEQUM   PROGRAM

```
      IF(T .LT. -273.2)GO TO 450
      X11REF = X11
      X12REF = X12
      X21RFF = X21
      X22REF = X22
      T = 273.2 + T
      DX = 0.00001
      M = 3
      M1 = M+1
      M3 = M+3
      L = 1000
      E = 0.00000000005
      KINC = 0
      MSIGN = 1
  405 CONTINUE
      XT(1) = X12REF
      XT(2) = X21REF
      XT(3) = X22REF
      CALL LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
  101 PRINT 4,X11,X12,X21,X22,X31,X32,Y(1)
      PRINT 9,DX
      GO TO 23
 450  CONTINUE
  500 CONTINUE
      STOP
      END
```

```
      SUBROUTINE FN(Y,XT)
      DIMENSION CACTCO(3,3),ALFA(3,3),GX(3,2),XT(3),DELX(3)
      DIMENSION TAOU(3,3),GT(3,3),G(3,3),GAMT(5),A(3),W(3),C(3),
     1D(3),CC(3),AA(3),BB(3),GLC(3)
      COMMON T,X11,X12,X21,X22,X31,X32,CACTCO,ALFA,NCOMP,YY
    5 FORMAT(1H0,T20, ' FREE ENERGY OF MIXING = ',F10.3)
      NFLAG = 0
      X12REF = XT(1)
      X22REF = XT(3)
      X21REF = XT(2)
      XT(1) = X11
      IF((XT(1) + XT(2)) .GT. 1.0)XT(2) = 1.0 - XT(1)
      IF(XT(2) .LT. 0.0)XT(2) = 0.0
      XT(3) = 1.0 - XT(1) - XT(2)
      X21 = XT(2)
      X31 = XT(3)
      GO TO 40
   30 CONTINUE
      XT(1) = X12REF
      IF(XT(1) .LT. 0.0)XT(1) = 0.0
      IF(XT(1) .GT. 1.0)XT(1) = 1.0
      XT(2) = X22REF
      IF(XT(2) .LT. 0.0)XT(2) = 0.0
      IF(XT(2) .GT. 1.0)XT(2) = 1.0
      IF((XT(1) + XT(2)) .GT. 1.0)XT(2) = 1.0 - XT(1)
      XT(3) = 1.0 - XT(1) - XT(2)
      X12 = XT(1)
      X22 = XT(2)
      X32 = XT(3)
   40 CONTINUE
   60 CONTINUE
C
C     THIS ROUTINE EVALUATES TERNARY GAMMAS USING BINARY CONSTANTS
C     FROM THE NRTL EQUATION.
C
      GMIX = 0.0
      YY = 0.0
      Y = 0.0
      DO 70 I = 1,NCOMP
      DO 70 J = 1,NCOMP
      GT(I,J) = CACTCO(I,J)
   70 CONTINUE
      RT=1.987*T
      DO 298 I = 1,NCOMP
      DO 298 J = 1,NCOMP
      ALFA(J,J) = 0.
      ALFA(J,I) = ALFA(I,J)
      TAOU(J,I) = (GT(J,I) - GT(I,I))/RT
      G(J,I) = EXP(-ALFA(J,I)*TAOU(J,I))
  298 CONTINUE
```

```
      DO 302 I = 1,NCOMP
      CC(I) = 0
      A(I) = 0.
      W(I) = 0.
      DO 301 J = 1,NCOMP
      C(J) = 0
      D(J) = 0
      DO 300 K = 1,NCOMP
      IF(J .GE. 2) GO TO 299
      A(I) = A(I) + TAOU(K,I)*G(K,I)*XT(K)
      W(I) = W(I) + G(K,I)*XT(K)
  299 C(J) = C(J) +XT(K)*TAOU(K,J)*G(K,J)
      D(J) = D(J) + G(K,J)*XT(K)
  300 CONTINUE
      AA(I) = A(I)/W(I)
      BB(J) = C(J)/D(J)
      CC(I) = CC(I) +((XT(J)*G(I,J))/D(J))*(TAOU(I,J) - BB(J))
  301 CONTINUE
      GLC(I) = AA(I) + CC(I)
      GAMT(I) = EXP(GLC(I))
  302 CONTINUE
      NFLAG = NFLAG + 1
      DO 100 I = 1,NCOMP
  100 GX(I,NFLAG) = XT(I)*GAMT(I)
      IF(NFLAG .LT. 2)GO TO 30
      DELX(1) = X11 - X12
      DELX(2) = X21 - X22
      DELX(3) = X31 - X32
      IF(DELX(1) .EQ. 0.0)DELX(1) = 1.0E-10
      IF(DELX(2) .EQ. 0.0)DELX(2) = 1.0E-10
      IF(DELX(3) .EQ. 0.0)DELX(3) = 1.0E-10
      DO 110 I = 1,NCOMP
      YY = YY + ABS(GX(I,1) - GX(I,2))
      Y = Y + ABS((GX(I,1) - GX(I,2))/DELX(I))
  110 CONTINUE
  500 CONTINUE
      XT(1) = X12REF
      XT(2) = X21REF
      XT(3) = X22REF
      RETURN
      END
```

```
      SUBROUTINE LSQ2(XT,X,DX,Y,M,M1,M3,L,E)
      DIMENSION XT(3),X(3,6),Y(4),JJ(3),A(3,3)
10    L1C = 0
      IF(L.LE.0) GO TO 50
      IHC = M1+1
      EN = M
      EN = EN*1.5
      L1 = L
      L = -L
      L2 = (3*M)/2+5
      K3 = 2
      IF(M.GE.3) K3=3
      K4 = K3-1
      G = K3*2
      G = 1.0/G
      DO 100 I=1,M
100   X(I,1) = XT(I)
      CALL FN(Y(1),XT)
      DO 106 J=2,M1
      XT(J-1) = XT(J-1)+DX
      DO 104 I=1,M
104   X(I,J) = XT(I)
      CALL FN(Y(J),XT)
      XT(J-1) = X(J-1,1)
106   CONTINUE
      L2C = 0
      FLG = 1.0
      GO TO 50
108   L1C = L1C +1
      IF(L1C.GE.L1) GO TO 400
50    YL = 1.0E38
      YH = -YL
      Y2 = YH
      Y3 = YL
      DO 110 J=1,M1
      IF(Y(J).LT.YH) GO TO 1091
      Y2 = YH
      I2 = IH
      YH = Y(J)
      IH = J
      GO TO 109
1091  IF(Y(J).LT.Y2) GO TO 109
      Y2 = Y(J)
      I2 = J
109   IF(Y(J).GT.YL) GO TO 1101
      Y3 = YL
      I3 = IL
      IL = J
      YL = Y(J)
      GO TO 110
```

```
1101 IF(Y(J).GT.Y3) GO TO 110
     Y3 = Y(J)
     I3 = J
110  CONTINUE
     L2C = L2C+1
     IF(L2C.LT.L2) GO TO 111
     L2C = 0
     JJ(1) = IL
     JJ(2) = I2
     JJ(3) = I3
     DO 60 K1=1,K3
     J1 = JJ(K1)
     DO 60 K2=K1,K3
     J2 = JJ(K2)
     S = 0.0
     DO 55 I=1,M
55   S = S+(X(I,J1)-X(I,IH))*(X(I,J2)-X(I,IH))
60   A(K1,K2) = S
     IF(A(1,1) .EQ. 0.0)A(1,1) = 1.0E-10
     D = A(1,1)*A(2,2)-A(1,2)**2
     GO TO(62,61),K4
61   D1 = A(1,1)*A(2,3)-A(1,2)*A(1,3)
     D = ((A(1,1)*A(3,3)-A(1,3)**2)*D-D1*D1)/(A(1,1)*9.0)
 62  IF(D .EQ. 0.0)GO TO 65
     IF(D .LE. 0.)D = ABS(D)
     D = (D/4.0)**G
     IF(D.LT.E) GO TO 65
     FLG = 1.0
     GO TO 111
65   IF(FLG.LT.0.0) GO TO 400
     FLG = -1.0
111  DO 115 I=1,M
     XT(I) = 0.0
     DO 112 J=1,M1
     IF(J.NE.IH) XT(I) = XT(I)+X(I,J)
112  CONTINUE
115  XT(I) = (3.0*XT(I)+X(I,I2)-X(I,IL))/EN-X(I,IH)
121  CALL FN(YT,XT)
     IF(YT.GE.Y2) GO TO 167
     IHC = M1+1
     IF(YT.GE.YL) GO TO 140
     YTT = YT
     DO 135 I=1,M
135  XT(I) = 1.5*XT(I)-0.5*X(I,IH)
     CALL FN(YT,XT)
     IF(YT.LE.YL ) GO TO 140
     DO 138 I=1,M
138  X(I,IH) = (2.0*XT(I)+X(I,IH))/3.0
     Y(IH) = YTT
     GO TO 108
```

```
140   DO 142 I=1,M
142   X(I,IH) = XT(I)
      Y(IH) = YT
      GO TO 108
167   IHC = IHC-1
      IF(IHC.EQ.0) GO TO 300
      IF(YT.GE.YH) GO TO 173
      DO 168 I=1,M
      XS = XT(I)
      XT(I) = X(I,IH)
168   X(I,IH) = XS
173   DO 174 I=1,M
174   XT(I)    = 0.75*X(I,IH)+0.25*XT(I)
      CALL FN(YT,XT)
      IF(YT.GT.YH) GO TO 180
      Y(IH) = YT
      DO 175 I=1,M
175   X(I,IH) = XT(I)
      GO TO 108
180   DO 185 J=1,M1
      IF(J.EQ.IL) GO TO 185
      DO 182 I=1,M
      XT(I) = (X(I,J)+X(I,IL))/2.0
182   X(I,J) = XT(I)
      CALL FN(Y(J),XT)
185   CONTINUE
      GO TO 108
300   IHC = 2*M1
      IF(M.GE.3) GO TO 350
      S = 0.0
      DO 302 I=1,M
      X(I,M+2) = X(I,IH)-X(I,IL)
      X(I,M+3) = X(I,IH)-X(I,I3)
302   S = S+X(I,M+2)**2
303   S = SQRT(S)
      IF(S .EQ. 0.0)S = 1.0E-5
304   U = -X(2,M+2)/S
      X(2,M+2) = X(1,M+2)/S
      X(1,M+2) = U
      S = X(1,M+2)*X(1,M+3)+X(2,M+2)*X(2,M+3)
      DO 305 I=1,M
305   X(I,M+2) = X(I,M+2)*S
306   DO 307 I=1,M
307   XT(I) = X(I,IH)+X(I,M+2)
      CALL FN(YT,XT)
      DO 309 I=1,M
309   XT(I) = X(I,IH)-X(I,M+2)
      CALL FN(YTT,XT)
      IF(YTT.LE.YT) GO TO 320
      DO 311 I=1,M
```

```
311  XT(I) = X(I,IH)+X(I,M+2)
     YTT = YT
320  Y(IH) = YTT
     DO 321 I=1,M
321  X(I,IH) = XT(I)
     GO TO 108
350  DO 352 I=1,M
     XT(I) = X(I,IH) - X(I,IL)
     X(I,M+2) = X(I,IH) - X(I,I2)
352  X(I,M+3) = X(I,IH) - X(I,I3)
     S = 0.0
     S1 = 0.0
     DO 355 I=1,M
     S = S+XT(I)**2
355  S1 = S1+X(I,M+3)**2
     S  = SQRT(S )
     IF(S .EQ. 0.0)S = 1.0E-5
     S1 = SQRT(S1)
     IF(S1 .EQ. 0.0)S1 = 1.0E-5
     S2 = 0.0
     DO 357 I=1,M
     XT(I) = XT(I)/S
     S2 = S2+XT(I)*X(I,M+2)
357  X(I,M+3) = X(I,M+3)/S1
     DO 360 I=1,M
360  X(I,M+2) = X(I,M+2)-XT(I)*S2
     S1 = 0.0
     DO 362 I=1,M
362  S1 = S1+X(I,M+2)**2
     S1 = SQRT(S1)
     IF(S1 .EQ. 0.0)S1 = 1.0E-10
     DO 365 I=1,M
365  X(I,M+2) = X(I,M+2)/S1
     S1 = 0.0
     S2 = 0.0
     DO 367 I=1,M
     S1 = S1+XT(I)*X(I,M+3)
367  S2 = S2+X(I,M+2)*X(I,M+3)
     DO 370 I=1,M
370  X(I,M+2) = S*(S1*XT(I)+S2*X(I,M+2)-X(I,M+3))
     GO TO 306
400  S = Y(1)
     Y(1) = Y(IL)
     Y(IL) = S
     DO 402 I=1,M
     XT(I) = X(I,IL)
     X(I,IL) = X(I,1)
402  X(I,1) = XT(I)
     RETURN
     END
```

APPENDIX C

CORRELATION OF BINARY DATA. DETAILED RESULTS

```
ORIGINAL NRTL EQUATION
ACETONE(1) CARBON TET(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)



A21ST =      0.0          A12ST =      0.0
A21 =    658.21           A12 =    -22.76
ALFA21 =  0.300           ALFA12 =  0.300
17 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0235



   X      TEMP      G1OBS     G1CAL  %ERROR      G2OBS     G2CAL  %ERROR

0.0115   50.00     2.4400    2.6072    6.85     1.0100    1.0002   -0.97
0.0201   50.00     2.5500    2.5490   -0.04     0.9900    1.0005    1.06
0.0385   50.00     2.4900    2.4320   -2.33     1.0100    1.0020   -0.80
0.0395   50.00     2.6700    2.4260   -9.14     0.9900    1.0021    1.22
0.0868   50.00     2.1900    2.1682   -0.99     1.0100    1.0096   -0.03
0.1699   50.00     1.8300    1.8268   -0.17     1.0600    1.0353   -2.33
0.2860   50.00     1.5000    1.5089    0.59     1.1000    1.0950   -0.45
0.4396   50.00     1.2600    1.2571   -0.23     1.2200    1.2139   -0.50
0.5073   50.00     1.1900    1.1845   -0.46     1.2700    1.2805    0.83
0.5610   50.00     1.1600    1.1387   -1.83     1.3100    1.3396    2.26
0.6465   50.00     1.0900    1.0831   -0.63     1.4300    1.4455    1.08
0.7031   50.00     1.0700    1.0559   -1.31     1.4800    1.5238    2.96
0.7649   50.00     1.0400    1.0334   -0.63     1.5800    1.6170    2.34
0.8293   50.00     1.0200    1.0168   -0.31     1.7000    1.7230    1.35
0.8759   50.00     1.0100    1.0086   -0.14     1.7800    1.8056    1.44
0.9470   50.00     1.0000    1.0015    0.15     1.9600    1.9414   -0.95
0.9763   50.00     1.0000    1.0003    0.03     2.0300    2.0010   -1.43
```

```
LEMF EQUATION
ACETONE(1) CARBON TET(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)



A21ST =      0.0           A12ST =      0.0
A21 =    127.46            A12 =    314.49
ALFA21 = -1.000            ALFA12 = -1.000
17 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0230



   X      TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0115   50.00     2.4400     2.6231    7.51     1.0100     1.0002   -0.97
0.0201   50.00     2.5500     2.5604    0.41     0.9900     1.0006    1.07
0.0385   50.00     2.4900     2.4355   -2.19     1.0100     1.0021   -0.78
0.0395   50.00     2.6700     2.4291   -9.02     0.9900     1.0022    1.23
0.0868   50.00     2.1900     2.1592   -1.41     1.0100     1.0101    0.01
0.1699   50.00     1.8300     1.8123   -0.97     1.0600     1.0363   -2.23
0.2860   50.00     1.5000     1.4988   -0.08     1.1000     1.0956   -0.40
0.4396   50.00     1.2600     1.2551   -0.39     1.2200     1.2110   -0.74
0.5073   50.00     1.1900     1.1848   -0.43     1.2700     1.2753    0.42
0.5610   50.00     1.1600     1.1403   -1.70     1.3100     1.3325    1.72
0.6465   50.00     1.0900     1.0856   -0.41     1.4300     1.4360    0.42
0.7031   50.00     1.0700     1.0583   -1.09     1.4800     1.5136    2.27
0.7649   50.00     1.0400     1.0354   -0.44     1.5800     1.6077    1.76
0.8293   50.00     1.0200     1.0182   -0.18     1.7000     1.7174    1.02
0.8759   50.00     1.0100     1.0095   -0.05     1.7800     1.8050    1.41
0.9470   50.00     1.0000     1.0017    0.17     1.9600     1.9540   -0.31
0.9763   50.00     1.0000     1.0003    0.03     2.0300     2.0214   -0.42
```

```
ORIGINAL NRTL EQUATION
ACETONE - CHLOROFORM AT 35.17 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0          A12ST =      0.0
A21 =      79.83          A12 =    -525.89
ALFA21 =  0.300           ALFA12 =  0.300
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0284


   X       TEMP      G1OBS       G1CAL  %ERROR     G2OBS      G2CAL  %ERROR

0.0821    35.17     0.4940      0.4571  -7.47     0.9750     0.9917    1.71
0.1953    35.17     0.5700      0.5712   0.21     0.9400     0.9570    1.81
0.2003    35.17     0.5430      0.5762   6.11     0.9470     0.9550    0.84
0.3365    35.17     0.6770      0.7054   4.20     0.8670     0.8871    2.32
0.4188    35.17     0.7460      0.7750   3.89     0.8150     0.8380    2.82
0.4484    35.17     0.7710      0.7981   3.51     0.8020     0.8194    2.17
0.4857    35.17     0.7990      0.8255   3.32     0.7760     0.7955    2.51
0.5070    35.17     0.8170      0.8403   2.85     0.7670     0.7817    1.92
0.5752    35.17     0.8630      0.8832   2.34     0.7190     0.7371    2.52
0.5950    35.17     0.8760      0.8944   2.10     0.7130     0.7242    1.57
0.6336    35.17     0.8940      0.9146   2.30     0.6890     0.6990    1.45
0.6432    35.17     0.9000      0.9192   2.13     0.6780     0.6927    2.17
0.7090    35.17     0.9280      0.9475   2.10     0.6480     0.6504    0.37
0.7296    35.17     0.9408      0.9550   1.51     0.6321     0.6373    0.83
0.7343    35.17     0.9370      0.9566   2.09     0.6498     0.6344   -2.38
0.8147    35.17     0.9637      0.9796   1.65     0.5880     0.5848   -0.54
0.8182    35.17     0.9628      0.9804   1.83     0.5949     0.5827   -2.05
0.8768    35.17     0.9721      0.9912   1.97     0.5657     0.5482   -3.09
0.9397    35.17     0.9767      0.9980   2.18     0.5369     0.5128   -4.49
0.9412    35.17     0.9769      0.9981   2.17     0.5337     0.5120   -4.08
```

```
LEMF EQUATION
ACETONE - CHLOROFORM AT 35.17 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0            A12ST =      0.0
A21 =    -489.23            A12 =    -258.43
ALFA21 = -1.000             ALFA12 = -1.000
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0342


   X       TEMP       G1OBS       G1CAL   %ERROR      G2OBS       G2CAL   %ERROR

0.0821    35.17      0.4940      0.4482   -9.27      0.9750      0.9889    1.42
0.1953    35.17      0.5700      0.5811    1.95      0.9400      0.9493    0.99
0.2003    35.17      0.5430      0.5865    8.01      0.9470      0.9471    0.01
0.3365    35.17      0.6770      0.7173    5.95      0.8670      0.8806    1.57
0.4188    35.17      0.7460      0.7823    4.86      0.8150      0.8356    2.53
0.4484    35.17      0.7710      0.8033    4.19      0.8020      0.8188    2.10
0.4857    35.17      0.7990      0.8281    3.64      0.7760      0.7973    2.75
0.5070    35.17      0.8170      0.8414    2.99      0.7670      0.7848    2.32
0.5752    35.17      0.8630      0.8805    2.03      0.7190      0.7440    3.48
0.5950    35.17      0.8760      0.8908    1.69      0.7130      0.7319    2.65
0.6336    35.17      0.8940      0.9096    1.74      0.6890      0.7080    2.75
0.6432    35.17      0.9000      0.9140    1.55      0.6780      0.7019    3.53
0.7090    35.17      0.9280      0.9414    1.44      0.6480      0.6600    1.85
0.7296    35.17      0.9408      0.9490    0.87      0.6321      0.6465    2.28
0.7343    35.17      0.9370      0.9506    1.46      0.6498      0.6435   -0.98
0.8147    35.17      0.9637      0.9751    1.18      0.5880      0.5897    0.28
0.8182    35.17      0.9628      0.9760    1.37      0.5949      0.5873   -1.28
0.8768    35.17      0.9721      0.9886    1.70      0.5657      0.5467   -3.36
0.9397    35.17      0.9767      0.9972    2.10      0.5369      0.5019   -6.52
0.9412    35.17      0.9769      0.9973    2.09      0.5337      0.5008   -6.16
```

```
ORIGINAL NRTL EQUATION
ACETONE(1) CHOROFORM(2) AT 50C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)



A21ST =      0.0           A12ST =      0.0
A21 =      36.77           A12 =   -453.06
ALFA21 =  0.300            ALFA12 =  0.300
10 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0277



   X       TEMP         G1OBS        G1CAL  %ERROR        G2OBS        G2CAL  %ERROR

0.1440    50.00        0.6069       0.5736   -5.48       0.9731       0.9805    0.76
0.2610    50.00        0.6775       0.6760   -0.22       0.9293       0.9406    1.22
0.3350    50.00        0.7243       0.7363    1.66       0.9050       0.9072    0.24
0.4310    50.00        0.8011       0.8071    0.75       0.8512       0.8571    0.69
0.5090    50.00        0.8600       0.8573   -0.32       0.8014       0.8125    1.38
0.5810    50.00        0.9189       0.8971   -2.37       0.7284       0.7695    5.64
0.6880    50.00        0.9536       0.9442   -0.98       0.6783       0.7043    3.83
0.7510    50.00        0.9549       0.9651    1.06       0.7138       0.6659   -6.70
0.8160    50.00        0.9786       0.9813    0.28       0.6255       0.6270    0.24
0.8710    50.00        0.9926       0.9910   -0.16       0.5778       0.5947    2.93
```

```
LEMF EQUATION
ACETONE(1) CHOROFORM(2) AT 50C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)


A21ST =      0.0           A12ST =      0.0
A21 =   -400.17            A12 =   -225.21
ALFA21 = -1.000            ALFA12 = -1.000
10 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0282


   X       TEMP       G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.1440   50.00      0.6069      0.5721   -5.74       0.9731      0.9773     0.43
0.2610   50.00      0.6775      0.6805    0.45       0.9293      0.9356     0.67
0.3350   50.00      0.7243      0.7407    2.26       0.9050      0.9026    -0.26
0.4310   50.00      0.8011      0.8089    0.97       0.8512      0.8547     0.41
0.5090   50.00      0.8600      0.8565   -0.41       0.8014      0.8125     1.39
0.5810   50.00      0.9189      0.8943   -2.67       0.7284      0.7715     5.92
0.6880   50.00      0.9536      0.9401   -1.41       0.6783      0.7075     4.31
0.7510   50.00      0.9549      0.9613    0.67       0.7138      0.6683    -6.37
0.8160   50.00      0.9786      0.9785   -0.01       0.6255      0.6268     0.21
0.8710   50.00      0.9926      0.9892   -0.34       0.5778      0.5909     2.26
```

```
ORIGINAL NRTL EQUATION
ACETONE(1) METHANOL(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)


A21ST =      0.0          A12ST =      0.0
A21 =    251.32           A12 =    126.07
ALFA21 =  0.300           ALFA12 =  0.300
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0329


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.1360   50.00      1.5879     1.5263   -3.88     1.0060     1.0112    0.52
0.2570   50.00      1.3386     1.3608    1.66     1.0564     1.0399   -1.56
0.5020   50.00      1.1037     1.1441    3.66     1.2242     1.1559   -5.58
0.6740   50.00      1.0715     1.0583   -1.23     1.2074     1.2916    6.98
0.7210   50.00      1.0407     1.0422    0.14     1.3359     1.3382    0.17
0.7980   50.00      1.0285     1.0217   -0.66     1.3366     1.4246    6.58
0.8810   50.00      0.9959     1.0074    1.16     1.5932     1.5335   -3.75
0.9240   50.00      0.9967     1.0030    0.63     1.6002     1.5972   -0.19
0.9490   50.00      0.9897     1.0014    1.18     1.6847     1.6367   -2.85
```

```
LEMF EQUATION
ACETONE(1) METHANOL(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)


A21ST =      0.0            A12ST =      0.0
A21 =    138.19             A12 =    180.74
ALFA21 = -1.000             ALFA12 = -1.000
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0323


   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.1360    50.00       1.5879      1.5292   -3.70      1.0060      1.0118    0.58
0.2570    50.00       1.3386      1.3592    1.54      1.0564      1.0413   -1.43
0.5020    50.00       1.1037      1.1432    3.58      1.2242      1.1568   -5.50
0.6740    50.00       1.0715      1.0586   -1.21      1.2074      1.2909    6.91
0.7210    50.00       1.0407      1.0426    0.18      1.3359      1.3370    0.08
0.7980    50.00       1.0285      1.0221   -0.62      1.3366      1.4233    6.49
0.8810    50.00       0.9959      1.0076    1.18      1.5932      1.5335   -3.75
0.9240    50.00       0.9967      1.0031    0.64      1.6002      1.5988   -0.09
0.9490    50.00       0.9897      1.0014    1.18      1.6847      1.6396   -2.67
```

```
ORIGINAL NRTL EQUATION
ACETONE - METHANOL AT 100 C
REFFERENCE, GRISWOLD ET AL., CHEM.ENG.PROGESS SYMP.SER.,#3,48(1952)


A21ST =      0.0             A12ST =      0.0
A21 =    -456.97             A12 =    1090.17
ALFA21 =  0.300              ALFA12 =  0.300
14 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0615


   X      TEMP        G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0470  100.00       1.4120      1.3770   -2.48       0.9840      1.0002     1.65
0.0680  100.00       1.3120      1.3705    4.46       0.9920      1.0005     0.86
0.1460  100.00       1.2900      1.3435    4.14       1.0200      1.0030    -1.67
0.2200  100.00       1.1970      1.3142    9.79       1.0320      1.0080    -2.33
0.3970  100.00       1.1340      1.2328    8.71       1.1100      1.0381    -6.48
0.5070  100.00       1.0830      1.1776    8.73       1.1520      1.0786    -6.37
0.5620  100.00       1.0540      1.1497    9.08       1.1910      1.1087    -6.91
0.6240  100.00       1.0380      1.1189    7.80       1.2320      1.1535    -6.37
0.6410  100.00       1.0430      1.1107    6.49       1.2180      1.1683    -4.08
0.6600  100.00       1.0410      1.1016    5.82       1.2340      1.1863    -3.87
0.7470  100.00       1.0140      1.0627    4.81       1.2930      1.2927    -0.03
0.8700  100.00       0.9730      1.0195    4.78       1.5350      1.5458     0.70
0.9520  100.00       0.9720      1.0030    3.19       1.8550      1.8317    -1.26
0.9770  100.00       0.9630      1.0007    3.92       2.2900      1.9485   -14.91
```

```
LEMF EQUATION
ACETONE - METHANOL AT 100 C
REFFERENCE, GRISWOLD ET AL., CHEM.ENG.PROGESS SYMP.SER.,#3,48(1952)



A21ST =      0.0          A12ST =      0.0
A21 =    498.24           A12 =   -425.55
ALFA21 = -1.000           ALFA12 = -1.000
14 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0601



   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0470  100.00      1.4120     1.3955   -1.17     0.9840     1.0004    1.66
0.0680  100.00      1.3120     1.3857    5.62     0.9920     1.0008    0.89
0.1460  100.00      1.2900     1.3490    4.57     1.0200     1.0041   -1.56
0.2200  100.00      1.1970     1.3134    9.73     1.0320     1.0101   -2.12
0.3970  100.00      1.1340     1.2266    8.17     1.1100     1.0422   -6.11
0.5070  100.00      1.0830     1.1726    8.27     1.1520     1.0820   -6.08
0.5620  100.00      1.0540     1.1460    8.73     1.1910     1.1109   -6.73
0.6240  100.00      1.0380     1.1168    7.59     1.2320     1.1536   -6.36
0.6410  100.00      1.0430     1.1090    6.33     1.2180     1.1676   -4.14
0.6600  100.00      1.0410     1.1004    5.70     1.2340     1.1847   -4.00
0.7470  100.00      1.0140     1.0632    4.85     1.2930     1.2863   -0.52
0.8700  100.00      0.9730     1.0204    4.87     1.5350     1.5356    0.04
0.9520  100.00      0.9720     1.0032    3.21     1.8550     1.8336   -1.15
0.9770  100.00      0.9630     1.0008    3.92     2.2900     1.9609  -14.37
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```
ORIGINAL NRTL EQUATION
ACETONE(1) METHYL ACETATE(2) AT 50C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)


A21ST =      0.0           A12ST =      0.0
A21 =    463.42            A12 =   -310.65
ALFA21 =  0.300            ALFA12 =  0.300
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0314


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0190    50.00      1.2840     1.1654   -9.24     0.9981     1.0001    0.20
0.0400    50.00      1.1000     1.1541    4.92     1.0000     1.0004    0.04
0.0870    50.00      1.1410     1.1311   -0.87     0.9956     1.0017    0.62
0.1890    50.00      1.0880     1.0909    0.27     0.9988     1.0075    0.87
0.2530    50.00      1.0700     1.0712    0.11     1.0030     1.0127    0.97
0.3130    50.00      1.0720     1.0559   -1.50     1.0010     1.0185    1.74
0.3710    50.00      1.0520     1.0437   -0.79     1.0110     1.0246    1.35
0.4540    50.00      1.0460     1.0297   -1.55     1.0170     1.0343    1.70
0.5540    50.00      1.0320     1.0176   -1.40     1.0320     1.0468    1.44
0.6280    50.00      1.0340     1.0111   -2.21     1.0270     1.0564    2.86
0.6880    50.00      1.0220     1.0073   -1.44     1.0510     1.0642    1.26
0.7480    50.00      1.0240     1.0044   -1.91     1.0420     1.0720    2.88
0.7780    50.00      1.0130     1.0033   -0.96     1.0660     1.0758    0.92
0.8030    50.00      1.0210     1.0025   -1.81     1.0370     1.0790    4.05
0.8370    50.00      1.0170     1.0016   -1.51     1.0380     1.0832    4.36
0.8710    50.00      1.0060     1.0010   -0.50     1.0910     1.0874   -0.33
0.9460    50.00      0.9943     1.0002    0.59     1.2220     1.0963  -10.29
0.9590    50.00      0.9994     1.0001    0.07     1.1590     1.0977   -5.29
0.9830    50.00      1.0000     1.0000    0.00     1.0910     1.1004    0.87
0.9910    50.00      1.0000     1.0000    0.00     1.0300     1.1013    6.93
```

```
LEMF EQUATION
ACETONE(1) METHYL ACETATE(2) AT 50C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)



A21ST =      0.0            A12ST =       0.0
A21 =    -180.66            A12 =      203.66
ALFA21 = -1.000             ALFA12 = -1.000
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =    0.0314



   X       TEMP        G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0190    50.00       1.2840      1.1569   -9.89       0.9981      1.0001     0.20
0.0400    50.00       1.1000      1.1468    4.25       1.0000      1.0003     0.03
0.0870    50.00       1.1410      1.1261   -1.31       0.9956      1.0016     0.60
0.1890    50.00       1.0880      1.0895    0.13       0.9988      1.0068     0.81
0.2530    50.00       1.0700      1.0713    0.12       1.0030      1.0117     0.86
0.3130    50.00       1.0720      1.0570   -1.40       1.0010      1.0170     1.60
0.3710    50.00       1.0520      1.0453   -0.64       1.0110      1.0229     1.18
0.4540    50.00       1.0460      1.0317   -1.36       1.0170      1.0323     1.50
0.5540    50.00       1.0320      1.0195   -1.21       1.0320      1.0449     1.25
0.6280    50.00       1.0340      1.0128   -2.05       1.0270      1.0548     2.71
0.6880    50.00       1.0220      1.0086   -1.31       1.0510      1.0633     1.17
0.7480    50.00       1.0240      1.0054   -1.82       1.0420      1.0720     2.88
0.7780    50.00       1.0130      1.0041   -0.88       1.0660      1.0764     0.98
0.8030    50.00       1.0210      1.0031   -1.75       1.0370      1.0802     4.16
0.8370    50.00       1.0170      1.0021   -1.47       1.0380      1.0853     4.56
0.8710    50.00       1.0060      1.0013   -0.47       1.0910      1.0905    -0.05
0.9460    50.00       0.9943      1.0002    0.59       1.2220      1.1020    -9.82
0.9590    50.00       0.9994      1.0001    0.07       1.1590      1.1041    -4.74
0.9830    50.00       1.0000      1.0000    0.00       1.0910      1.1078     1.54
0.9910    50.00       1.0000      1.0000    0.00       1.0300      1.1091     7.68
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```
ORIGINAL NRTL EQUATION
ACETONE(1), TOLUENE(2) AT 45 C
REFFERENCE, ORYE,R.V.,DOCTORAL DISSERTATION, UNIV. CALIFORNIA, BERKELEY (1965)



A21ST =      0.0          A12ST =      0.0
A21 =    205.39           A12 =    237.55
ALFA21 =  0.300           ALFA12 =  0.300
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0003



  X      TEMP       G1OBS      G1CAL  %ERROR       G2OBS      G2CAL  %ERROR

0.0120   45.00     1.9060     1.9057   -0.02      1.0000     1.0001    0.01
0.0340   45.00     1.8530     1.8525   -0.03      1.0010     1.0008   -0.02
0.0490   45.00     1.8170     1.8178    0.05      1.0020     1.0016   -0.04
0.0930   45.00     1.7220     1.7227    0.04      1.0060     1.0057   -0.03
0.1180   45.00     1.6720     1.6729    0.05      1.0090     1.0092    0.02
0.1330   45.00     1.6450     1.6443   -0.04      1.0120     1.0117   -0.03
0.1570   45.00     1.6010     1.6005   -0.03      1.0160     1.0163    0.03
0.2010   45.00     1.5260     1.5264    0.02      1.0270     1.0269   -0.01
0.2350   45.00     1.4730     1.4740    0.07      1.0370     1.0369   -0.01
0.3070   45.00     1.3760     1.3757   -0.02      1.0640     1.0639   -0.01
0.4440   45.00     1.2290     1.2290    0.00      1.1390     1.1385   -0.04
0.5080   45.00     1.1760     1.1757   -0.02      1.1850     1.1853    0.03
0.5370   45.00     1.1540     1.1543    0.03      1.2100     1.2094   -0.05
0.6240   45.00     1.0990     1.0997    0.06      1.2940     1.2933   -0.05
0.6310   45.00     1.0960     1.0959   -0.01      1.3010     1.3009   -0.01
0.7770   45.00     1.0340     1.0343    0.03      1.4930     1.4929   -0.00
0.8720   45.00     1.0110     1.0112    0.02      1.6600     1.6597   -0.02
0.8760   45.00     1.0110     1.0105   -0.05      1.6680     1.6676   -0.02
0.9610   45.00     1.0010     1.0010    0.00      1.8550     1.8551    0.00
0.9710   45.00     1.0010     1.0006   -0.04      1.8800     1.8798   -0.01
```

```
LEMF EQUATION
ACETONE(1), TOLUENE(2) AT 45 C
REFFERENCE, DRYE,R.V.,DOCTORAL DISSERTATION, UNIV. CALIFORNIA, BERKELEY (1965)


A21ST =      0.0           A12ST =      0.0
A21 =    187.15            A12 =    177.40
ALFA21 = -1.000            ALFA12 = -1.000
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0024


   X       TEMP       G1OBS      G1CAL   %ERROR     G2OBS      G2CAL   %ERROR

0.0120    45.00      1.9060     1.9165     0.55     1.0000     1.0001     0.01
0.0340    45.00      1.8530     1.8593     0.34     1.0010     1.0008    -0.02
0.0490    45.00      1.8170     1.8223     0.29     1.0020     1.0017    -0.03
0.0930    45.00      1.7220     1.7220     0.00     1.0060     1.0060     0.00
0.1180    45.00      1.6720     1.6702    -0.11     1.0090     1.0097     0.07
0.1330    45.00      1.6450     1.6407    -0.26     1.0120     1.0122     0.02
0.1570    45.00      1.6010     1.5958    -0.32     1.0160     1.0170     0.10
0.2010    45.00      1.5260     1.5206    -0.36     1.0270     1.0278     0.08
0.2350    45.00      1.4730     1.4679    -0.34     1.0370     1.0379     0.09
0.3070    45.00      1.3760     1.3703    -0.41     1.0640     1.0648     0.08
0.4440    45.00      1.2290     1.2266    -0.19     1.1390     1.1381    -0.08
0.5080    45.00      1.1760     1.1747    -0.11     1.1850     1.1837    -0.11
0.5370    45.00      1.1540     1.1538    -0.01     1.2100     1.2072    -0.24
0.6240    45.00      1.0990     1.1004     0.12     1.2940     1.2891    -0.38
0.6310    45.00      1.0960     1.0966     0.06     1.3010     1.2966    -0.34
0.7770    45.00      1.0340     1.0353     0.13     1.4930     1.4869    -0.41
0.8720    45.00      1.0110     1.0118     0.08     1.6600     1.6569    -0.19
0.8760    45.00      1.0110     1.0111     0.01     1.6680     1.6651    -0.17
0.9610    45.00      1.0010     1.0011     0.01     1.8550     1.8626     0.41
0.9710    45.00      1.0010     1.0006    -0.04     1.8800     1.8892     0.49
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```
ORIGINAL NRTL EQUATION
ACETONE - WATER AT 25.0 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0          A12ST =      0.0
A21 =    802.19           A12 =    432.24
ALFA21 =  0.300           ALFA12 =  0.300
13 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0733


   X      TEMP      G1OBS     G1CAL  %ERROR     G2OBS     G2CAL  %ERROR

0.0194   25.00     5.9690    6.3269    6.00    1.0210    1.0009   -1.97
0.0289   25.00     5.8590    6.0472    3.21    1.0100    1.0020   -0.79
0.0449   25.00     5.7140    5.6152   -1.73    1.0100    1.0049   -0.51
0.0556   25.00     5.5180    5.3510   -3.03    0.9810    1.0075    2.70
0.0939   25.00     4.9160    4.5420   -7.61    0.9590    1.0209    6.45
0.0951   25.00     4.9110    4.5197   -7.97    0.9260    1.0214   10.30
0.1310   25.00     4.1540    3.9221   -5.58    0.9590    1.0400    8.45
0.1470   25.00     3.9290    3.6942   -5.98    0.9090    1.0501   15.52
0.1791   25.00     3.4240    3.2956   -3.75    0.9900    1.0737    8.46
0.2654   25.00     2.5640    2.5123   -2.01    1.1440    1.1600    1.40
0.3538   25.00     2.0340    1.9949   -1.92    1.2450    1.2861    3.30
0.5808   25.00     1.3670    1.3152   -3.79    1.6670    1.8473   10.82
0.7852   25.00     1.1140    1.0725   -3.73    2.3980    2.8613   19.32
```

```
LEMF EQUATION
ACETONE - WATER AT 25.0 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0           A12ST =      0.0
A21 =    390.10            A12 =    397.53
ALFA21 = -1.000            ALFA12 = -1.000
13 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0759



   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0194    25.00      5.9690     6.4331    7.77     1.0210     1.0011   -1.95
0.0289    25.00      5.8590     6.1133    4.34     1.0100     1.0023   -0.76
0.0449    25.00      5.7140     5.6298   -1.47     1.0100     1.0055   -0.45
0.0556    25.00      5.5180     5.3403   -3.22     0.9810     1.0083    2.78
0.0939    25.00      4.9160     4.4829   -8.81     0.9590     1.0226    6.63
0.0951    25.00      4.9110     4.4599   -9.19     0.9260     1.0232   10.49
0.1310    25.00      4.1540     3.8543   -7.21     0.9590     1.0423    8.69
0.1470    25.00      3.9290     3.6291   -7.63     0.9090     1.0525   15.79
0.1791    25.00      3.4240     3.2420   -5.31     0.9900     1.0759    8.67
0.2654    25.00      2.5640     2.5037   -2.35     1.1440     1.1579    1.21
0.3538    25.00      2.0340     2.0252   -0.43     1.2450     1.2731    2.26
0.5808    25.00      1.3670     1.3752    0.60     1.6670     1.7858    7.12
0.7852    25.00      1.1140     1.1035   -0.95     2.3980     2.8886   20.46
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ORIGINAL NRTL EQUATION
ACETONE - WATER AT 100 C
REFFERENCE, GRISWOLD ET AL.,CHEM.ENG.PROG.SYMP.SER.,48,#3,18(1952)



A21ST =      0.0           A12ST =      0.0
A21 =    1475.35           A12 =    174.02
ALFA21 =  0.300            ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0329



   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0480  100.00      6.8640     6.4834   -5.55     1.0570     1.0082   -4.62
0.0820  100.00      4.9240     5.2553    6.73     1.0180     1.0230    0.49
0.1080  100.00      4.3860     4.5425    3.57     1.1130     1.0387   -6.67
0.2200  100.00      2.6460     2.7375    3.46     1.1450     1.1455    0.05
0.3080  100.00      1.9980     2.0495    2.58     1.3000     1.2701   -2.30
0.3970  100.00      1.6440     1.6431   -0.05     1.4910     1.4316   -3.98
0.5260  100.00      1.3080     1.3121    0.31     1.8120     1.7333   -4.35
0.4800  100.00      1.4550     1.4062   -3.35     1.6680     1.6160   -3.12
0.6950  100.00      1.1080     1.1027   -0.48     2.2990     2.2682   -1.34
0.7420  100.00      1.0740     1.0698   -0.39     2.4360     2.4500    0.58
0.8540  100.00      1.0170     1.0202    0.31     3.0300     2.9522   -2.57
0.9440  100.00      0.9950     1.0028    0.78     3.5090     3.4369   -2.06
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```
LEMF EQUATION
ACETONE - WATER AT 100 C
REFFERENCE, GRISWOLD ET AL.,CHEM.ENG.PROG.SYMP.SER.,48,#3,18(1952)



A21ST =      0.0          A12ST =      0.0
A21 =    285.76           A12 =    617.95
ALFA21 = -1.000           ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0316



   X      TEMP      G1OBS      G1CAL  %ERROR     G2OBS      G2CAL  %ERROR

0.0480  100.00     6.8640     6.6842   -2.62     1.0570     1.0097   -4.48
0.0820  100.00     4.9240     5.2690    7.01     1.0180     1.0264    0.83
0.1080  100.00     4.3360     4.4899    2.37     1.1130     1.0438   -6.22
0.2200  100.00     2.6460     2.6550    0.34     1.1450     1.1546    0.84
0.3080  100.00     1.9980     2.0038    0.29     1.3000     1.2762   -1.83
0.3970  100.00     1.6440     1.6274   -1.01     1.4910     1.4284   -4.20
0.5260  100.00     1.3080     1.3192    0.85     1.8120     1.7076   -5.76
0.4800  100.00     1.4550     1.4076   -3.26     1.6680     1.5992   -4.13
0.6950  100.00     1.1080     1.1146    0.59     2.2990     2.2190   -3.48
0.7420  100.00     1.0740     1.0802    0.58     2.4360     2.4036   -1.33
0.8540  100.00     1.0170     1.0250    0.79     3.0300     2.9560   -2.44
0.9440  100.00     0.9950     1.0037    0.87     3.5090     3.5653    1.60
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```
ORIGINAL NRTL EQUATION
ACETONE - WATER AT 150 C
REFFERENCE, GRISWOLD ET AL.,CHEM.ENG.PROG.SYMP.SER.,48,#3,18(1952)



A21ST =      0.0            A12ST =      0.0
A21 =   1780.77             A12 =     -15.48
ALFA21 =  0.300             ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0518



   X       TEMP        G1OBS      G1CAL  %ERROR       G2OBS      G2CAL  %ERROR

0.0710  150.00       4.6860     4.9601    5.85       1.1020     1.0179   -7.63
0.1630  150.00       2.8130     3.0628    8.88       1.2130     1.0839  -10.64
0.3490  150.00       1.5960     1.6742    4.90       1.4680     1.3252   -9.73
0.4300  150.00       1.3870     1.4254    2.77       1.5960     1.4678   -8.03
0.5780  150.00       1.1750     1.1752    0.02       1.8790     1.7810   -5.22
0.6860  150.00       1.0880     1.0820   -0.55       2.1400     2.0504   -4.19
0.7220  150.00       1.0660     1.0612   -0.45       2.2590     2.1475   -4.93
0.7630  150.00       1.0510     1.0421   -0.85       2.3770     2.2626   -4.81
0.8180  150.00       1.0340     1.0232   -1.04       2.4820     2.4240   -2.34
0.8540  150.00       1.0190     1.0143   -0.46       2.6760     2.5341   -5.30
0.9120  150.00       1.0040     1.0049    0.09       2.7660     2.7186   -1.72
0.9530  150.00       0.9980     1.0013    0.33       2.7680     2.8541    3.11
```

```
LEMF EQUATION
ACETONE - WATER AT 150 C
REFFERENCE, GRISWOLD ET AL.,CHEM.ENG.PROG.SYMP.SER.,48,#3,18(1952)


A21ST =      0.0           A12ST =      0.0
A21 =    192.57            A12 =    709.90
ALFA21 = -1.000            ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0526


   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0710  150.00      4.6860     5.0490    7.75     1.1020     1.0204   -7.41
0.1630  150.00      2.8130     3.0098    6.99     1.2130     1.0912  -10.05
0.3490  150.00      1.5960     1.6512    3.46     1.4680     1.3307   -9.35
0.4300  150.00      1.3370     1.4165    2.13     1.5960     1.4667   -8.10
0.5780  150.00      1.1750     1.1788    0.33     1.8790     1.7635   -6.15
0.6860  150.00      1.0880     1.0872   -0.07     2.1400     2.0247   -5.39
0.7220  150.00      1.0660     1.0661    0.01     2.2590     2.1216   -6.08
0.7630  150.00      1.0510     1.0464   -0.44     2.3770     2.2388   -5.81
0.8180  150.00      1.0340     1.0262   -0.75     2.4820     2.4086   -2.96
0.8540  150.00      1.0190     1.0165   -0.24     2.6760     2.5285   -5.51
0.9120  150.00      1.0040     1.0058    0.18     2.7660     2.7382   -1.00
0.9530  150.00      0.9980     1.0016    0.36     2.7680     2.9003    4.78
```

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ORIGINAL NRTL EQUATION
ACETONE - WATER AT  200 C
REFFERENCE, GRISWOLD ET AL.,CHEM.ENG.PROG.SYMP.SER.,48,#3,18(1952)



A21ST =      0.0           A12ST =      0.0
A21 =   2070.45            A12 =   -283.10
ALFA21 =  0.300            ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0609



   X      TEMP        G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0450  200.00       4.5160     4.7172    4.46     1.0600     1.0073   -4.98
0.0920  200.00       3.2770     3.5679    8.88     1.1070     1.0280   -7.14
0.2260  200.00       1.9380     2.0329    4.90     1.2350     1.1396   -7.72
0.3620  200.00       1.4070     1.4545    3.37     1.4440     1.3067   -9.51
0.4460  200.00       1.2580     1.2754    1.38     1.5730     1.4276   -9.24
0.5120  200.00       1.1860     1.1832   -0.23     1.6770     1.5291   -8.82
0.5510  200.00       1.1530     1.1425   -0.91     1.7560     1.5911   -9.39
0.6340  200.00       1.0940     1.0799   -1.29     1.8770     1.7261   -8.04
0.7350  200.00       1.0560     1.0346   -2.02     2.0570     1.8926   -7.99
0.7720  200.00       1.0420     1.0240   -1.73     2.1100     1.9533   -7.43
0.8670  200.00       1.0180     1.0069   -1.09     2.1840     2.1063   -3.56
0.9400  200.00       0.9920     1.0012    0.93     2.1000     2.2192    5.68
```

```
LEMF EQUATION
ACETONE - WATER AT  200 C
REFFERENCE, GRISWOLD ET AL.,CHEM.ENG.PROG.SYMP.SER.,48,#3,18(1952)


A21ST =      0.0          A12ST =      0.0
A21 =     26.30           A12 =    776.36
ALFA21 = -1.000           ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0627


   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0450  200.00     4.5160     4.7708    5.64     1.0600     1.0079   -4.92
0.0920  200.00     3.2770     3.5490    8.30     1.1070     1.0298   -6.97
0.2260  200.00     1.9380     2.0050    3.46     1.2350     1.1429   -7.46
0.3620  200.00     1.4070     1.4469    2.83     1.4440     1.3056   -9.59
0.4460  200.00     1.2580     1.2749    1.34     1.5730     1.4218   -9.61
0.5120  200.00     1.1860     1.1857   -0.02     1.6770     1.5194   -9.40
0.5510  200.00     1.1530     1.1460   -0.61     1.7560     1.5793  -10.06
0.6340  200.00     1.0940     1.0840   -0.91     1.8770     1.7116   -8.81
0.7350  200.00     1.0560     1.0378   -1.72     2.0570     1.8798   -8.61
0.7720  200.00     1.0420     1.0266   -1.48     2.1100     1.9432   -7.91
0.8670  200.00     1.0180     1.0080   -0.98     2.1840     2.1096   -3.41
0.9400  200.00     0.9920     1.0015    0.96     2.1000     2.2406    6.69
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```
ORIGINAL NRTL EQUATION
ACETONITRILE(1)-TOLUENE(2) AT 45C
REFFERENCE, DRYE,R.V.,DOCTORAL DISSERTATION, UNIV. CALIFORNIA, BERKELEY (1965)


A21ST =      0.0          A12ST =      0.0
A21 =     358.89          A12 =     507.60
ALFA21 =  0.300           ALFA12 =  0.300
18 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0221


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0200    45.00      3.2620     3.1656   -2.95     1.0010     1.0005   -0.05
0.0270    45.00      3.1970     3.1155   -2.55     1.0010     1.0009   -0.01
0.0310    45.00      3.1590     3.0874   -2.27     1.0020     1.0011   -0.09
0.0400    45.00      3.0700     3.0254   -1.45     1.0030     1.0019   -0.11
0.0660    45.00      2.8510     2.8565    0.19     1.0070     1.0051   -0.19
0.0980    45.00      2.6240     2.6673    1.65     1.0140     1.0113   -0.27
0.2130    45.00      2.0390     2.1263    4.28     1.0620     1.0544   -0.72
0.2820    45.00      1.8070     1.8826    4.18     1.1050     1.0975   -0.68
0.3010    45.00      1.7550     1.8239    3.93     1.1180     1.1118   -0.55
0.3180    45.00      1.7090     1.7742    3.81     1.1320     1.1257   -0.55
0.4790    45.00      1.3940     1.4086    1.05     1.2960     1.3119    1.23
0.5110    45.00      1.3480     1.3545    0.48     1.3390     1.3632    1.81
0.7350    45.00      1.1110     1.0978   -1.19     1.8520     1.9325    4.34
0.5960    45.00      1.2420     1.2342   -0.63     1.4820     1.5300    3.24
0.8660    45.00      1.0310     1.0249   -0.59     2.5110     2.5473    1.45
0.8910    45.00      1.0210     1.0165   -0.44     2.6940     2.7034    0.35
0.9340    45.00      1.0080     1.0061   -0.19     3.0840     3.0109   -2.37
0.9730    45.00      1.0010     1.0010    0.00     3.5440     3.3405   -5.74
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```
LEMF EQUATION
ACETONITRILE(1)-TOLUENE(2) AT 45C
REFFERENCE, ORYE,R.V.,DOCTORAL DISSERTATION, UNIV. CALIFORNIA, BERKELEY (1965)


A21ST =      0.0          A12ST =      0.0
A21 =    331.33           A12 =    282.82
ALFA21 = -1.000           ALFA12 = -1.000
18 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0109


  X       TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0200   45.00     3.2620     3.2176   -1.36     1.0010     1.0006   -0.04
0.0270   45.00     3.1970     3.1578   -1.23     1.0010     1.0010    0.00
0.0310   45.00     3.1590     3.1245   -1.09     1.0020     1.0013   -0.07
0.0400   45.00     3.0700     3.0519   -0.59     1.0030     1.0022   -0.08
0.0660   45.00     2.8510     2.8579    0.24     1.0070     1.0059   -0.11
0.0980   45.00     2.6240     2.6479    0.91     1.0140     1.0128   -0.12
0.2130   45.00     2.0390     2.0847    2.24     1.0620     1.0581   -0.37
0.2820   45.00     1.8070     1.8467    2.20     1.1050     1.1011   -0.36
0.3010   45.00     1.7550     1.7906    2.03     1.1180     1.1151   -0.26
0.3150   45.00     1.7090     1.7433    2.01     1.1320     1.1286   -0.30
0.4790   45.00     1.3940     1.4013    0.53     1.2960     1.3042    0.63
0.5110   45.00     1.3480     1.3509    0.22     1.3390     1.3519    0.96
0.7350   45.00     1.1110     1.1047   -0.56     1.8520     1.8914    2.13
0.5960   45.00     1.2420     1.2377   -0.35     1.4820     1.5070    1.69
0.8660   45.00     1.0310     1.0286   -0.24     2.5110     2.5261    0.60
0.8910   45.00     1.0210     1.0192   -0.17     2.6940     2.6984    0.16
0.9340   45.00     1.0080     1.0073   -0.07     3.0840     3.0521   -1.03
0.9730   45.00     1.0010     1.0013    0.03     3.5440     3.4535   -2.55
```

```
ORIGINAL NRTL EQUATION
BENZENE - N-HEPTANE AT 400 MM. PRESS.
REFFERENCE, NIELSEN, ET AL.,J. CHEM.ENG.DATA,4,#2,145(1959)


A21ST =      0.0            A12ST =      0.0
A21 =    -267.04            A12 =     710.96
ALFA21 =  0.300             ALFA12 =  0.300
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0023


   X       TEMP       G1OBS      G1CAL  %ERROR       G2OBS      G2CAL  %ERROR

0.1000    73.90      1.3900     1.3857   -0.31      1.0000     1.0023    0.23
0.2000    70.50      1.3300     1.3267   -0.25      1.0100     1.0104    0.04
0.3000    68.00      1.2700     1.2682   -0.14      1.0300     1.0262   -0.37
0.4000    66.00      1.2100     1.2115    0.12      1.0500     1.0524    0.23
0.5000    64.40      1.1600     1.1579   -0.18      1.0900     1.0929    0.27
0.6000    63.30      1.1100     1.1089   -0.10      1.1500     1.1532    0.28
0.7000    62.10      1.0700     1.0663   -0.35      1.2400     1.2417    0.14
0.8000    61.40      1.0300     1.0320    0.20      1.3700     1.3714    0.10
0.9000    60.80      1.0100     1.0088   -0.12      1.5600     1.5637    0.23
```

```
LEMF EQUATION
BENZENE - N-HEPTANE AT 400 MM. PRESS.
REFFERENCE, NIELSEN, ET AL.,J. CHEM.ENG.DATA,4,#2,145(1959)



A21ST =      0.0          A12ST =      0.0
A21 =    289.28           A12 =     -34.94
ALFA21 = -1.000           ALFA12 = -1.000
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0032



   X       TEMP       G1OBS       G1CAL   %ERROR       G2OBS       G2CAL  %ERROR

0.1000    73.90      1.3900      1.3839   -0.44      1.0000      1.0025    0.25
0.2000    70.50      1.3300      1.3245   -0.41      1.0100      1.0110    0.10
0.3000    68.00      1.2700      1.2660   -0.32      1.0300      1.0273   -0.26
0.4000    66.00      1.2100      1.2096   -0.04      1.0500      1.0540    0.38
0.5000    64.40      1.1600      1.1566   -0.30      1.0900      1.0948    0.44
0.6000    63.30      1.1100      1.1081   -0.17      1.1500      1.1551    0.44
0.7000    62.10      1.0700      1.0661   -0.36      1.2400      1.2435    0.28
0.8000    61.40      1.0300      1.0321    0.21      1.3700      1.3729    0.21
0.9000    60.80      1.0100      1.0089   -0.11      1.5600      1.5662    0.40
```

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ORIGINAL NRTL EQUATION
NBUTANOL - WATER AT 760 MM. PRESS.
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)



A21ST =      0.0          A12ST =     0.0
A21 =    2686.82          A12 =     94.78
ALFA21 =  0.300           ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =    0.0754



   X       TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0150    93.40    37.1390    32.8660  -11.51     0.9956     1.0024    0.68
0.0200    93.00    30.6910    29.8375   -2.78     0.9910     1.0042    1.33
0.0250    92.70    25.2620    27.1472    7.46     1.0015     1.0064    0.49
0.4230    92.80     1.4990     1.4907   -0.55     1.6820     1.8260    8.56
0.4480    92.90     1.4094     1.4168    0.53     1.7514     1.8988    8.42
0.4940    93.40     1.3020     1.3092    0.55     1.8510     2.0363   10.01
0.5040    93.50     1.2902     1.2897   -0.04     1.8714     2.0668   10.44
0.6950    96.30     1.0680     1.0745    0.61     2.4750     2.6906    8.71
0.7250    97.20     1.0482     1.0578    0.91     2.5740     2.7950    8.59
0.7430    97.90     1.0280     1.0491    2.06     2.6360     2.8583    8.43
0.9300   108.60     0.9464     1.0029    5.97     3.7321     3.5613   -4.58
0.9610   111.50     0.9400     1.0009    6.48     4.6540     3.6869  -20.78
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LEMF EQUATION
NBUTANOL - WATER AT 760 MM. PRESS.
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)


A21ST =      0.0            A12ST =      0.0
A21 =    175.52             A12 =    830.03
ALFA21 = -1.000             ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0749


   X       TEMP       G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0150    93.40     37.1390     32.4616  -12.59      0.9956      1.0024    0.68
0.0200    93.00     30.6910     29.5863   -3.60      0.9910      1.0042    1.33
0.0250    92.70     25.2620     26.9962    6.86      1.0015      1.0064    0.49
0.4230    92.80      1.4990      1.5315    2.17      1.6820      1.8126    7.76
0.4480    92.90      1.4094      1.4549    3.23      1.7514      1.8852    7.64
0.4940    93.40      1.3020      1.3420    3.07      1.8510      2.0221    9.24
0.5040    93.50      1.2902      1.3214    2.42      1.8714      2.0528    9.69
0.6950    96.30      1.0680      1.0882    1.89      2.4750      2.6980    9.01
0.7250    97.20      1.0482      1.0691    2.00      2.5740      2.8081    9.09
0.7430    97.90      1.0280      1.0591    3.03      2.6360      2.8744    9.04
0.9300   108.80      0.9464      1.0037    6.06      3.7321      3.6092   -3.29
0.9610   111.50      0.9400      1.0011    6.50      4.6540      3.7367  -19.71
```

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ORIGINAL NRTL EQUATION
CARBON TETRACHLORIDE - BENZENE AT 49.99 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =     0.0           A12ST =     0.0
A21 =    375.58           A12 =   -234.65
ALFA21 =  0.300           ALFA12 =  0.300
16 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0129



   X       TEMP      G1OBS      G1CAL   %ERROR      G2OBS      G2CAL   %ERROR

0.0507    49.99     1.2160     1.1662   -4.09      0.9890     1.0006    1.17
0.0507    49.99     1.1730     1.1662   -0.58      0.9890     1.0006    1.17
0.1170    49.99     1.1300     1.1351    0.45      0.9950     1.0031    0.81
0.1745    49.99     1.1130     1.1121   -0.09      0.9950     1.0066    1.16
0.1772    49.99     1.1040     1.1110    0.64      0.9980     1.0068    0.88
0.2506    49.99     1.0730     1.0863    1.24      1.0040     1.0129    0.89
0.2525    49.99     1.0780     1.0857    0.72      1.0000     1.0131    1.31
0.2947    49.99     1.0750     1.0736   -0.13      1.0040     1.0174    1.34
0.3947    49.99     1.0640     1.0498   -1.34      1.0180     1.0294    1.12
0.3959    49.99     1.0630     1.0495   -1.27      1.0110     1.0296    1.64
0.5561    49.99     1.0360     1.0235   -1.21      1.0390     1.0532    1.37
0.5600    49.99     1.0280     1.0230   -0.49      1.0480     1.0538    0.55
0.6737    49.99     1.0240     1.0115   -1.22      1.0640     1.0730    0.84
0.6774    49.99     1.0220     1.0113   -1.05      1.0630     1.0736    1.00
0.7646    49.99     1.0160     1.0056   -1.02      1.0750     1.0892    1.32
0.7658    49.99     1.0170     1.0055   -1.13      1.0740     1.0895    1.44
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LEMF EQUATION
CARBON TETRACHLORIDE - BENZENE AT 49.99 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0            A12ST =      0.0
A21 =    -250.24            A12 =     248.89
ALFA21 = -1.000             ALFA12 = -1.000
16 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0128


   X       TEMP      G1OBS      G1CAL   %ERROR     G2OBS      G2CAL   %ERROR

0.0507    49.99     1.2160     1.1688   -3.88     0.9890     1.0007    1.18
0.0507    49.99     1.1730     1.1688   -0.36     0.9890     1.0007    1.18
0.1170    49.99     1.1300     1.1356    0.49     0.9950     1.0033    0.83
0.1745    49.99     1.1130     1.1115   -0.14     0.9950     1.0069    1.20
0.1772    49.99     1.1040     1.1104    0.58     0.9980     1.0072    0.92
0.2506    49.99     1.0730     1.0851    1.12     1.0040     1.0135    0.94
0.2525    49.99     1.0780     1.0845    0.60     1.0000     1.0137    1.37
0.2947    49.99     1.0750     1.0722   -0.26     1.0040     1.0180    1.40
0.3947    49.99     1.0640     1.0485   -1.45     1.0180     1.0300    1.18
0.3959    49.99     1.0630     1.0483   -1.38     1.0110     1.0301    1.89
0.5561    49.99     1.0360     1.0228   -1.28     1.0390     1.0532    1.37
0.5600    49.99     1.0280     1.0223   -0.55     1.0480     1.0538    0.56
0.6737    49.99     1.0240     1.0112   -1.25     1.0640     1.0724    0.79
0.6774    49.99     1.0220     1.0110   -1.08     1.0630     1.0730    0.94
0.7646    49.99     1.0160     1.0055   -1.04     1.0750     1.0881    1.22
0.7658    49.99     1.0170     1.0054   -1.14     1.0740     1.0884    1.34
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ORIGINAL NRTL EQUATION
CARBON TET BENZENE AT 760 MM PRESS
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)



A21ST =     0.0           A12ST =     0.0
A21 =     54.06           A12 =     20.68
ALFA21 =  0.300           ALFA12 =  0.300
 9 DATA POINTS
STD, DEV, OF CALCULATED GAMMAS =   0.0040



  X       TEMP       G1OBS      G1CAL   %ERROR      G2OBS      G2CAL   %ERROR

0.1360   79.30      1.0860     1.0824   -0.33      1.0020     1.0020   -0.00
0.2160   78.80      1.0630     1.0673    0.40      1.0090     1.0050   -0.39
0.2570   78.60      1.0690     1.0602   -0.82      1.0060     1.0071    0.11
0.2940   78.50      1.0460     1.0541    0.78      1.0120     1.0093   -0.26
0.3634   78.20      1.0410     1.0437    0.26      1.0150     1.0143   -0.07
0.4060   78.00      1.0420     1.0380   -0.39      1.0160     1.0178    0.18
0.5270   77.60      1.0230     1.0238    0.08      1.0330     1.0301   -0.28
0.6200   77.40      1.0180     1.0153   -0.27      1.0370     1.0418    0.47
0.7220   77.10      1.0130     1.0081   -0.48      1.0560     1.0570    0.10
```

```
LEMF EQUATION
CARBON TET BENZENE AT 760 MM PRESS
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)


A21ST =      0.0            A12ST =      0.0
A21 =      29.29            A12 =      42.73
ALFA21 = -1.000             ALFA12 = -1.000
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =    0.0040


   X       TEMP       G1OBS      G1CAL   %ERROR      G2OBS      G2CAL   %ERROR

0.1360    79.30      1.0860     1.0824    -0.33     1.0020     1.0020     0.00
0.2160    78.80      1.0630     1.0672     0.40     1.0090     1.0051    -0.39
0.2570    78.60      1.0690     1.0601    -0.83     1.0060     1.0072     0.11
0.2940    78.50      1.0460     1.0540     0.77     1.0120     1.0094    -0.26
0.3634    78.20      1.0410     1.0436     0.25     1.0150     1.0143    -0.07
0.4060    78.00      1.0420     1.0379    -0.40     1.0160     1.0179     0.18
0.5270    77.60      1.0230     1.0238     0.07     1.0330     1.0302    -0.27
0.6200    77.40      1.0180     1.0152    -0.27     1.0370     1.0419     0.47
0.7220    77.10      1.0130     1.0081    -0.48     1.0560     1.0570     0.09
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ORIGINAL NRTL EQUATION
CHLOROFORM - BENZENE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =     0.0          A12ST =      0.0
A21 =   -133.58          A12 =     -10.39
ALFA21 =  0.300          ALFA12 =   0.300
14 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0272



   X      TEMP      G1OBS     G1CAL  %ERROR     G2OBS     G2CAL  %ERROR

0.0532   79.60     0.8240    0.8310    0.84    0.9940    0.9994    0.55
0.0559   79.55     0.8230    0.8318    1.07    0.9950    0.9994    0.44
0.1313   78.25     0.8480    0.8541    0.71    0.9960    0.9966    0.06
0.1459   78.05     0.8530    0.8583    0.62    0.9930    0.9958    0.28
0.2404   76.45     0.8500    0.8846    4.07    0.9990    0.9884   -1.06
0.2512   76.20     0.8610    0.8875    3.07    0.9970    0.9873   -0.97
0.2853   75.60     0.8770    0.8964    2.21    0.9900    0.9836   -0.65
0.3542   74.35     0.8730    0.9137    4.66    1.0010    0.9746   -2.64
0.4216   73.00     0.9090    0.9294    2.24    0.9760    0.9638   -1.25
0.4777   71.95     0.9140    0.9415    3.01    0.9740    0.9534   -2.12
0.6353   68.75     0.9400    0.9703    3.22    0.9690    0.9169   -5.38
0.7099   67.20     0.9630    0.9808    1.85    0.9210    0.8961   -2.71
0.7994   65.40     0.9740    0.9906    1.71    0.9000    0.8682   -3.53
0.9126   63.10     0.9870    0.9982    1.13    0.8900    0.8287   -6.88
```

```
LEMF EQUATION
CHLOROFORM - BENZENE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0            A12ST =      0.0
A21 =     -49.60            A12 =    -109.07
ALFA21 = -1.000             ALFA12 = -1.000
14 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0271


   X      TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0532   79.60     0.8240     0.8318    0.95     0.9940     0.9995    0.55
0.0559   79.55     0.8230     0.8326    1.17     0.9950     0.9994    0.44
0.1313   78.25     0.8480     0.8544    0.76     0.9960     0.9967    0.07
0.1459   78.05     0.8530     0.8586    0.65     0.9930     0.9959    0.29
0.2404   76.45     0.8500     0.8844    4.04     0.9990     0.9887   -1.03
0.2512   76.20     0.8610     0.8872    3.04     0.9970     0.9876   -0.94
0.2853   75.60     0.8770     0.8960    2.17     0.9900     0.9840   -0.61
0.3542   74.35     0.8730     0.9130    4.59     1.0010     0.9751   -2.59
0.4216   73.00     0.9090     0.9296    2.15     0.9760     0.9644   -1.19
0.4777   71.95     0.9140     0.9406    2.91     0.9740     0.9540   -2.05
0.6353   68.75     0.9400     0.9695    3.14     0.9690     0.9175   -5.32
0.7099   67.20     0.9630     0.9802    1.79     0.9210     0.8964   -2.67
0.7994   65.40     0.9740     0.9903    1.67     0.9000     0.8679   -3.57
0.9126   63.10     0.9870     0.9981    1.12     0.8900     0.8270   -7.08
```

```
ORIGINAL NRTL EQUATION
CHLOROFORM - ETHYL ACETATE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0           A12ST =      0.0
A21 =    -772.61           A12 =     380.32
ALFA21 =  0.300            ALFA12 =  0.300
18 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0095



   X       TEMP       G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0710    77.50      0.5560      0.5555   -0.09       0.9880      0.9979    1.00
0.1100    77.60      0.5710      0.5736    0.45       0.9860      0.9947    0.88
0.1400    77.70      0.5870      0.5880    0.17       0.9810      0.9912    1.04
0.1740    77.80      0.6010      0.6048    0.63       0.9740      0.9860    1.24
0.2230    77.80      0.6220      0.6297    1.24       0.9660      0.9762    1.06
0.2590    77.50      0.6420      0.6483    0.99       0.9660      0.9670    0.11
0.3010    77.30      0.6650      0.6709    0.89       0.9560      0.9541   -0.20
0.3650    76.80      0.7020      0.7063    0.62       0.9360      0.9295   -0.70
0.4480    76.00      0.7480      0.7540    0.81       0.8940      0.8879   -0.69
0.5040    75.10      0.7790      0.7867    0.99       0.8670      0.8532   -1.59
0.5280    74.70      0.7920      0.8008    1.12       0.8500      0.8367   -1.57
0.5810    73.50      0.8310      0.8318    0.09       0.8050      0.7964   -1.07
0.6500    71.80      0.8690      0.8714    0.28       0.7490      0.7365   -1.66
0.7040    70.40      0.9000      0.9012    0.13       0.6800      0.6841    0.60
0.7510    68.90      0.9240      0.9255    0.16       0.6400      0.6346   -0.85
0.7900    67.70      0.9430      0.9442    0.13       0.5880      0.5913    0.56
0.8560    65.60      0.9680      0.9714    0.35       0.5130      0.5143    0.26
0.9220    63.70      0.9820      0.9909    0.90       0.4460      0.4350   -2.47
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LEMF EQUATION
CHLOROFORM - ETHYL ACETATE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0          A12ST =      0.0
A21 =   -230.59           A12 =   -614.94
ALFA21 = -1.000           ALFA12 = -1.000
18 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0141



   X      TEMP      G1OBS      G1CAL   %ERROR     G2OBS      G2CAL   %ERROR

0.0710   77.50     0.5560     0.5415   -2.61     0.9880     0.9970    0.91
0.1100   77.60     0.5710     0.5648   -1.08     0.9860     0.9928    0.69
0.1400   77.70     0.5870     0.5826   -0.75     0.9810     0.9884    0.76
0.1740   77.80     0.6010     0.6026    0.26     0.9740     0.9823    0.85
0.2230   77.80     0.6220     0.6310    1.44     0.9660     0.9711    0.53
0.2590   77.50     0.6420     0.6515    1.49     0.9660     0.9612   -0.50
0.3010   77.30     0.6650     0.6754    1.56     0.9560     0.9478   -0.86
0.3650   76.80     0.7020     0.7112    1.31     0.9360     0.9235   -1.34
0.4480   76.00     0.7480     0.7571    1.22     0.8940     0.8844   -1.08
0.5040   75.10     0.7790     0.7876    1.11     0.8670     0.8527   -1.64
0.5280   74.70     0.7920     0.8006    1.09     0.8500     0.8378   -1.44
0.5810   73.50     0.8310     0.8290   -0.24     0.8050     0.8015   -0.44
0.6500   71.80     0.8690     0.8655   -0.40     0.7490     0.7468   -0.29
0.7040   70.40     0.9000     0.8935   -0.72     0.6800     0.6976    2.59
0.7510   68.90     0.9240     0.9170   -0.76     0.6400     0.6496    1.50
0.7900   67.70     0.9430     0.9358   -0.77     0.5880     0.6058    3.03
0.8560   65.60     0.9680     0.9647   -0.34     0.5130     0.5234    2.02
0.9220   63.70     0.9820     0.9878    0.59     0.4460     0.4306   -3.46
```

```
ORIGINAL NRTL EQUATION
CHLOROFORM(1) METHANOL(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)


A21ST =      0.0            A12ST =      0.0
A21 =   -167.37             A12 =   1496.32
ALFA21 =  0.300             ALFA12 =  0.300
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0210


   X      TEMP      G1OBS     G1CAL  %ERROR      G2OBS     G2CAL  %ERROR

0.1000   50.00     2.2981    2.2838   -0.62     0.9923    1.0039    1.17
0.1780   50.00     2.0900    2.1450    2.63     1.0215    1.0143   -0.71
0.2660   50.00     2.0230    1.9846   -1.90     1.0212    1.0372    1.57
0.4270   50.00     1.7461    1.6911   -3.15     1.0933    1.1313    3.47
0.5540   50.00     1.4126    1.4715    4.17     1.3333    1.2956   -2.82
0.6530   50.00     1.2953    1.3159    1.59     1.5166    1.5382    1.42
0.7040   50.00     1.2194    1.2433    1.96     1.7485    1.7344   -0.81
0.7850   50.00     1.1294    1.1417    1.09     2.2154    2.2274    0.54
0.9350   50.00     1.0109    1.0163    0.53     4.7651    4.7093   -1.17
```

```
LEMF EQUATION
CHLOROFORM(1) METHANOL(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)


A21ST =      0.0           A12ST =      0.0
A21 =     552.97           A12 =      38.66
ALFA21 = -1.000            ALFA12 = -1.000
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0224


   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.1000    50.00       2.2981      2.3087    0.46      0.9923      1.0048    1.26
0.1780    50.00       2.0900      2.1489    2.82      1.0215      1.0166   -0.48
0.2660    50.00       2.0230      1.9755   -2.35      1.0212      1.0414    1.98
0.4270    50.00       1.7461      1.6784   -3.87      1.0933      1.1373    4.02
0.5540    50.00       1.4126      1.4654    3.73      1.3333      1.2982   -2.64
0.6530    50.00       1.2953      1.3155    1.56      1.5166      1.5320    1.02
0.7040    50.00       1.2194      1.2451    2.11      1.7485      1.7209   -1.58
0.7850    50.00       1.1294      1.1454    1.42      2.2154      2.1993   -0.73
0.9350    50.00       1.0109      1.0176    0.66      4.7651      4.7364   -0.60
```

```
ORIGINAL NRTL EQUATION
CHLOROFORM - METHANOL AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =       0.0          A12ST =        0.0
A21 =    -139.46           A12 =    1358.91
ALFA21 =  0.300            ALFA12 =  0.300
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =    0.0193


   X      TEMP       G1OBS       G1CAL   %ERROR      G2OBS       G2CAL   %ERROR

0.0650   62.00      2.3140      2.3230     0.39     0.9850      1.0019     1.71
0.1460   59.30      2.2150      2.1673    -2.15     0.9860      1.0104     2.48
0.1960   57.80      2.1530      2.0717    -3.78     0.9940      1.0201     2.63
0.2300   57.00      2.0930      2.0068    -4.12     0.9990      1.0292     3.02
0.2870   55.90      1.9540      1.8990    -2.82     1.0270      1.0496     2.20
0.3320   55.30      1.8500      1.8149    -1.90     1.0480      1.0714     2.23
0.3830   54.70      1.7420      1.7216    -1.17     1.0850      1.1037     1.73
0.4250   54.30      1.6620      1.6466    -0.92     1.1220      1.1379     1.41
0.4590   54.00      1.5980      1.5875    -0.66     1.1630      1.1716     0.74
0.5200   53.80      1.4860      1.4850    -0.07     1.2370      1.2495     1.01
0.5570   53.70      1.4200      1.4257     0.40     1.3050      1.3106     0.43
0.6280   53.50      1.3170      1.3191     0.16     1.4680      1.4684     0.02
0.6360   53.50      1.3060      1.3077     0.13     1.4870      1.4904     0.23
0.6670   53.50      1.2630      1.2650     0.16     1.5850      1.5860     0.06
0.7530   53.70      1.1600      1.1588    -0.11     1.9410      1.9680     1.39
0.7970   53.90      1.1160      1.1125    -0.31     2.2160      2.2637     2.15
0.8550   54.40      1.0660      1.0615    -0.42     2.7450      2.8272     3.00
0.9040   55.20      1.0330      1.0287    -0.41     3.4490      3.5477     2.86
0.9370   56.30      1.0160      1.0129    -0.30     4.0730      4.2263     3.76
0.9700   57.90      1.0040      1.0031    -0.09     5.3340      5.1316    -3.80
```

```
LEMF EQUATION
CHLOROFORM - METHANOL AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0           A12ST =      0.0
A21 =    521.70            A12 =      78.64
ALFA21 = -1.000            ALFA12 = -1.000
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0206


  X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0650   62.00       2.3140      2.3398    1.12      0.9850      1.0022    1.75
0.1460   59.30       2.2150      2.1690   -2.08      0.9860      1.0122    2.66
0.1960   57.80       2.1530      2.0676   -3.97      0.9940      1.0231    2.93
0.2300   57.00       2.0930      1.9997   -4.46      0.9990      1.0330    3.40
0.2870   55.90       1.9540      1.8887   -3.34      1.0270      1.0549    2.72
0.3320   55.30       1.8500      1.8035   -2.51      1.0480      1.0777    2.84
0.3830   54.70       1.7420      1.7105   -1.81      1.0850      1.1109    2.39
0.4250   54.30       1.6620      1.6367   -1.52      1.1220      1.1454    2.09
0.4590   54.00       1.5980      1.5790   -1.19      1.1630      1.1792    1.39
0.5200   53.80       1.4860      1.4793   -0.45      1.2370      1.2561    1.54
0.5570   53.70       1.4200      1.4220    0.14      1.3050      1.3158    0.82
0.6280   53.50       1.3170      1.3190    0.15      1.4680      1.4692    0.08
0.6360   53.50       1.3060      1.3080    0.15      1.4870      1.4906    0.24
0.6670   53.50       1.2630      1.2665    0.28      1.5850      1.5832   -0.11
0.7530   53.70       1.1600      1.1624    0.20      1.9410      1.9546    0.70
0.7970   53.90       1.1160      1.1163    0.03      2.2160      2.2450    1.31
0.8550   54.40       1.0660      1.0646   -0.13      2.7450      2.8067    2.25
0.9040   55.20       1.0330      1.0307   -0.23      3.4490      3.5409    2.66
0.9370   56.30       1.0160      1.0140   -0.20      4.0730      4.2445    4.21
0.9700   57.90       1.0040      1.0033   -0.06      5.3340      5.1999   -2.51
```

```
ORIGINAL NRTL EQUATION
CYCLOHEXANE - N-HEPTANE AT 25 C
REFFERENCE, KATAYAMA, ET AL.,A.I.CH.E.J.,11,925(1965)


A21ST =       0.0            A12ST =       0.0
A21 =    -205.12             A12 =    305.67
ALFA21 =  0.300              ALFA12 =  0.300
11 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0097


   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0468   25.00      1.0958     1.0936   -0.20     0.9837     1.0001    1.67
0.1010   25.00      1.0875     1.0858   -0.16     0.9907     1.0007    1.01
0.1877   25.00      1.0349     1.0734   -1.06     1.0011     1.0027    0.16
0.3005   25.00      1.0605     1.0579   -0.25     1.0091     1.0074   -0.17
0.3821   25.00      1.0447     1.0472    0.24     1.0065     1.0127    0.62
0.5001   25.00      1.0374     1.0330   -0.43     1.0355     1.0238   -1.13
0.5819   25.00      1.0183     1.0241    0.57     1.0177     1.0342    1.63
0.6999   25.00      1.0052     1.0133    0.80     1.0520     1.0542    0.21
0.7879   25.00      0.9981     1.0070    0.89     1.0497     1.0735    2.27
0.8998   25.00      0.9921     1.0017    0.96     1.1212     1.1049   -1.45
0.9459   25.00      0.9973     1.0005    0.32     1.1183     1.1205    0.19
```

```
LEMF EQUATION
CYCLOHEXANE - N-HEPTANE AT 25 C
REFFERENCE, KATAYAMA, ET AL.,A.I.CH.E.J.,11,925(1965)


A21ST =      0.0           A12ST =      0.0
A21 =    136.98            A12 =    -94.00
ALFA21 = -1.000            ALFA12 = -1.000
11 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0097


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0468   25.00      1.0958     1.0936   -0.20     0.9837     1.0002    1.67
0.1010   25.00      1.0875     1.0856   -0.17     0.9907     1.0007    1.01
0.1877   25.00      1.0849     1.0732   -1.08     1.0011     1.0027    0.16
0.3005   25.00      1.0605     1.0577   -0.26     1.0091     1.0074   -0.16
0.3821   25.00      1.0447     1.0471    0.23     1.0065     1.0127    0.62
0.5001   25.00      1.0374     1.0330   -0.43     1.0355     1.0237   -1.14
0.5819   25.00      1.0183     1.0242    0.58     1.0177     1.0341    1.61
0.6999   25.00      1.0052     1.0134    0.82     1.0520     1.0539    0.18
0.7879   25.00      0.9981     1.0071    0.90     1.0497     1.0733    2.25
0.8998   25.00      0.9921     1.0017    0.97     1.1212     1.1051   -1.44
0.9459   25.00      0.9973     1.0005    0.32     1.1183     1.1209    0.23
```

```
ORIGINAL NRTL EQUATION
ETHANOL - BENZENE AT 400 MM. PRESS.
REFFERENCE, NIELSEN, ET AL.,J. CHEM.ENG.DATA,4,#2,145(1959)


A21ST =      0.0          A12ST =      0.0
A21 =   1051.90           A12 =    543.88
ALFA21 =  0.470           ALFA12 =  0.470
10 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0123


   X      TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.1000   52.80     4.7800     4.7053   -1.56     1.0300     1.0326    0.26
0.2000   51.60     2.9600     3.0185    1.98     1.1300     1.1164   -1.20
0.3000   51.30     2.1500     2.1885    1.79     1.2500     1.2420   -0.64
0.3990   51.20     1.7100     1.7293    1.13     1.4100     1.4089   -0.08
0.4000   51.20     1.7100     1.7257    0.92     1.4200     1.4108   -0.65
0.5000   51.30     1.4500     1.4433   -0.46     1.5900     1.6319    2.64
0.6000   51.60     1.2700     1.2607   -0.73     1.9000     1.9237    1.25
0.7000   52.20     1.1400     1.1396   -0.03     2.3000     2.3175    0.76
0.8000   54.10     1.0600     1.0607    0.07     2.8800     2.8622   -0.62
0.9000   56.30     1.0200     1.0153   -0.47     3.7300     3.6506   -2.13
```

```
LEMF EQUATION
ETHANOL - BENZENE AT 400 MM. PRESS.
REFFERENCE, NIELSEN, ET AL.,J. CHEM.ENG.DATA,4,#2,145(1959)


A21ST =      0.0           A12ST =      0.0
A21 =    332.34            A12 =    503.92
ALFA21 = -1.000            ALFA12 = -1.000
10 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0115


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.1000    52.80      4.7800     4.7074   -1.52     1.0300     1.0334    0.33
0.2000    51.60      2.9600     3.0138    1.82     1.1300     1.1184   -1.03
0.3000    51.30      2.1500     2.1862    1.68     1.2500     1.2443   -0.45
0.3990    51.20      1.7100     1.7312    1.24     1.4100     1.4099   -0.00
0.4000    51.20      1.7100     1.7277    1.04     1.4200     1.4118   -0.57
0.5000    51.30      1.4500     1.4483   -0.12     1.5900     1.6298    2.50
0.6000    51.60      1.2700     1.2668   -0.25     1.9000     1.9170    0.90
0.7000    52.20      1.1400     1.1450    0.44     2.3000     2.3071    0.31
0.8000    54.10      1.0600     1.0641    0.39     2.8800     2.8504   -1.03
0.9000    56.30      1.0200     1.0164   -0.35     3.7300     3.6588   -1.91
```

```
ORIGINAL NRTL EQUATION
ETHANOL - BENZENE AT 40.0 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0          A12ST =      0.0
A21 =    1236.72          A12 =     515.58
ALFA21 =  0.470           ALFA12 =  0.470
11 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0435



   X       TEMP       G1OBS      G1CAL   %ERROR      G2OBS      G2CAL  %ERROR

0.0200    40.00     11.0790    10.4014    -6.12     0.9905     1.0021    1.17
0.0950    40.00      5.1578     5.6233     9.02     1.0379     1.0391    0.12
0.2040    40.00      2.9533     3.1128     5.40     1.1371     1.1501    1.14
0.3780    40.00      1.7587     1.8006     2.38     1.4079     1.4312    1.65
0.4900    40.00      1.4189     1.4526     2.38     1.6356     1.6856    3.06
0.5920    40.00      1.2231     1.2624     3.21     1.9511     1.9880    1.89
0.7020    40.00      1.0823     1.1319     4.58     2.4306     2.4272   -0.14
0.8020    40.00      1.0096     1.0572     4.71     2.9835     2.9860    0.08
0.8800    40.00      0.9832     1.0211     3.86     3.5383     3.5881    1.41
0.9430    40.00      0.9795     1.0048     2.59     4.1338     4.2352    2.45
0.9870    40.00      0.9832     1.0003     1.73     5.4340     4.8071  -11.54
```

```
LEMF EQUATION
ETHANOL - BENZENE AT 40.0 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0            A12ST =      0.0
A21 =     292.95            A12 =     536.41
ALFA21 = -1.000             ALFA12 = -1.000
11 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0450


   X       TEMP      G1OBS      G1CAL   %ERROR     G2OBS      G2CAL  %ERROR

0.0200    40.00    11.0790    10.1351   -8.52     0.9905     1.0020    1.16
0.0950    40.00     5.1578     5.6056    8.68     1.0379     1.0377   -0.02
0.2040    40.00     2.9533     3.1276    5.90     1.1371     1.1471    0.88
0.3780    40.00     1.7587     1.8048    2.62     1.4079     1.4291    1.51
0.4900    40.00     1.4189     1.4538    2.46     1.6356     1.6853    3.04
0.5920    40.00     1.2231     1.2627    3.24     1.9511     1.9886    1.92
0.7020    40.00     1.0823     1.1323    4.62     2.4306     2.4277   -0.12
0.8020    40.00     1.0096     1.0576    4.75     2.9835     2.9862    0.09
0.8800    40.00     0.9832     1.0214    3.88     3.5383     3.5909    1.49
0.9430    40.00     0.9795     1.0049    2.60     4.1338     4.2466    2.73
0.9870    40.00     0.9832     1.0003    1.74     5.4340     4.8323  -11.07
```

```
ORIGINAL NRTL EQUATION
ETHYL ALCOHOL - ETHYL ACETATE AT 760 MM PRESS.
REFFERENCE, GRISWOLD ET AL.,IND.ENG.CHEM.,41,2352(1949)



A21ST =      0.0           A12ST =      0.0
A21 =    248.90            A12 =    370.80
ALFA21 =  0.300            ALFA12 =  0.300
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0140



   X      TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.1550   73.90       1.7700      1.8060    2.03      1.0300      1.0193   -1.04
0.2720   72.70       1.5500      1.5601    0.65      1.0700      1.0613   -0.82
0.3090   72.40       1.4900      1.4955    0.37      1.0900      1.0800   -0.92
0.5270   71.90       1.2500      1.2134   -2.93      1.2700      1.2560   -1.11
0.5580   72.00       1.2000      1.1847   -1.27      1.3100      1.2919   -1.38
0.6280   72.30       1.1500      1.1287   -1.85      1.3900      1.3859   -0.30
0.7360   73.30       1.0500      1.0637    1.30      1.6100      1.5717   -2.38
0.8360   74.60       1.0200      1.0244    0.43      1.7800      1.8006    1.16
0.9210   76.10       1.0100      1.0057   -0.43      2.0400      2.0516    0.57
```

```
LEMF EQUATION
ETHYL ALCOHOL - ETHYL ACETATE AT 760 MM PRESS.
REFFERENCE, GRISWOLD ET AL.,IND.ENG.CHEM.,41,2352(1949)


A21ST =      0.0           A12ST =      0.0
A21 =     256.84           A12 =     233.25
ALFA21 = -1.000            ALFA12 = -1.000
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0143


   X       TEMP       G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.1550   73.90      1.7700      1.8105    2.29      1.0300      1.0212   -0.86
0.2720   72.70      1.5500      1.5550    0.32      1.0700      1.0649   -0.47
0.3090   72.40      1.4900      1.4899   -0.01      1.0900      1.0840   -0.55
0.5270   71.90      1.2500      1.2125   -3.00      1.2700      1.2576   -0.98
0.5580   72.00      1.2000      1.1846   -1.28      1.3100      1.2926   -1.33
0.6280   72.30      1.1500      1.1299   -1.75      1.3900      1.3842   -0.42
0.7360   73.30      1.0500      1.0655    1.48      1.6100      1.5669   -2.68
0.8360   74.60      1.0200      1.0257    0.56      1.7800      1.7975    0.98
0.9210   76.10      1.0100      1.0061   -0.39      2.0400      2.0592    0.94
```

```
ORIGINAL NRTL EQUATION
ETHANOL - N-HEPTANE AT 400 MM. PRESS.
REFFERENCE, KATZ, ET AL.,IND.ENG.CHEM.,48,#1,137(1956)


A21ST =      0.0           A12ST =      0.0
A21 =   1345.44            A12 =   1196.56
ALFA21 =  0.470            ALFA12 =  0.470
16 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0314


   X      TEMP       G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.9550   57.25      1.0400      1.0084   -3.04      9.8800      9.3117   -5.75
0.9060   56.00      1.0700      1.0335   -3.41      6.2500      6.7122    7.40
0.8070   54.75      1.1400      1.1226   -1.53      4.1100      4.0783   -0.77
0.7030   55.00      1.2800      1.2625   -1.36      2.8200      2.8280    0.28
0.6630   54.80      1.3400      1.3300   -0.75      2.5300      2.5289   -0.05
0.4700   55.75      1.8700      1.8126   -3.07      1.6000      1.6813    5.08
0.3770   55.50      2.2500      2.2196   -1.35      1.4600      1.4497   -0.71
0.3510   55.50      2.3900      2.3717   -0.77      1.3800      1.3958    1.14
0.2830   56.25      2.8800      2.8968    0.58      1.2700      1.2716    0.12
0.2780   56.25      2.9400      2.9452    0.18      1.2200      1.2634    3.55
0.2450   56.25      3.2300      3.3109    2.51      1.2100      1.2121    0.18
0.2040   56.25      3.8500      3.9118    1.61      1.1700      1.1551   -1.27
0.1830   56.75      4.2000      4.3047    2.49      1.1100      1.1285    1.67
0.1750   56.40      4.2400      4.4775    5.60      1.1200      1.1191   -0.08
0.1330   58.00      5.2600      5.6030    6.52      1.0600      1.0735    1.27
0.0350   63.10     12.2000     11.3846   -6.68      1.0000      1.0061    0.61
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LEMF EQUATION
ETHANOL - N-HEPTANE AT 400 MM. PRESS.
REFFERENCE, KATZ, ET AL.,IND.ENG.CHEM.,48,#1,137(1956)



A21ST =      0.0             A12ST =      0.0
A21 =     504.51             A12 =     550.44
ALFA21 = -1.000              ALFA12 = -1.000
16 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0460



   X       TEMP       G1OBS       G1CAL   %ERROR       G2OBS      G2CAL   %ERROR

0.9550    57.25      1.0400      1.0073    -3.14      9.8800     8.7618  -11.32
0.9060    56.00      1.0700      1.0299    -3.75      6.2500     6.5772    5.24
0.8070    54.75      1.1400      1.1134    -2.34      4.1100     4.1481    0.93
0.7030    55.00      1.2800      1.2500    -2.34      2.8200     2.8904    2.50
0.6630    54.80      1.3400      1.3178    -1.65      2.5300     2.5824    2.07
0.4700    55.75      1.8700      1.8172    -2.82      1.6000     1.6864    5.40
0.3770    55.50      2.2500      2.2482    -0.08      1.4600     1.4442   -1.08
0.3510    55.50      2.3900      2.4087     0.78      1.3800     1.3883    0.60
0.2830    56.25      2.8800      2.9523     2.51      1.2700     1.2607   -0.73
0.2780    56.25      2.9400      3.0024     2.12      1.2200     1.2525    2.66
0.2450    56.25      3.2300      3.3786     4.60      1.2100     1.2013   -0.72
0.2040    56.25      3.8500      3.9870     3.56      1.1700     1.1451   -2.13
0.1830    56.75      4.2000      4.3691     4.03      1.1100     1.1192    0.83
0.1750    56.40      4.2400      4.5459     7.21      1.1200     1.1103   -0.87
0.1330    58.00      5.2600      5.5897     6.27      1.0600     1.0666    0.62
0.0350    63.10     12.2000     10.2929   -15.63      1.0000     1.0053    0.53
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ORIGINAL NRTL EQUATION
ETHANOL - WATER AT 50 MM. PRESS.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0           A12ST =      0.0
A21 =     482.86           A12 =     279.94
ALFA21 =  0.300            ALFA12 =  0.300
19 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0934


   X       TEMP      G1OBS      G1CAL   %ERROR      G2OBS      G2CAL   %ERROR

0.0197    38.15     2.2666     3.0768    35.74     0.9038     1.0005    10.70
0.0442    32.80     2.7960     2.9421     5.22     1.0776     1.0026    -6.96
0.0640    30.90     3.1063     2.8168    -9.32     1.0614     1.0055    -5.27
0.0860    29.40     3.0873     2.6818   -13.14     1.0496     1.0099    -3.78
0.1110    28.15     2.9429     2.5370   -13.79     1.0425     1.0165    -2.49
0.1420    27.10     2.6707     2.3711   -11.22     1.0534     1.0270    -2.50
0.1670    26.25     2.5280     2.2502   -10.99     1.0681     1.0374    -2.87
0.2020    25.60     2.2691     2.0953    -7.66     1.0952     1.0547    -3.69
0.2400    25.05     2.0164     1.9471    -3.44     1.1524     1.0774    -6.51
0.2780    24.60     1.8450     1.8172    -1.51     1.1895     1.1042    -7.17
0.3220    24.30     1.6695     1.6861     1.00     1.2316     1.1405    -7.39
0.3790    23.90     1.4847     1.5434     3.95     1.3268     1.1969    -9.79
0.4250    23.60     1.3814     1.4467     4.73     1.3956     1.2506   -10.39
0.4780    23.25     1.2942     1.3525     4.50     1.4764     1.3226   -10.42
0.5440    22.90     1.2093     1.2565     3.90     1.5802     1.4293    -9.55
0.6120    22.60     1.1176     1.1780     5.41     1.7976     1.5620   -13.11
0.6870    22.25     1.0962     1.1115     1.40     1.8337     1.7409    -5.06
0.7800    21.95     1.0518     1.0531     0.13     2.0385     2.0210    -0.86
0.8850    21.70     1.0278     1.0141    -1.33     2.2692     2.4392     7.49

XT(2) =     1296.861) =     1254.74
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LEMF EQUATION
ETHANOL - WATER AT 50 MM. PRESS.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0          A12ST =      0.0
A21 =     254.68          A12 =     296.90
ALFA21 = -1.000           ALFA12 = -1.000
19 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0965



  X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0197   38.15      2.2666     3.0908   36.36     0.9038     1.0006   10.71
0.0442   32.80      2.7960     2.9524    5.59     1.0776     1.0030   -6.93
0.0640   30.90      3.1063     2.8175   -9.30     1.0614     1.0062   -5.20
0.0860   29.40      3.0873     2.6731  -13.42     1.0496     1.0111   -3.67
0.1110   28.15      2.9429     2.5200  -14.37     1.0425     1.0182   -2.33
0.1420   27.10      2.6707     2.3474  -12.11     1.0534     1.0294   -2.28
0.1670   26.25      2.5280     2.2240  -12.03     1.0681     1.0403   -2.60
0.2020   25.60      2.2691     2.0680   -8.86     1.0952     1.0582   -3.38
0.2400   25.05      2.0164     1.9214   -4.71     1.1524     1.0811   -6.19
0.2780   24.60      1.8450     1.7949   -2.72     1.1895     1.1078   -6.87
0.3220   24.30      1.6695     1.6688   -0.04     1.2316     1.1434   -7.16
0.3790   23.90      1.4847     1.5330    3.25     1.3268     1.1977   -9.73
0.4250   23.60      1.3814     1.4416    4.36     1.3956     1.2490  -10.51
0.4780   23.25      1.2942     1.3525    4.50     1.4764     1.3173  -10.78
0.5440   22.90      1.2093     1.2610    4.28     1.5802     1.4183  -10.24
0.6120   22.60      1.1176     1.1853    6.06     1.7976     1.5451  -14.04
0.6870   22.25      1.0962     1.1195    2.13     1.8337     1.7195   -6.23
0.7800   21.95      1.0518     1.0594    0.72     2.0385     2.0041   -1.69
0.8850   21.70      1.0278     1.0167   -1.08     2.2692     2.4630    8.54
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ORIGINAL NRTL EQUATION
ETHANOL WATER AT 380 MM. PRESS.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0          A12ST =      0.0
A21 =   1341.21           A12 =   -175.57
ALFA21 =  0.300           ALFA12 =  0.300
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0584



   X       TEMP        G1OBS       G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0160   78.10       4.6190      4.7251    2.30      0.9990     1.0008    0.18
0.0315   76.00       4.3360      4.3570    0.48      0.9720     1.0030    3.19
0.0600   72.40       3.9430      3.7822   -4.08      0.9680     1.0105    4.39
0.0855   69.30       3.5830      3.3620   -6.17      1.0380     1.0208   -1.66
0.1465   67.70       2.5990      2.5932   -0.22      1.0450     1.0567    1.12
0.2060   67.50       2.0160      2.1080    4.57      1.0400     1.1045    6.20
0.2360   67.10       1.8500      1.9294    4.29      1.0560     1.1328    7.28
0.3495   65.30       1.4300      1.4875    4.02      1.2370     1.2618    2.01
0.4675   64.70       1.1820      1.2478    5.57      1.3740     1.4235    3.61
0.4875   64.30       1.1560      1.2201    5.54      1.4480     1.4536    0.39
0.5800   64.40       1.0370      1.1233    8.32      1.5300     1.5969    4.37
0.6525   64.20       0.9790      1.0741    9.71      1.6500     1.7157    3.98
0.7000   63.80       0.9590      1.0509    9.59      1.7720     1.7960    1.35
0.7175   63.20       0.9840      1.0439    6.08      1.7910     1.8267    1.99
0.7890   63.80       0.9210      1.0218   10.95      1.9010     1.9479    2.47
0.8420   62.70       0.9460      1.0113    6.90      2.1350     2.0409   -4.41
0.8749   62.50       0.9490      1.0067    6.08      2.2170     2.0976   -5.39
0.8967   63.60       0.9040      1.0045   11.11      2.1300     2.1332    0.15
0.9485   63.50       0.9030      1.0010   10.86      2.3410     2.2214   -5.11
0.9727   63.00       0.9230      1.0003    8.37      2.4840     2.2628   -8.91
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LEMF EQUATION
ETHANOL WATER AT 380 MM. PRESS.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =     0.0            A12ST =     0.0
A21 =     41.38            A12 =    526.86
ALFA21 = -1.000            ALFA12 = -1.000
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0577


   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0160   78.10      4.6190     4.7467    2.77     0.9990     1.0009    0.19
0.0315   76.00      4.3360     4.3694    0.77     0.9720     1.0033    3.22
0.0600   72.40      3.9430     3.7839   -4.03     0.9680     1.0115    4.49
0.0855   69.30      3.5830     3.3601   -6.22     1.0380     1.0227   -1.48
0.1465   67.70      2.5990     2.5666   -1.25     1.0450     1.0606    1.49
0.2060   67.50      2.0160     2.0781    3.08     1.0400     1.1095    6.69
0.2360   67.10      1.8500     1.9028    2.85     1.0560     1.1382    7.78
0.3495   65.30      1.4300     1.4759    3.21     1.2370     1.2664    2.37
0.4675   64.70      1.1820     1.2456    5.38     1.3740     1.4236    3.61
0.4875   64.30      1.1560     1.2191    5.45     1.4480     1.4531    0.35
0.5800   64.40      1.0370     1.1250    8.49     1.5300     1.5918    4.04
0.6525   64.20      0.9790     1.0766    9.97     1.6500     1.7085    3.55
0.7000   63.80      0.9590     1.0535    9.85     1.7720     1.7894    0.98
0.7175   63.20      0.9840     1.0464    6.34     1.7910     1.8216    1.71
0.7890   63.80      0.9210     1.0237   11.15     1.9010     1.9447    2.30
0.8420   62.70      0.9460     1.0125    7.03     2.1350     2.0464   -4.15
0.8749   62.50      0.9490     1.0076    6.17     2.2170     2.1090   -4.87
0.8967   63.60      0.9040     1.0050   11.18     2.1300     2.1447    0.69
0.9485   63.50      0.9030     1.0012   10.87     2.3410     2.2452   -4.09
0.9727   63.00      0.9230     1.0003    8.38     2.4840     2.2958   -7.58
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ORIGINAL NRTL EQUATION
ETHANOL - WATER AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0            A12ST =      0.0
A21 =    1391.99            A12 =    -177.43
ALFA21 =  0.300             ALFA12 =  0.300
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0166



   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0673    88.40       3.7010      3.6359   -1.76      1.0300      1.0129   -1.66
0.0871    87.20       3.2750      3.3142    1.20      1.0380      1.0212   -1.62
0.1260    85.40       2.7840      2.8048    0.75      1.0410      1.0424    0.13
0.1430    84.50       2.6370      2.6250   -0.45      1.0600      1.0536   -0.60
0.1720    84.00       2.3150      2.3602    1.95      1.0790      1.0750   -0.37
0.2060    83.40       2.0740      2.1108    1.78      1.0940      1.1037    0.89
0.2100    83.00       2.0530      2.0858    1.60      1.1240      1.1075   -1.47
0.2550    82.30       1.8170      1.8368    1.09      1.1610      1.1514   -0.83
0.2840    82.00       1.6950      1.7095    0.85      1.1810      1.1826    0.13
0.3210    81.40       1.5840      1.5760   -0.50      1.2200      1.2255    0.45
0.3240    81.50       1.5640      1.5663    0.15      1.2200      1.2290    0.74
0.3450    81.20       1.4980      1.5034    0.36      1.2590      1.2549   -0.32
0.4050    80.90       1.3400      1.3588    1.40      1.3240      1.3335    0.72
0.4300    80.50       1.3070      1.3111    0.31      1.3600      1.3686    0.63
0.4490    80.20       1.2800      1.2788   -0.10      1.3980      1.3959   -0.15
0.5060    80.00       1.1950      1.1989    0.33      1.4520      1.4807    1.98
0.5450    79.50       1.1510      1.1563    0.46      1.5510      1.5418   -0.59
0.6630    78.60       1.0580      1.0693    1.07      1.7590      1.7361   -1.30
0.7350    78.50       1.0220      1.0381    1.57      1.9000      1.8597   -2.12
0.8040    78.40       0.9850      1.0187    3.42      2.1310      1.9800   -7.08
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LEMF EQUATION
ETHANOL - WATER AT 760 MM, HG,
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =     0.0          A12ST =     0.0
A21 =     64.20          A12 =    544.87
ALFA21 = -1.000          ALFA12 = -1.000
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0154



   X      TEMP      G1OBS      G1CAL   %ERROR      G2OBS      G2CAL   %ERROR

0.0673   88.40     3.7010     3.6480   -1.43      1.0300     1.0140   -1.56
0.0871   87.20     3.2750     3.3161    1.25      1.0380     1.0228   -1.47
0.1260   85.40     2.7840     2.7956    0.42      1.0410     1.0451    0.39
0.1430   84.50     2.6370     2.6149   -0.84      1.0600     1.0568   -0.30
0.1720   84.00     2.3150     2.3473    1.40      1.0790     1.0789   -0.01
0.2060   83.40     2.0740     2.0984    1.18      1.0940     1.1081    1.29
0.2100   83.00     2.0530     2.0745    1.05      1.1240     1.1120   -1.07
0.2550   82.30     1.8170     1.8287    0.64      1.1610     1.1563   -0.41
0.2840   82.00     1.6950     1.7037    0.51      1.1810     1.1874    0.54
0.3210   81.40     1.5840     1.5736   -0.66      1.2200     1.2301    0.83
0.3240   81.50     1.5640     1.5639   -0.01      1.2200     1.2335    1.11
0.3450   81.20     1.4980     1.5026    0.31      1.2590     1.2592    0.01
0.4050   80.90     1.3400     1.3615    1.61      1.3240     1.3364    0.93
0.4300   80.50     1.3070     1.3151    0.62      1.3600     1.3710    0.81
0.4490   80.20     1.2800     1.2837    0.29      1.3980     1.3981    0.01
0.5060   80.00     1.1950     1.2051    0.84      1.4520     1.4816    2.04
0.5450   79.50     1.1510     1.1630    1.04      1.5510     1.5426   -0.54
0.6630   78.80     1.0580     1.0752    1.62      1.7590     1.7397   -1.10
0.7350   78.50     1.0220     1.0425    2.00      1.9000     1.8699   -1.58
0.8040   78.40     0.9850     1.0215    3.71      2.1310     2.0011   -6.09
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ORIGINAL NRTL EQUATION
ETHANOL - WATER AT 760 MM. PRESS.
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)



A21ST =      0.0           A12ST =      0.0
A21 =    1360.31           A12 =    -147.58
ALFA21 =   0.300           ALFA12 =   0.300
10 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =    0.0188



    X       TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

 0.0720    89.00     3.5570     3.5842    0.76     0.9810     1.0144    3.41
 0.1240    85.30     2.8590     2.8681    0.32     1.0370     1.0406    0.35
 0.2340    82.70     1.9270     1.9746    2.47     1.1290     1.1292    0.02
 0.3270    81.50     1.5390     1.5792    2.61     1.2360     1.2323   -0.30
 0.3960    80.70     1.3790     1.3949    1.15     1.3200     1.3226    0.20
 0.5080    79.80     1.1910     1.2073    1.37     1.4890     1.4897    0.04
 0.5730    79.30     1.1210     1.1385    1.56     1.6110     1.5966   -0.90
 0.6760    78.74     1.0470     1.0671    1.92     1.7980     1.7775   -1.14
 0.7470    78.41     1.0160     1.0367    2.04     1.9500     1.9089   -2.11
 0.8940    78.15     0.9810     1.0052    2.47     2.2820     2.1910   -3.99
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LEMF EQUATION
ETHANOL - WATER AT 760 MM. PRESS.
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)


A21ST =      0.0           A12ST =      0.0
A21 =      76.44           A12 =     544.26
ALFA21 = -1.000            ALFA12 = -1.000
10 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0175


   X      TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0720   89.00     3.5570     3.5937    1.03     0.9810     1.0158    3.55
0.1240   85.30     2.8590     2.8556   -0.12     1.0370     1.0440    0.67
0.2340   82.70     1.9270     1.9541    1.40     1.1290     1.1356    0.58
0.3270   81.50     1.5390     1.5678    1.87     1.2360     1.2387    0.22
0.3960   80.70     1.3790     1.3900    0.80     1.3200     1.3276    0.57
0.5080   79.80     1.1910     1.2088    1.50     1.4890     1.4908    0.12
0.5730   79.30     1.1210     1.1417    1.85     1.6110     1.5958   -0.94
0.6760   78.74     1.0470     1.0708    2.27     1.7980     1.7764   -1.20
0.7470   78.41     1.0160     1.0397    2.33     1.9500     1.9114   -1.98
0.8940   78.15     0.9810     1.0060    2.55     2.2820     2.2179   -2.81
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ORIGINAL NRTL EQUATION
NHEPTANE - TOLUENE AT 760 MM. HG.
REFFERENCE, STEINHAUSER, ET AL.,IND.ENG.CHEM.,41,2912(1949)



A21ST =      0.0            A12ST =      0.0
A21 =      28.76            A12 =     218.48
ALFA21 =  0.300             ALFA12 =  0.300
19 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0357



   X      TEMP       G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0250  110.75      1.3877      1.3320    -4.02      1.0009      1.0002    -0.07
0.0620  108.60      1.2874      1.3075     1.57      1.0086      1.0011    -0.74
0.1290  106.80      1.2459      1.2642     1.47      1.0186      1.0048    -1.36
0.1850  105.65      1.2039      1.2307     2.22      1.0271      1.0100    -1.66
0.2350  104.80      1.1754      1.2027     2.32      1.0320      1.0163    -1.53
0.2500  104.50      1.1676      1.1948     2.33      1.0363      1.0185    -1.72
0.2860  103.83      1.1803      1.1764    -0.33      1.0301      1.0245    -0.55
0.3540  102.95      1.1210      1.1441     2.06      1.0566      1.0382    -1.74
0.4120  102.25      1.0909      1.1193     2.60      1.0767      1.0526    -2.24
0.4480  101.78      1.0912      1.1052     1.28      1.0765      1.0630    -1.25
0.4550  101.72      1.0745      1.1025     2.61      1.0947      1.0651    -2.71
0.4970  101.35      1.0622      1.0874     2.37      1.1031      1.0787    -2.21
0.5680  100.70      1.0457      1.0646     1.81      1.1238      1.1054    -1.64
0.5800  100.60      1.0430      1.0611     1.73      1.1275      1.1104    -1.51
0.6920   99.73      1.0283      1.0330     0.47      1.1537      1.1641     0.90
0.8430   98.90      1.0072      1.0087     0.15      1.2235      1.2604     3.02
0.9400   98.50      1.0025      1.0013    -0.12      1.2394      1.3398     8.11
0.9750   98.40      0.9977      1.0002     0.25      1.3772      1.3725    -0.34
0.9940   98.33      0.9977      1.0000     0.23      1.6769      1.3912   -17.04
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LEMF EQUATION
NHEPTANE - TOLUENE AT 760 MM. HG.
REFFERENCE, STEINHAUSER, ET AL.,IND.ENG.CHEM.,41,2912(1949)



A21ST =      0.0          A12ST =      0.0
A21 =    135.72           A12 =      84.48
ALFA21 = -1.000           ALFA12 = -1.000
19 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0355



   X       TEMP       G1OBS      G1CAL   %ERROR      G2OBS      G2CAL  %ERROR

0.0250   110.75      1.3877     1.3330   -3.95      1.0009     1.0002   -0.07
0.0620   108.60      1.2874     1.3081    1.61      1.0086     1.0011   -0.74
0.1290   106.80      1.2459     1.2642    1.46      1.0186     1.0049   -1.35
0.1850   105.65      1.2039     1.2303    2.19      1.0271     1.0101   -1.65
0.2350   104.80      1.1754     1.2022    2.28      1.0320     1.0165   -1.51
0.2500   104.50      1.1676     1.1942    2.28      1.0363     1.0187   -1.70
0.2860   103.83      1.1803     1.1758   -0.38      1.0301     1.0247   -0.53
0.3540   102.95      1.1210     1.1436    2.01      1.0566     1.0385   -1.71
0.4120   102.25      1.0909     1.1189    2.56      1.0767     1.0529   -2.21
0.4480   101.78      1.0912     1.1048    1.25      1.0765     1.0632   -1.23
0.4550   101.72      1.0745     1.1022    2.58      1.0947     1.0653   -2.68
0.4970   101.35      1.0622     1.0871    2.34      1.1031     1.0789   -2.19
0.5680   100.70      1.0457     1.0644    1.79      1.1238     1.1055   -1.63
0.5800   100.60      1.0430     1.0609    1.72      1.1275     1.1104   -1.51
0.6920    99.73      1.0283     1.0331    0.47      1.1537     1.1639    0.89
0.8430    98.90      1.0072     1.0088    0.16      1.2235     1.2602    3.00
0.9400    98.50      1.0025     1.0013   -0.12      1.2394     1.3403    8.14
0.9750    98.40      0.9977     1.0002    0.25      1.3772     1.3733   -0.28
0.9940    98.33      0.9977     1.0000    0.23      1.6769     1.3924  -16.97
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ORIGINAL NRTL EQUATION
METHANOL BENZENE AT 55 C
REFFERENCE, SCATCHARD, ET AL.,J. AM.CHEM.SOC.,74,3724(1952)


A21ST =      0.0            A12ST =      0.0
A21 =    1193.04            A12 =     671.35
ALFA21 =  0.470             ALFA12 =  0.470
 5 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0073


   X       TEMP        G1OBS       G1CAL   %ERROR      G2OBS       G2CAL   %ERROR

0.0400    55.00       8.3470      8.3261   -0.25      1.0170      1.0069   -0.99
0.0640    55.00       6.9770      6.9602   -0.24      1.0280      1.0168   -1.09
0.0770    55.00       6.3250      6.3636    0.61      1.0330      1.0237   -0.90
0.2300    55.00       2.9340      2.9486    0.50      1.1710      1.1705   -0.04
0.5990    55.00       1.3120      1.2985   -1.03      2.0300      2.0273   -0.13
```

```
LEMF EQUATION
METHANOL BENZENE AT 55 C
REFFERENCE, SCATCHARD, ET AL.,J. AM.CHEM.SOC.,74,3724(1952)


A21ST =      0.0          A12ST =      0.0
A21 =     368.49          A12 =     539.92
ALFA21 = -1.000           ALFA12 = -1.000
 5 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0073


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0400    55.00      8.3470     8.3183   -0.34     1.0170     1.0068   -1.00
0.0640    55.00      6.9770     6.9608   -0.23     1.0280     1.0167   -1.10
0.0770    55.00      6.3250     6.3663    0.65     1.0330     1.0236   -0.91
0.2300    55.00      2.9340     2.9489    0.51     1.1710     1.1705   -0.04
0.5990    55.00      1.3120     1.3000   -0.92     2.0300     2.0242   -0.28
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ORIGINAL NRTL EQUATION
METHYL ALCOHOL - BENZENE AT 55 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0           A12ST =      0.0
A21 =    1205.11           A12 =     709.68
ALFA21 =  0.470            ALFA12 =  0.470
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0172


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0304    55.00      9.0320     9.2865    2.82     1.0240     1.0041   -1.94
0.0493    55.00      8.4050     7.9847   -5.00     1.0060     1.0104    0.44
0.1031    55.00      5.4100     5.5272    2.17     1.0460     1.0412   -0.46
0.3297    55.00      2.1400     2.1831    2.01     1.3440     1.3261   -1.33
0.4874    55.00      1.5510     1.5494   -0.10     1.6660     1.6766    0.63
0.4984    55.00      1.5210     1.5206   -0.02     1.6980     1.7074    0.55
0.6076    55.00      1.2980     1.2962   -0.14     2.0640     2.0797    0.76
0.7896    55.00      1.0810     1.0838    0.26     3.1700     3.1546   -0.49
0.9014    55.00      1.0170     1.0193    0.22     4.4670     4.4244   -0.95
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```
LEMF EQUATION
METHYL ALCOHOL - BENZENE AT 55 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0           A12ST =      0.0
A21 =     380.40           A12 =     542.48
ALFA21 = -1.000            ALFA12 = -1.000
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0172


   X       TEMP       G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0304    55.00      9.0320      9.2668     2.60      1.0240      1.0041   -1.95
0.0493    55.00      8.4050      7.9799    -5.06      1.0060      1.0103    0.43
0.1031    55.00      5.4100      5.5353     2.32      1.0460      1.0409   -0.49
0.3297    55.00      2.1400      2.1822     1.97      1.3440      1.3266   -1.29
0.4874    55.00      1.5510      1.5487    -0.15      1.6660      1.6771    0.67
0.4984    55.00      1.5210      1.5200    -0.06      1.6980      1.7079    0.58
0.6076    55.00      1.2980      1.2968    -0.09      2.0640      2.0781    0.68
0.7896    55.00      1.0810      1.0850     0.37      3.1700      3.1480   -0.69
0.9014    55.00      1.0170      1.0198     0.28      4.4670      4.4313   -0.80
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ORIGINAL NRTL EQUATION
METHYL ALCOHOL - CARBON TETRACHLORIDE AT 55 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0          A12ST =      0.0
A21 =   1357.13           A12 =     812.02
ALFA21 =  0.470           ALFA12 =  0.470
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0868


  X       TEMP      G1OBS     G1CAL  %ERROR     G2OBS     G2CAL  %ERROR

0.0254   55.00    16.0340   12.1080  -24.49    1.0240    1.0035   -2.00
0.0579   55.00     7.1970    8.8979   23.63    1.0750    1.0169   -5.40
0.1493   55.00     4.5800    4.6780    2.14    1.1350    1.0932   -3.68
0.3647   55.00     2.0520    2.0630    0.54    1.4770    1.4316   -3.08
0.4893   55.00     1.5790    1.5844    0.34    1.7910    1.7408   -2.80
0.4946   55.00     1.5650    1.5697    0.30    1.8070    1.7566   -2.79
0.6448   55.00     1.2520    1.2621    0.80    2.4300    2.3437   -3.55
0.7903   55.00     1.0810    1.0935    1.15    3.5500    3.3812   -4.75
0.9087   55.00     1.0150    1.0191    0.41    5.2190    5.0544   -3.15
```

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LEMF EQUATION
METHYL ALCOHOL - CARBON TETRACHLORIDE AT 55 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1966


A21ST =      0.0          A12ST =      0.0
A21 =    401.29           A12 =    571.85
ALFA21 = -1.000           ALFA12 = -1.000
 9 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0888


   X       TEMP        G1OBS       G1CAL   %ERROR       G2OBS       G2CAL  %ERROR

0.0254'   55.00      16.0340     11.7612  -26.65       1.0240      1.0033   -2.02
0.0579    55.00       7.1970      8.8146   22.48       1.0750      1.0158   -5.50
0.1493    55.00       4.5800      4.7393    3.48       1.1350      1.0895   -4.01
0.3647    55.00       2.0520      2.0763    1.18       1.4770      1.4313   -3.09
0.4893    55.00       1.5790      1.5846    0.35       1.7910      1.7486   -2.37
0.4946    55.00       1.5650      1.5696    0.29       1.8070      1.7647   -2.34
0.6448    55.00       1.2520      1.2587    0.53       2.4300      2.3622   -2.79
0.7903    55.00       1.0810      1.0915    0.97       3.5500      3.3986   -4.26
0.9087    55.00       1.0150      1.0187    0.36       5.2190      5.0404   -3.42
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ORIGINAL NRTL EQUATION
METHANOL CARBON TET AT 55 C
REFFERENCE, SCATCHARD, ET AL.,J. AM.CHEM.SOC.,74,3724(1952)


A21ST =      0.0          A12ST =      0.0
A21 =   1742.05           A12 =   3101.53
ALFA21 =  0.470           ALFA12 =  0.470
 6 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0824


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0230    55.00     17.4020    16.2043   -6.88     0.9910     1.0045    1.36
0.0340    55.00     13.1240    13.7506    4.77     1.0040     1.0093    0.53
0.0520    55.00     10.2270    10.8181    5.78     1.0370     1.0202   -1.62
0.1730    55.00      4.0480     3.9548   -2.30     1.1520     1.1488   -0.28
0.5450    55.00      1.4460     1.6460   13.83     1.9670     1.7473  -11.17
0.8700    55.00      1.0140     1.1939   17.74     4.6850     4.6088   -1.63
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LEMF EQUATION
METHANOL CARBON TET AT 55 C
REFFERENCE, SCATCHARD, ET AL.,J. AM.CHEM.SOC.,74,3724(1952)


A21ST =      0.0            A12ST =      0.0
A21 =     375.71            A12 =     615.33
ALFA21 = -1.000             ALFA12 = -1.000
 6 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0593


   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0230    55.00      17.4020     15.1297  -13.06      0.9910      1.0032    1.24
0.0340    55.00      13.1240     13.3660    1.84      1.0040      1.0069    0.29
0.0520    55.00      10.2270     11.0721    8.26      1.0370      1.0154   -2.08
0.1730    55.00       4.0480      4.4230    9.26      1.1520      1.1350   -1.47
0.5450    55.00       1.4460      1.4213   -1.71      1.9670      2.0206    2.73
0.8700    55.00       1.0140      1.0333    1.90      4.6850      4.4033   -6.01
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ORIGINAL NRTL EQUATION
METHANOL - ETHANOL AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =     0.0           A12ST =     0.0
A21 =    123.11           A12 =   -136.13
ALFA21 =  0.300           ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0508



   X        TEMP        G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.1340     76.60       0.8680      0.9779    12.66      0.9820      0.9994     1.77
0.2420     75.00       0.9060      0.9832     8.53      0.9840      0.9981     1.43
0.3200     73.60       0.9450      0.9866     4.40      0.9840      0.9967     1.29
0.4010     72.30       0.9770      0.9897     1.30      0.9680      0.9949     2.78
0.4350     71.70       0.9850      0.9909     0.60      0.9680      0.9941     2.69
0.5420     70.00       1.0040      0.9941    -0.99      0.9550      0.9909     3.76
0.6520     68.60       0.9870      0.9966     0.98      0.9890      0.9871    -0.20
0.7280     67.70       0.9790      0.9980     1.94      1.0190      0.9840    -3.43
0.7900     66.90       0.9810      0.9988     1.81      1.0360      0.9814    -5.27
0.8140     66.60       0.9820      0.9991     1.74      1.0420      0.9803    -5.92
0.8730     65.80       0.9910      0.9996     0.86      1.0230      0.9776    -4.44
0.9100     65.60       0.9770      0.9998     2.33      1.1320      0.9758   -13.80
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LEMF EQUATION
METHANOL - ETHANOL AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0           A12ST =      0.0
A21 =    -582.82           A12 =     266.61
ALFA21 = -1.000            ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0416



   X       TEMP        G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.1340   76.60      0.8680      0.9223    6.25      0.9820      0.9880     0.61
0.2420   75.00      0.9060      0.9847    8.69      0.9840      0.9739    -1.02
0.3200   73.60      0.9450      1.0063    6.49      0.9840      0.9661    -1.82
0.4010   72.30      0.9770      1.0161    4.00      0.9680      0.9614    -0.68
0.4350   71.70      0.9850      1.0177    3.32      0.9680      0.9606    -0.77
0.5420   70.00      1.0040      1.0168    1.28      0.9550      0.9623     0.76
0.6520   68.60      0.9870      1.0117    2.50      0.9890      0.9706    -1.86
0.7280   67.70      0.9790      1.0076    2.93      1.0190      0.9799    -3.84
0.7900   66.90      0.9810      1.0047    2.42      1.0360      0.9895    -4.49
0.8140   66.60      0.9820      1.0038    2.22      1.0420      0.9937    -4.64
0.8730   65.80      0.9910      1.0018    1.09      1.0230      1.0050    -1.76
0.9100   65.60      0.9770      1.0009    2.45      1.1320      1.0125   -10.56
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ORIGINAL NRTL EQUATION
METHANOL - ETHYL ACETATE AT 760MM.HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0           A12ST =      0.0
A21 =     388.69           A12 =     337.02
ALFA21 =  0.300            ALFA12 =  0.300
17 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0217



   X       TEMP        G1OBS       G1CAL  %ERROR      G2OBS       G2CAL  %ERROR

0.0240    74.00       2.6940      2.5511   -5.30     1.0240      1.0006   -2.29
0.1810    67.10       1.8990      1.9416    2.24     1.0490      1.0342   -1.41
0.3110    64.70       1.5510      1.5985    3.07     1.1180      1.1037   -1.28
0.3500    64.20       1.4850      1.5179    2.22     1.1390      1.1328   -0.55
0.4030    63.60       1.4140      1.4218    0.55     1.1690      1.1791    0.87
0.5660    62.60       1.2020      1.2043    0.19     1.3530      1.3800    2.00
0.6160    62.40       1.1740      1.1567   -1.47     1.3900      1.4632    5.27
0.6460    62.40       1.1250      1.1317    0.60     1.4940      1.5189    1.67
0.7080    62.30       1.0600      1.0879    0.73     1.6310      1.6502    1.18
0.7200    62.10       1.0780      1.0806    0.24     1.6830      1.6788   -0.25
0.7340    62.30       1.0510      1.0725    2.04     1.7530      1.7123   -2.32
0.7430    62.50       1.0520      1.0675    1.47     1.7060      1.7344    1.67
0.7440    62.60       1.0480      1.0669    1.80     1.7000      1.7367    2.16
0.8100    62.50       1.0270      1.0364    0.91     1.9020      1.9219    1.04
0.8150    62.40       1.0310      1.0345    0.34     1.9160      1.9377    1.13
0.8890    62.80       1.0040      1.0123    0.83     2.2440      2.1932   -2.26
0.9390    63.30       0.9960      1.0037    0.77     2.5270      2.3983   -5.09
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LEMF EQUATION
METHANOL - ETHYL ACETATE AT 760MM.HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =     0.0          A12ST =     0.0
A21 =    268.09          A12 =    284.95
ALFA21 = -1.000          ALFA12 = -1.000
17 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0185



   X       TEMP      G1OBS      G1CAL  %ERROR     G2OBS      G2CAL  %ERROR

0.0240    74.00     2.6940     2.6020   -3.42    1.0240     1.0007   -2.28
0.1810    67.10     1.8990     1.9346    1.87    1.0490     1.0373   -1.11
0.3110    64.70     1.5510     1.5879    2.38    1.1180     1.1084   -0.86
0.3500    64.20     1.4850     1.5089    1.61    1.1390     1.1373   -0.15
0.4030    63.60     1.4140     1.4157    0.12    1.1690     1.1829    1.19
0.5660    62.60     1.2020     1.2061    0.34    1.3530     1.3773    1.80
0.6160    62.40     1.1740     1.1598   -1.21    1.3900     1.4579    4.89
0.6460    62.40     1.1250     1.1353    0.92    1.4940     1.5121    1.21
0.7080    62.30     1.0800     1.0919    1.10    1.6310     1.6413    0.63
0.7200    62.10     1.0780     1.0846    0.62    1.6830     1.6699   -0.78
0.7340    62.30     1.0510     1.0764    2.42    1.7530     1.7033   -2.84
0.7430    62.50     1.0520     1.0713    1.83    1.7060     1.7253    1.13
0.7440    62.60     1.0480     1.0707    2.17    1.7000     1.7276    1.62
0.8100    62.50     1.0270     1.0394    1.20    1.9020     1.9168    0.78
0.8150    62.40     1.0310     1.0374    0.62    1.9160     1.9333    0.90
0.8890    62.80     1.0040     1.0137    0.97    2.2440     2.2057   -1.71
0.9390    63.30     0.9960     1.0042    0.83    2.5270     2.4344   -3.66
```

```
ORIGINAL NRTL EQUATION
METHANOL NHEPTANE AT 760 MM, PRESS,
REFFERENCE, BENEDICT, ET AL.,TRANS. AM.INST.CHEM.ENG.,41,37(1945)



A21ST =      0.0           A12ST =      0.0
A21 =   1692.38            A12 =   1659.75
ALFA21 =  0.470            ALFA12 =  0.470
 7 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0426



   X       TEMP        G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.1380   60.60       6.0201     5.9857   -0.57     1.1084     1.1031   -0.48
0.1780   59.47       4.9660     4.6752   -5.86     1.1570     1.1557   -0.11
0.3900   58.93       2.3341     2.2260   -4.63     1.5554     1.5278   -1.78
0.6680   86.82       1.3814     1.3816    0.02     2.7941     2.5919   -7.24
0.8100   58.81       1.1430     1.1688    2.26     4.8460     4.3846   -9.52
0.8850   59.01       1.0600     1.0745    1.37     7.4200     7.0459   -5.04
0.9460   59.90       1.0122     1.0198    0.75    12.4660    12.5199    0.43
```

```
LEMF EQUATION
METHANOL NHEPTANE AT 760 MM. PRESS.
REFFERENCE, BENEDICT, ET AL.,TRANS. AM.INST.CHEM.ENG.,41,37(1945)


A21ST =      0.0           A12ST =      0.0
A21 =    592.14            A12 =    559.65
ALFA21 = -1.000            ALFA12 = -1.000
 7 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0380


   X       TEMP        G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.1380 '  60.60       6.0201      6.2225     3.36      1.1084      1.0729    -3.21
0.1780    59.47       4.9660      5.0930     2.56      1.1570      1.1160    -3.54
0.3900    58.93       2.3341      2.4187     3.62      1.5554      1.4892    -4.26
0.6680    88.82       1.3814      1.3372    -3.20      2.7941      2.5299    -9.46
0.8100    58.81       1.1430      1.1460     0.26      4.8460      4.8928     0.97
0.8850    59.01       1.0600      1.0596    -0.04      7.4200      7.5827     2.19
0.9460    59.90       1.0122      1.0147     0.24     12.4660     12.0706    -3.17
```

```
ORIGINAL NRTL EQUATION
METHANOL TOLUENE AT 760 MM. PRESS.
REFFERENCE, BENEDICT, ET AL.,TRANS. AM.INST.CHEM.ENG.,41,37(1945)


A21ST =      0.0           A12ST =      0.0
A21 =    1129.22           A12 =     855.73
ALFA21 =  0.470            ALFA12 =  0.470
 6 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0150


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.1300    70.25      4.5650     4.6429    1.71     1.0740     1.0546   -1.81
0.2660    66.44      2.7070     2.7303    0.86     1.2400     1.2029   -2.99
0.4070    65.58      1.8760     1.8867    0.57     1.4340     1.4499    1.11
0.5930    64.47      1.3690     1.3647   -0.31     2.0030     2.0053    0.12
0.6920    64.10      1.2040     1.2068    0.23     2.5380     2.5039   -1.34
0.7790    63.79      1.1030     1.1088    0.53     3.2470     3.1729   -2.28
```

```
LEMF EQUATION
METHANOL TOLUENE AT 760 MM. PRESS.
REFFERENCE, BENEDICT, ET AL.,TRANS. AM.INST.CHEM.ENG.,41,37(1945)



A21ST =      0.0            A12ST =      0.0
A21 =    441.38             A12 =    534.31
ALFA21 = -1.000             ALFA12 = -1.000
 6 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0134



   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.1300   70.25       4.5650      4.6145    1.08      1.0740      1.0555   -1.72
0.2660   66.44       2.7070      2.7251    0.67      1.2400      1.2068   -2.68
0.4070   65.58       1.8760      1.8839    0.42      1.4340      1.4559    1.53
0.5930   64.47       1.3690      1.3666   -0.18      2.0030      2.0124    0.47
0.6920   64.10       1.2040      1.2094    0.45      2.5380      2.5116   -1.04
0.7790   63.79       1.1030      1.1112    0.74      3.2470      3.1865   -1.86

XT(2) =    2021.291) =    1862.65
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ORIGINAL NRTL EQUATION
METHYL ALCOHOL - TOLUENE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0          A12ST =      0.0
A21 =    862.82           A12 =   1021.01
ALFA21 =  0.470           ALFA12 =  0.470
14 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =    0.1351



   X       TEMP       G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0460    89.90      4.6260      5.5266    19.47      0.9330      1.0050     7.72
0.0580    84.80      5.2200      5.3322     2.15      0.8660      1.0080    16.39
0.0700    80.40      5.6220      5.1352    -8.66      0.8080      1.0117    25.20
0.0940    74.75      5.6180      4.7268   -15.86      0.7610      1.0210    34.16
0.1140    71.30      5.3500      4.4077   -17.61      0.8170      1.0307    26.15
0.1320    69.70      4.9480      4.1330   -16.47      0.8500      1.0408    22.44
0.2340    66.75      3.1600      2.9701    -6.01      1.0100      1.1223    11.12
0.3300    65.75      2.3520      2.3104    -1.77      1.1410      1.2395     8.63
0.4390    65.10      1.8250      1.8332     0.45      1.3500      1.4331     6.15
0.6750    64.15      1.2510      1.2701     1.53      2.2200      2.2870     3.02
0.8300    63.70      1.0650      1.0812     1.52      3.6680      3.7658     2.67
0.8700    63.60      1.0340      1.0494     1.49      4.3870      4.4624     1.72
0.9300    63.70      1.0000      1.0154     1.54      5.8700      6.0127     2.43
0.9740    64.10      0.9870      1.0023     1.55      7.6330      7.7878     2.03
```

```
LEMF EQUATION
METHYL ALCOHOL - TOLUENE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0          A12ST =      0.0
A21 =    493.20           A12 =    468.73
ALFA21 = -1.000           ALFA12 = -1.000
14 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.1346



   X      TEMP       G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0460    89.90     4.6260      5.4421   17.64      0.9330      1.0054    7.76
0.0580    84.80     5.2200      5.3102    1.73      0.8660      1.0087   16.48
0.0700    80.40     5.6220      5.1608   -8.20      0.8080      1.0128   25.35
0.0940    74.75     5.6180      4.7909  -14.72      0.7610      1.0232   34.45
0.1140    71.30     5.3500      4.4822  -16.22      0.8170      1.0340   26.56
0.1320    69.70     4.9480      4.1979  -15.16      0.8500      1.0451   22.96
0.2340    66.75     3.1600      2.9733   -5.91      1.0100      1.1330   12.18
0.3300    65.75     2.3520      2.2978   -2.30      1.1410      1.2557   10.05
0.4390    65.10     1.8250      1.8211   -0.21      1.3500      1.4541    7.71
0.6750    64.15     1.2510      1.2678    1.34      2.2200      2.3102    4.06
0.8300    63.70     1.0650      1.0813    1.53      3.6680      3.7880    3.27
0.8700    63.60     1.0340      1.0496    1.51      4.3870      4.4877    2.30
0.9300    63.70     1.0000      1.0156    1.56      5.8700      6.0496    3.06
0.9740    64.10     0.9870      1.0023    1.55      7.6330      7.8409    2.72
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```
ORIGINAL NRTL EQUATION
METHANOL WATER AT 760 MM. PRESS.
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)


A21ST =      0.0           A12ST =      0.0
A21 =     846.04           A12 =    -223.31
ALFA21 =  0.300            ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0083


   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0600    91.20       1.9800      1.9874    0.38      1.0150      1.0044   -1.05
0.1000    87.70       1.8270      1.8363    0.51      1.0120      1.0119   -0.01
0.1500    84.40       1.6790      1.6771   -0.12      1.0090      1.0258    1.67
0.2000    81.70       1.5440      1.5465    0.17      1.0390      1.0445    0.53
0.3000    78.00       1.3420      1.3516    0.72      1.0950      1.0939   -0.10
0.4000    75.30       1.2130      1.2206    0.63      1.1530      1.1569    0.34
0.5000    73.10       1.1210      1.1326    1.04      1.2380      1.2311   -0.55
0.6000    71.20       1.0600      1.0743    1.35      1.3280      1.3145   -1.02
0.7000    69.30       1.0270      1.0369    0.96      1.4260      1.4052   -1.46
0.8000    67.60       1.0060      1.0146    0.85      1.5050      1.5011   -0.26
0.9000    66.00       0.9940      1.0032    0.93      1.5950      1.6002    0.33
0.9500    65.00       0.9990      1.0008    0.18      1.6670      1.6506   -0.98
```

```
LEMF EQUATION
METHANOL WATER AT 760 MM. PRESS.
REFFERENCE, PERRY, ET AL.,CHEM.ENG.HANDBOOK,4TH ED.,MC GRAW HILL,N.Y.,(1963)


A21ST =      0.0           A12ST =      0.0
A21 =     -12.57           A12 =    372.58
ALFA21 = -1.000            ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0077


   X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0600    91.20      1.9800     1.9886    0.43     1.0150     1.0047   -1.01
0.1000    87.70      1.8270     1.8331    0.34     1.0120     1.0128    0.08
0.1500    84.40      1.6790     1.6702   -0.52     1.0090     1.0276    1.85
0.2000    81.70      1.5440     1.5382   -0.38     1.0390     1.0472    0.79
0.3000    78.00      1.3420     1.3434    0.10     1.0950     1.0981    0.28
0.4000    75.30      1.2130     1.2146    0.13     1.1530     1.1618    0.77
0.5000    73.10      1.1210     1.1291    0.72     1.2380     1.2359   -0.17
0.6000    71.20      1.0600     1.0726    1.19     1.3280     1.3185   -0.71
0.7000    69.30      1.0270     1.0364    0.91     1.4260     1.4086   -1.22
0.8000    67.60      1.0060     1.0145    0.85     1.5050     1.5046   -0.03
0.9000    66.00      0.9940     1.0033    0.93     1.5950     1.6056    0.66
0.9500    65.00      0.9990     1.0008    0.18     1.6670     1.6583   -0.52
```

```
ORIGINAL NRTL EQUATION
METHANOL - WATER AT 100.0C
REFFERENCE, GRISWOLD ET AL., CHEM.ENG.PROGESS SYMP.SER.,#3,48(1952)



A21ST =     0.0           A12ST =      0.0
A21 =    986.21           A12 =    -344.56
ALFA21 =  0.300           ALFA12 =  0.300
15 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0537



   X       TEMP        G1OBS       G1CAL  %ERROR        G2OBS       G2CAL  %ERROR

0.0110  100.00        2.4670      2.1515  -12.79       1.0060      1.0002   -0.58
0.0350  100.00        1.9280      2.0234    4.95       1.0270      1.0016   -2.47
0.0530  100.00        1.7690      1.9377    9.54       1.0520      1.0036   -4.60
0.0740  100.00        1.7270      1.8476    6.98       1.0450      1.0068   -3.65
0.1210  100.00        1.6910      1.6779   -0.78       1.0470      1.0173   -2.83
0.1630  100.00        1.5360      1.5563    1.32       1.0490      1.0300   -1.81
0.2810  100.00        1.2900      1.3189    2.24       1.0710      1.0792    0.77
0.3520  100.00        1.1650      1.2260    5.23       1.1140      1.1162    0.20
0.5220  100.00        1.0320      1.0916    5.77       1.2950      1.2195   -5.83
0.6060  100.00        1.0130      1.0544    4.09       1.4110      1.2751   -9.63
0.6670  100.00        0.9970      1.0354    3.85       1.4700      1.3163  -10.45
0.8260  100.00        0.9820      1.0076    2.61       1.5860      1.4236  -10.24
0.9320  100.00        0.9940      1.0010    0.70       1.5280      1.4921   -2.35
0.9460  100.00        0.9950      1.0006    0.56       1.4920      1.5009    0.59
0.9580  100.00        0.9880      1.0004    1.25       1.4980      1.5083    0.69
```

```
LEMF EQUATION
METHANOL - WATER AT 100.0C
REFFERENCE, GRISWOLD ET AL., CHEM.ENG.PROGESS SYMP.SER.,#3,48(1952)



A21ST =      0.0          A12ST =      0.0
A21 =    -87.37           A12 =     398.52
ALFA21 = -1.000           ALFA12 = -1.000
15 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0538



   X      TEMP        G1OBS      G1CAL  %ERROR       G2OBS      G2CAL  %ERROR

0.0110  100.00       2.4670     2.1616  -12.38      1.0060     1.0002   -0.58
0.0350  100.00       1.9280     2.0273    5.15      1.0270     1.0017   -2.47
0.0530  100.00       1.7690     1.9382    9.57      1.0520     1.0037   -4.59
0.0740  100.00       1.7270     1.8452    6.85      1.0450     1.0071   -3.63
0.1210  100.00       1.6910     1.6722   -1.11      1.0470     1.0178   -2.79
0.1630  100.00       1.5360     1.5498    0.90      1.0490     1.0307   -1.75
0.2810  100.00       1.2900     1.3144    1.89      1.0710     1.0796    0.80
0.3520  100.00       1.1650     1.2234    5.01      1.1140     1.1159    0.17
0.5220  100.00       1.0320     1.0920    5.81      1.2950     1.2168   -6.04
0.6060  100.00       1.0130     1.0554    4.18      1.4110     1.2715   -9.89
0.6670  100.00       0.9970     1.0364    3.95      1.4700     1.3124  -10.72
0.8260  100.00       0.9820     1.0081    2.66      1.5860     1.4216  -10.37
0.9320  100.00       0.9940     1.0011    0.71      1.5280     1.4948   -2.17
0.9460  100.00       0.9950     1.0007    0.57      1.4920     1.5045    0.83
0.9580  100.00       0.9880     1.0004    1.26      1.4980     1.5127    0.98
```

```
ORIGINAL NRTL EQUATION
METHYL ACETATE - BENZENE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =     0.0           A12ST =     0.0
A21 =    216.86           A12 =     -0.07
ALFA21 =  0.300           ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =  0.0268


   X       TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0550    76.90     1.3130     1.3170    0.30     1.0140     1.0010   -1.28
0.0760    75.90     1.2360     1.3007    1.14     1.0170     1.0020   -1.48
0.1390    73.50     1.2140     1.2548    3.36     1.0240     1.0065   -1.71
0.1890    71.80     1.1840     1.2219    3.20     1.0290     1.0120   -1.65
0.2120    71.00     1.1750     1.2077    2.79     1.0340     1.0151   -1.82
0.3380    67.50     1.1160     1.1402    2.17     1.0630     1.0384   -2.32
0.3620    66.80     1.0990     1.1293    2.75     1.0880     1.0440   -4.04
0.5050    63.80     1.0550     1.0744    1.84     1.1430     1.0858   -5.01
0.6200    61.80     1.0310     1.0424    1.11     1.1950     1.1298   -5.46
0.7352    60.10     1.0200     1.0200    0.00     1.2190     1.1837   -2.90
0.8630    58.40     1.0090     1.0052   -0.38     1.2830     1.2559   -2.11
0.8950    57.90     1.0100     1.0030   -0.69     1.3280     1.2762   -3.90
```

```
LEMF EQUATION
METHYL ACETATE - BENZENE AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0            A12ST =      0.0
A21 =      55.66            A12 =     134.74
ALFA21 = -1.000             ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0266


   X       TEMP       G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0550    76.90      1.3130      1.3194    0.48      1.0140      1.0011   -1.28
0.0760    75.90      1.2860      1.3025    1.29      1.0170      1.0020   -1.47
0.1390    73.50      1.2140      1.2553    3.40      1.0240      1.0068   -1.68
0.1890    71.80      1.1840      1.2217    3.18      1.0290      1.0124   -1.61
0.2120    71.00      1.1750      1.2073    2.75      1.0340      1.0156   -1.78
0.3380    67.50      1.1160      1.1391    2.07      1.0630      1.0392   -2.24
0.3620    66.80      1.0990      1.1281    2.65      1.0880      1.0449   -3.96
0.5050    63.80      1.0550      1.0734    1.74      1.1430      1.0867   -4.92
0.6200    61.80      1.0310      1.0418    1.05      1.1950      1.1305   -5.40
0.7352    60.10      1.0200      1.0197   -0.03      1.2190      1.1838   -2.89
0.8630    58.40      1.0090      1.0051   -0.38      1.2830      1.2550   -2.18
0.8950    57.90      1.0100      1.0030   -0.69      1.3280      1.2751   -3.98
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```
ORIGINAL NRTL EQUATION
METHYL ACETATE - CHLOROFORM AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0          A12ST =      0.0
A21 =     454.85          A12 =    -718.90
ALFA21 =  0.300           ALFA12 =  0.300
15 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0155



  X       TEMP       G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0640   62.20      0.5280      0.5150   -2.47      0.9950      0.9953    0.03
0.1590   63.50      0.5960      0.6158    3.32      0.9780      0.9740   -0.41
0.1710   63.70      0.6120      0.6280    2.62      0.9710      0.9703   -0.07
0.2240   64.20      0.6750      0.6794    0.66      0.9500      0.9520    0.21
0.2630   64.60      0.7010      0.7151    2.01      0.9330      0.9368    0.41
0.3350   64.70      0.7600      0.7748    1.95      0.9080      0.9054   -0.28
0.4060   64.70      0.8150      0.8264    1.40      0.8690      0.8718    0.32
0.4630   64.20      0.8570      0.8622    0.61      0.8460      0.8434   -0.31
0.5320   63.70      0.8940      0.8994    0.60      0.8080      0.8084    0.05
0.5630   63.20      0.9140      0.9139   -0.02      0.7950      0.7924   -0.32
0.6400   62.40      0.9400      0.9443    0.46      0.7540      0.7534   -0.08
0.7060   61.40      0.9680      0.9644   -0.37      0.7090      0.7203    1.60
0.7820   60.30      0.9780      0.9815    0.35      0.6920      0.6835   -1.23
0.8510   59.20      0.9890      0.9918    0.28      0.6680      0.6513   -2.50
0.9200   58.10      0.9970      0.9977    0.07      0.6520      0.6205   -4.82
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LEMF EQUATION
METHYL ACETATE - CHLOROFORM AT 760 MM. HG.
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0            A12ST =      0.0
A21 =    -453.24            A12 =    -132.13
ALFA21 = -1.000             ALFA12 = -1.000
15 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0177



   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0640    62.20       0.5280      0.5098   -3.45      0.9950      0.9946   -0.04
0.1590    63.50       0.5960      0.6180    3.69      0.9780      0.9715   -0.66
0.1710    63.70       0.6120      0.6306    3.05      0.9710      0.9677   -0.34
0.2240    64.20       0.6750      0.6833    1.22      0.9500      0.9490   -0.10
0.2630    64.60       0.7010      0.7189    2.55      0.9330      0.9338    0.09
0.3350    64.70       0.7600      0.7777    2.33      0.9080      0.9031   -0.53
0.4060    64.70       0.8150      0.8275    1.54      0.8690      0.8708    0.21
0.4630    64.20       0.8570      0.8620    0.58      0.8460      0.8438   -0.27
0.5320    63.70       0.8940      0.8977    0.41      0.8080      0.8103    0.29
0.5630    63.20       0.9140      0.9117   -0.26      0.7950      0.7951    0.01
0.6400    62.40       0.9400      0.9414    0.15      0.7540      0.7571    0.41
0.7060    61.40       0.9680      0.9616   -0.66      0.7090      0.7242    2.15
0.7820    60.30       0.9780      0.9793    0.13      0.6920      0.6864   -0.81
0.8510    59.20       0.9890      0.9905    0.15      0.6680      0.6521   -2.38
0.9200    58.10       0.9970      0.9973    0.03      0.6520      0.6179   -5.24
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ORIGINAL NRTL EQUATION
METHYL ACETATE(1) METHANOL(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)



A21ST =      0.0           A12ST =      0.0
A21 =     295.62           A12 =     431.36
ALFA21 =  0.300            ALFA12 =  0.300
15 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0205



   X      TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0050   50.00     2.6130     2.7174    4.00     1.0020     1.0000   -0.20
0.0125   50.00     2.7430     2.6782   -2.36     1.0020     1.0002   -0.18
0.0315   50.00     2.6400     2.5826   -2.17     1.0010     1.0010   -0.00
0.0600   50.00     2.5900     2.4488   -5.45     1.0000     1.0035    0.35
0.1880   50.00     1.9500     1.9651    0.77     1.0200     1.0353    1.50
0.2590   50.00     1.7300     1.7622    1.86     1.0600     1.0683    0.78
0.4280   50.00     1.4000     1.4114    0.81     1.1700     1.2001    2.57
0.5000   50.00     1.2800     1.3047    1.93     1.2900     1.2846   -0.42
0.6080   50.00     1.1700     1.1809    0.93     1.4400     1.4541    0.98
0.7290   50.00     1.0800     1.0846    0.42     1.6800     1.7267    2.78
0.7830   50.00     1.0500     1.0540    0.38     1.8300     1.8867    3.10
0.8160   50.00     1.0400     1.0388   -0.11     1.9600     1.9992    2.00
0.8640   50.00     1.0200     1.0212    0.12     2.1500     2.1867    1.71
0.9110   50.00     1.0100     1.0091   -0.09     2.4200     2.4024   -0.73
0.9720   50.00     1.0000     1.0009    0.09     2.8700     2.7409   -4.50
```

```
LEMF EQUATION
METHYL ACETATE(1) METHANOL(2) AT 50 C
REFFERENCE, SEVERNS, ET AL.,A.I.CH.E.J.,1,401(1955)


A21ST =      0.0            A12ST =      0.0
A21 =    294.38             A12 =    246.57
ALFA21 = -1.000             ALFA12 = -1.000
15 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0178


   X       TEMP       G1OBS      G1CAL  %ERROR       G2OBS      G2CAL  %ERROR

 0.0050   50.00      2.6130     2.7482    5.17      1.0020     1.0000   -0.20
 0.0125   50.00      2.7430     2.7032   -1.45      1.0020     1.0002   -0.18
 0.0315   50.00      2.6400     2.5949   -1.71      1.0010     1.0011    0.01
 0.0600   50.00      2.5900     2.4467   -5.53      1.0000     1.0039    0.39
 0.1880   50.00      1.9500     1.9401   -0.51      1.0200     1.0372    1.69
 0.2590   50.00      1.7300     1.7396    0.56      1.0600     1.0703    0.97
 0.4280   50.00      1.4000     1.4039    0.28      1.1700     1.1972    2.33
 0.5000   50.00      1.2800     1.3029    1.79      1.2900     1.2772   -1.00
 0.6080   50.00      1.1700     1.1845    1.24      1.4400     1.4378   -0.15
 0.7290   50.00      1.0800     1.0896    0.89      1.6900     1.7023    1.33
 0.7830   50.00      1.0500     1.0584    0.80      1.8300     1.8629    1.80
 0.8160   50.00      1.0400     1.0425    0.25      1.9600     1.9787    0.95
 0.8640   50.00      1.0200     1.0238    0.37      2.1500     2.1770    1.26
 0.9110   50.00      1.0100     1.0105    0.05      2.4200     2.4143   -0.23
 0.9720   50.00      1.0000     1.0011    0.11      2.8700     2.8080   -2.16

XT(2) =     1267.221) =     1735.03
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ORIGINAL NRTL EQUATION
METHYL ETHYL KETONE - NHEPTANE AT 760 MM. HG.
REFFERENCE, STEINHAUSER, ET AL.,IND.ENG.CHEM.,41,2912(1949)



A21ST =      0.0            A12ST =      0.0
A21 =    734.73             A12 =    267.44
ALFA21 =  0.300             ALFA12 =  0.300
17 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.1300



   X       TEMP      G1OBS      G1CAL   %ERROR     G2OBS      G2CAL   %ERROR

0.0033    96.10    11.5771     3.7328  -67.76     1.0067     1.0000   -0.66
0.0270    93.70     3.5286     3.4871   -1.18     1.0127     1.0012   -1.14
0.0740    89.40     2.8927     3.0622    5.86     1.0106     1.0089   -0.17
0.1220    86.40     2.4980     2.6962    7.93     1.0233     1.0240    0.07
0.2300    82.25     1.9720     2.0862    5.79     1.0782     1.0841    0.55
0.3540    79.95     1.5904     1.6408    3.17     1.1746     1.1991    2.09
0.3690    80.05     1.5367     1.5995    4.08     1.1820     1.2164    2.92
0.4750    78.35     1.3785     1.3691   -0.68     1.3110     1.3655    4.15
0.5070    78.20     1.3246     1.3153   -0.70     1.3536     1.4195    4.87
0.6115    77.45     1.2056     1.1792   -2.19     1.5336     1.6321    6.43
0.6930    77.00     1.1358     1.1059   -2.64     1.7406     1.8425    5.85
0.7060    77.15     1.1233     1.0963   -2.41     1.7486     1.8796    7.49
0.7650    77.00     1.0877     1.0595   -2.59     1.9280     2.0671    7.22
0.8640    77.25     1.0342     1.0191   -1.46     2.3972     2.4502    2.21
0.9320    78.10     1.0177     1.0047   -1.28     2.5515     2.7713    8.61
0.9730    78.70     1.0044     1.0007   -0.36     3.1492     2.9930   -4.96
0.9940    79.05     1.0058     1.0000   -0.57     3.9582     3.1156  -21.29
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LEMF EQUATION
METHYL ETHYL KETONE - NHEPTANE AT 760 MM. HG.
REFFERENCE, STEINHAUSER, ET AL.,IND.ENG.CHEM.,41,2912(1949)


A21ST =      0.0            A12ST =      0.0
A21 =    280.16             A12 =    412.18
ALFA21 = -1.000             ALFA12 = -1.000
17 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.1259


   X       TEMP      G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

 0.0033   96.10    11.5771     3.8721  -66.55     1.0067     1.0000   -0.66
 0.0270   93.70     3.5286     3.5780    1.40     1.0127     1.0014   -1.12
 0.0740   89.40     2.8927     3.0887    6.78     1.0106     1.0104   -0.03
 0.1220   86.40     2.4980     2.6852    7.49     1.0233     1.0273    0.39
 0.2300   82.25     1.9720     2.0519    4.05     1.0782     1.0914    1.22
 0.3540   79.95     1.5904     1.6184    1.76     1.1746     1.2066    2.72
 0.3690   80.05     1.5367     1.5790    2.75     1.1820     1.2233    3.50
 0.4750   78.35     1.3785     1.3623   -1.17     1.3110     1.3664    4.22
 0.5070   78.20     1.3246     1.3117   -0.97     1.3536     1.4176    4.72
 0.6115   77.45     1.2056     1.1826   -1.90     1.5336     1.6192    5.59
 0.6930   77.00     1.1358     1.1112   -2.17     1.7406     1.8221    4.68
 0.7060   77.15     1.1233     1.1016   -1.93     1.7486     1.8583    6.27
 0.7650   77.00     1.0877     1.0645   -2.13     1.9280     2.0452    6.08
 0.8640   77.25     1.0342     1.0217   -1.21     2.3972     2.4475    2.10
 0.9320   78.10     1.0177     1.0055   -1.19     2.5515     2.8095   10.11
 0.9730   78.70     1.0044     1.0009   -0.35     3.1492     3.0748   -2.36
 0.9940   79.05     1.0058     1.0000   -0.57     3.9582     3.2273  -18.47

XT(2) =    1120.511) =    1191.10
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ORIGINAL NRTL EQUATION
METHYL ETHYL KETONE - TOLUENE AT 760 MM. HG.
REFFERENCE, STEINHAUSER, ET AL.,IND.ENG.CHEM.,41,2912(1949)


A21ST =      0.0          A12ST =      0.0
A21 =    190.16           A12 =    121.39
ALFA21 =  0.300           ALFA12 =  0.300
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0481


   X       TEMP        G1OBS      G1CAL   %ERROR      G2OBS      G2CAL   %ERROR

0.0045   110.20       1.4148     1.4885     5.21     1.0025     1.0000    -0.25
0.0085   109.88       1.5635     1.4841    -5.08     1.0005     1.0000    -0.04
0.0175   109.25       1.4740     1.4742     0.01     1.0002     1.0001    -0.01
0.0405   107.20       1.5403     1.4500    -5.86     1.0025     1.0007    -0.18
0.0850   104.20       1.4448     1.4044    -2.79     1.0072     1.0030    -0.41
0.1190   102.28       1.3996     1.3713    -2.02     1.0074     1.0060    -0.14
0.1800    99.25       1.2829     1.3162     2.59     1.0209     1.0137    -0.71
0.2359    97.10       1.2399     1.2701     2.43     1.0337     1.0238    -0.96
0.3127    94.30       1.1754     1.2141     3.29     1.0617     1.0422    -1.83
0.3982    91.85       1.1146     1.1607     4.14     1.0884     1.0694    -1.74
0.4682    89.90       1.0859     1.1236     3.47     1.1089     1.0974    -1.04
0.5479    87.85       1.0590     1.0880     2.73     1.1400     1.1358    -0.37
0.6420    85.80       1.0313     1.0543     2.23     1.1817     1.1910     0.79
0.7012    84.40       1.0283     1.0376     0.91     1.2061     1.2320     2.14
0.7846    83.15       1.0060     1.0193     1.33     1.2425     1.2981     4.48
0.8015    82.65       1.0111     1.0164     0.52     1.2549     1.3131     4.64
0.8611    81.80       1.0014     1.0080     0.66     1.2700     1.3691     7.80
0.9350    80.50       0.9954     1.0017     0.64     1.4642     1.4481    -1.10
0.9774    79.85       0.9954     1.0002     0.48     1.4161     1.4985     5.82
0.9939    79.50       1.0000     1.0000     0.00     2.0022     1.5194   -24.11
```

```
LEMF EQUATION
METHYL ETHYL KETONE - TOLUENE AT 760 MM. HG.
REFFERENCE, STEINHAUSER, ET AL.,IND.ENG.CHEM.,41,2912(1949)


A21ST =      0.0            A12ST =      0.0
A21 =     125.08            A12 =     149.24
ALFA21 = -1.000             ALFA12 = -1.000
20 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0478


   X        TEMP        G1OBS       G1CAL   %ERROR      G2OBS       G2CAL   %ERROR

0.0045    110.20       1.4148      1.4898     5.30     1.0025      1.0000    -0.25
0.0085    109.88       1.5635      1.4853    -5.00     1.0005      1.0000    -0.04
0.0175    109.25       1.4740      1.4751     0.07     1.0002      1.0001    -0.01
0.0405    107.20       1.5403      1.4504    -5.83     1.0025      1.0007    -0.18
0.0850    104.20       1.4448      1.4039    -2.83     1.0072      1.0031    -0.40
0.1190    102.28       1.3996      1.3704    -2.09     1.0074      1.0061    -0.13
0.1800     99.25       1.2829      1.3147     2.48     1.0209      1.0140    -0.68
0.2359     97.10       1.2399      1.2685     2.30     1.0337      1.0242    -0.92
0.3127     94.30       1.1754      1.2126     3.16     1.0617      1.0427    -1.79
0.3982     91.85       1.1146      1.1596     4.04     1.0884      1.0699    -1.70
0.4682     89.90       1.0859      1.1229     3.40     1.1089      1.0977    -1.01
0.5479     87.85       1.0590      1.0877     2.71     1.1400      1.1359    -0.36
0.6420     85.80       1.0313      1.0544     2.24     1.1817      1.1908     0.77
0.7012     84.40       1.0283      1.0378     0.92     1.2061      1.2316     2.11
0.7846     83.15       1.0060      1.0196     1.35     1.2425      1.2978     4.45
0.8015     82.65       1.0111      1.0166     0.54     1.2549      1.3129     4.62
0.8611     81.80       1.0014      1.0081     0.68     1.2700      1.3694     7.83
0.9350     80.50       0.9954      1.0018     0.64     1.4642      1.4501    -0.96
0.9774     79.85       0.9954      1.0002     0.48     1.4161      1.5020     6.07
0.9939     79.50       1.0000      1.0000     0.00     2.0022      1.5237   -23.90
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ORIGINAL NRTL EQUATION
NITROETHANE(1), TOLUENE(2) AT 45 C
REFFERENCE, ORYE,R.V.,DOCTORAL DISSERTATION, UNIV. CALIFORNIA, BERKELEY (1965)


A21ST =      0.0          A12ST =     0.0
A21 =     495.29          A12 =     52.74
ALFA21 =  0.300           ALFA12 =  0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0081


   X       TEMP         G1OBS       G1CAL  %ERROR        G2OBS       G2CAL  %ERROR

0.0410   45.00        2.2160      2.1815   -1.56       1.0020      1.0018   -0.02
0.0750   45.00        2.0550      2.0427   -0.60       1.0070      1.0058   -0.12
0.1170   45.00        1.8880      1.8934    0.29       1.0160      1.0139   -0.20
0.1200   45.00        1.8770      1.8836    0.35       1.0170      1.0147   -0.23
0.1410   45.00        1.8060      1.8177    0.65       1.0230      1.0201   -0.28
0.2530   45.00        1.5170      1.5371    1.32       1.0670      1.0627   -0.40
0.3030   45.00        1.4250      1.4423    1.21       1.0930      1.0891   -0.36
0.5000   45.00        1.1890      1.1895    0.04       1.2320      1.2380    0.49
0.5500   45.00        1.1510      1.1477   -0.28       1.2770      1.2879    0.85
0.6730   45.00        1.0790      1.0718   -0.67       1.4140      1.4339    1.41
0.8270   45.00        1.0230      1.0185   -0.44       1.6590      1.6695    0.64
0.9300   45.00        1.0040      1.0029   -0.11       1.9030      1.8656   -1.97
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LEMF EQUATION
NITROETHANE(1), TOLUENE(2) AT 45 C
REFFERENCE, DRYE,R.V.,DOCTORAL DISSERTATION, UNIV. CALIFORNIA, BERKELEY (1965)



A21ST =      0.0          A12ST =      0.0
A21 =     148.48          A12 =     266.50
ALFA21 = -1.000           ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0054



   X       TEMP       G1OBS      G1CAL   %ERROR      G2OBS      G2CAL   %ERROR

0.0410    45.00      2.2160     2.1946   -0.97      1.0020     1.0019   -0.01
0.0750    45.00      2.0550     2.0468   -0.40      1.0070     1.0062   -0.08
0.1170    45.00      1.8880     1.8910    0.16      1.0160     1.0147   -0.13
0.1200    45.00      1.8770     1.8808    0.21      1.0170     1.0154   -0.16
0.1410    45.00      1.8060     1.8131    0.39      1.0230     1.0210   -0.19
0.2530    45.00      1.5170     1.5304    0.89      1.0670     1.0641   -0.27
0.3030    45.00      1.4250     1.4369    0.83      1.0930     1.0902   -0.25
0.5000    45.00      1.1890     1.1901    0.10      1.2320     1.2356    0.30
0.5500    45.00      1.1510     1.1493   -0.15      1.2770     1.2843    0.57
0.6730    45.00      1.0790     1.0742   -0.45      1.4140     1.4280    0.99
0.8270    45.00      1.0230     1.0198   -0.31      1.6590     1.6680    0.54
0.9300    45.00      1.0040     1.0032   -0.08      1.9030     1.8783   -1.30
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ORIGINAL NRTL EQUATION
NITROMETHANE(1)-CARBON TET(2) AT 45 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0           A12ST =      0.0
A21 =   1130.77            A12 =     841.00
ALFA21 =  0.470            ALFA12 =  0.470
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0205


  X       TEMP       G1OBS     G1CAL  %ERROR     G2OBS     G2CAL  %ERROR

0.0459   45.00      8.3977    8.3662   -0.38    1.0083    1.0086    0.03
0.0918   45.00      6.0408    6.1388    1.62    1.0542    1.0318   -2.13
0.1954   45.00      3.5336    3.6318    2.78    1.1267    1.1249   -0.16
0.2829   45.00      2.6041    2.6467    1.64    1.2400    1.2417    0.13
0.3656   45.00      2.0909    2.1036    0.61    1.3853    1.3858    0.03
0.4659   45.00      1.6870    1.6934    0.38    1.6303    1.6163   -0.86
0.5366   45.00      1.5049    1.4965   -0.56    1.8616    1.8299   -1.70
0.6065   45.00      1.3280    1.3489    1.58    2.1200    2.1018   -0.86
0.6835   45.00      1.1953    1.2248    2.47    2.5295    2.5052   -0.96
0.8043   45.00      1.0593    1.0895    2.85    3.5737    3.5275   -1.29
0.9039   45.00      1.0999    1.0233   -6.97    5.2374    5.1101   -2.43
0.9488   45.00      1.0046    1.0069    0.23    6.2671    6.2624   -0.07
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```
LEMF EQUATION
NITROMETHANE(1)-CARBON TET(2) AT 45 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0          A12ST =      0.0
A21 =     421.24          A12 =     513.28
ALFA21 = -1.000           ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0207


  X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0459   45.00      8.3977     8.3541   -0.52     1.0083     1.0085    0.02
0.0918   45.00      6.0408     6.1421    1.68     1.0542     1.0316   -2.15
0.1954   45.00      3.5336     3.6352    2.88     1.1267     1.1246   -0.19
0.2829   45.00      2.6041     2.6467    1.63     1.2400     1.2417    0.14
0.3656   45.00      2.0909     2.1021    0.53     1.3853     1.3863    0.07
0.4659   45.00      1.6870     1.6918    0.28     1.6303     1.6172   -0.81
0.5366   45.00      1.5049     1.4954   -0.63     1.8616     1.8304   -1.67
0.6065   45.00      1.3280     1.3485    1.54     2.1200     2.1012   -0.89
0.6835   45.00      1.1953     1.2250    2.48     2.5295     2.5024   -1.07
0.8043   45.00      1.0593     1.0900    2.90     3.5737     3.5200   -1.50
0.9039   45.00      1.0999     1.0236   -6.94     5.2374     5.1071   -2.49
0.9488   45.00      1.0046     1.0070    0.24     6.2671     6.2743    0.11
```

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ORIGINAL NRTL EQUATION
1-PROPANOL - BENZENE AT 45 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =       0.0           A12ST =      0.0
A21 =    1088.39            A12 =     345.98
ALFA21 =  0.470             ALFA12 =  0.470
11 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0238


   X       TEMP        G1OBS       G1CAL  %ERROR       G2OBS       G2CAL  %ERROR

0.0470    45.00       6.2210      5.9765   -3.93      1.0150      1.0084   -0.65
0.0977    45.00       4.2920      4.3671    1.75      1.0450      1.0331   -1.14
0.2144    45.00       2.5460      2.5863    1.58      1.1460      1.1358   -0.89
0.2973    45.00       2.0110      1.9994   -0.58      1.2420      1.2401   -0.15
0.4061    45.00       1.6110      1.5664   -2.77      1.4010      1.4142    0.95
0.4807    45.00       1.4290      1.3845   -3.12      1.5370      1.5600    1.50
0.5252    45.00       1.3510      1.3031   -3.55      1.6320      1.6586    1.63
0.6053    45.00       1.2350      1.1921   -3.47      1.8280      1.8615    1.84
0.7033    45.00       1.1390      1.1005   -3.38      2.1310      2.1648    1.58
0.7982    45.00       1.0820      1.0443   -3.49      2.4970      2.5345    1.50
0.9140    45.00       1.0390      1.0078   -3.00      3.0540      3.1300    2.49
```

```
LEMF EQUATION
1-PROPANOL - BENZENE AT 45 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0           A12ST =      0.0
A21 =     232.36           A12 =     505.35
ALFA21 = -1.000            ALFA12 = -1.000
11 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =    0.0232


  X       TEMP        G1OBS       G1CAL   %ERROR        G2OBS       G2CAL   %ERROR

0.0470   45.00       6.2210      5.9724   -4.00        1.0150      1.0084   -0.65
0.0977   45.00       4.2920      4.3604    1.59        1.0450      1.0332   -1.13
0.2144   45.00       2.5460      2.5814    1.39        1.1460      1.1359   -0.88
0.2973   45.00       2.0110      1.9971   -0.69        1.2420      1.2400   -0.16
0.4061   45.00       1.6110      1.5668   -2.74        1.4010      1.4130    0.85
0.4807   45.00       1.4290      1.3861   -3.00        1.5370      1.5575    1.33
0.5252   45.00       1.3510      1.3052   -3.39        1.6320      1.6551    1.42
0.6053   45.00       1.2350      1.1946   -3.27        1.8280      1.8565    1.56
0.7033   45.00       1.1390      1.1028   -3.18        2.1310      2.1590    1.31
0.7982   45.00       1.0820      1.0458   -3.34        2.4970      2.5326    1.42
0.9140   45.00       1.0390      1.0082   -2.96        3.0540      3.1489    3.11
```

```
ORIGINAL NRTL EQUATION
1-PROPANOL(1), ETHYL ACETATE(2) AT 60 C
REFFERENCE, MURTI ET AL.,IND.ENG.CHEM.,CHEM,ENG.DATA SER.,3,72(1958)


A21ST =      0.0           A12ST =      0.0
A21 =    285.91            A12 =    201.30
ALFA21 =  0.300            ALFA12 =  0.300
13 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0235


   X       TEMP      G1OBS      G1CAL   %ERROR     G2OBS      G2CAL   %ERROR

0.0843    60.00     1.7770     1.8040    1.52     0.9982     1.0053     0.71
0.1860    60.00     1.5740     1.5872    0.84     1.0330     1.0255    -0.72
0.2977    60.00     1.4050     1.4060    0.07     1.0850     1.0659    -1.76
0.3738    60.00     1.3690     1.3092   -4.37     1.1010     1.1051     0.37
0.4716    60.00     1.2110     1.2099   -0.09     1.1770     1.1707    -0.53
0.5842    60.00     1.1500     1.1243   -2.23     1.3020     1.2708    -2.40
0.6375    60.00     1.1260     1.0929   -2.94     1.3220     1.3286     0.50
0.7230    60.00     1.0790     1.0530   -2.41     1.4770     1.4379    -2.64
0.7811    60.00     1.0680     1.0327   -3.31     1.5220     1.5254     0.22
0.8404    60.00     1.0300     1.0172   -1.24     1.6780     1.6274    -3.02
0.8825    60.00     1.0490     1.0093   -3.79     1.7340     1.7086    -1.47
0.9095    60.00     1.0410     1.0055   -3.41     1.7140     1.7648     2.96
0.9362    60.00     1.0240     1.0027   -2.08     1.7540     1.8239     3.99
```

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LEMF EQUATION
1-PROPANOL(1), ETHYL ACETATE(2) AT 60 C
REFFERENCE, MURTI ET AL.,IND.ENG.CHEM.,CHEM,ENG.DATA SER.,3,72(1958)



A21ST =     0.0            A12ST =     0.0
A21 =    185.60            A12 =    212.78
ALFA21 = -1.000            ALFA12 = -1.000
13 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0241



  X       TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0843   60.00      1.7770     1.8113    1.93     0.9982     1.0057    0.75
0.1860   60.00      1.5740     1.5843    0.65     1.0330     1.0268   -0.60
0.2977   60.00      1.4050     1.4012   -0.27     1.0850     1.0678   -1.59
0.3738   60.00      1.3690     1.3054   -4.65     1.1010     1.1067    0.52
0.4716   60.00      1.2110     1.2081   -0.24     1.1770     1.1712   -0.49
0.5842   60.00      1.1500     1.1245   -2.22     1.3020     1.2690   -2.54
0.6375   60.00      1.1260     1.0936   -2.88     1.3220     1.3257    0.28
0.7230   60.00      1.0790     1.0541   -2.31     1.4770     1.4336   -2.94
0.7811   60.00      1.0680     1.0337   -3.21     1.5220     1.5211   -0.06
0.8404   60.00      1.0300     1.0180   -1.17     1.6780     1.6246   -3.18
0.8825   60.00      1.0490     1.0098   -3.74     1.7340     1.7083   -1.48
0.9095   60.00      1.0410     1.0058   -3.38     1.7140     1.7670    3.09
0.9362   60.00      1.0240     1.0029   -2.06     1.7540     1.8295    4.30

XT(2) =     997.711) =    2734.88
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ORIGINAL NRTL EQUATION
1-PROPANOL - WATER AT40.0 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)



A21ST =      0.0            A12ST =     0.0
A21 =    1734.67            A12 =      -2.29
ALFA21 =  0.300             ALFA12 =   0.300
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0890



   X       TEMP        G1OBS       G1CAL  %ERROR      G2OBS       G2CAL  %ERROR

0.0805    40.00       7.1630      6.8623   -4.20     1.1070      1.0347   -6.53
0.1295    40.00       4.6820      4.6737   -0.18     1.1540      1.0820   -6.24
0.1525    40.00       4.0430      4.0109   -0.79     1.1740      1.1095   -5.50
0.3050    40.00       2.1640      1.9863   -8.21     1.3740      1.3572   -1.22
0.3980    40.00       1.7170      1.5459   -9.96     1.5590      1.5530   -0.39
0.4700    40.00       1.5330      1.3489  -12.01     1.6980      1.7233    1.49
0.5755    40.00       1.3370      1.1769  -11.98     1.9930      1.9985    0.28
0.6660    40.00       1.2350      1.0925  -11.54     2.2540      2.2557    0.08
0.7385    40.00       1.1760      1.0503  -10.69     2.5810      2.4741   -4.14
0.8440    40.00       1.1230      1.0154   -9.59     2.8280      2.8088   -0.68
0.8500    40.00       1.1710      1.0141  -13.40     2.2890      2.8284   23.56
0.8975    40.00       1.1430      1.0062  -11.97     2.9930      2.9853   -0.26
```

```
LEMF EQUATION
1-PROPANOL - WATER AT40.0 C
REFFERENCE, HALA ET AL.,V.-L. EQUIL. DATA AT NORMAL PRESS.,PERGAMON PRESS,N.Y. (1968)


A21ST =      0.0            A12ST =      0.0
A21 =     124.31            A12 =     621.04
ALFA21 = -1.000             ALFA12 = -1.000
12 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0889


   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0805   40.00      7.1630     6.9703   -2.69     1.1070     1.0386   -6.18
0.1295   40.00      4.6820     4.6316   -1.08     1.1540     1.0891   -5.62
0.1525   40.00      4.0430     3.9517   -2.26     1.1740     1.1178   -4.78
0.3050   40.00      2.1640     1.9587   -9.49     1.3740     1.3659   -0.59
0.3980   40.00      1.7170     1.5388  -10.38     1.5590     1.5549   -0.26
0.4700   40.00      1.5330     1.3504  -11.91     1.6980     1.7179    1.17
0.5755   40.00      1.3370     1.1836  -11.47     1.9930     1.9825   -0.53
0.6660   40.00      1.2350     1.0993  -10.98     2.2540     2.2359   -0.80
0.7385   40.00      1.1760     1.0558  -10.22     2.5810     2.4588   -4.74
0.8440   40.00      1.1230     1.0179   -9.35     2.8230     2.8208   -0.25
0.8500   40.00      1.1710     1.0165  -13.19     2.2890     2.8429   24.20
0.8975   40.00      1.1430     1.0074  -11.86     2.9930     3.0246    1.06
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ORIGINAL NRTL EQUATION
1-PROPANOL(1), WATER(2) AT 60 C
REFFERENCE, MURTI ET AL.,IND.ENG.CHEM.,CHEM,ENG.DATA SER.,3,72(1958)



A21ST =      0.0           A12ST =      0.0
A21 =   1793.68            A12 =    -20.05
ALFA21 =  0.300            ALFA12 =  0.300
18 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0589



   X      TEMP         G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0390   60.00        9.7320      9.4491    -2.91      1.0140      1.0084    -0.55
0.0650   60.00        8.1400      7.3757    -9.39      1.0240      1.0222    -0.18
0.1545   60.00        3.6000      3.8086     5.79      1.1400      1.1069    -2.90
0.1790   60.00        3.1900      3.3115     3.81      1.1730      1.1383    -2.96
0.1960   60.00        2.9000      3.0304     4.50      1.1840      1.1618    -1.87
0.2620   60.00        2.3090      2.2691    -1.73      1.2710      1.2654    -0.44
0.3000   60.00        2.0000      1.9858    -0.71      1.3280      1.3330     0.38
0.4090   60.00        1.5550      1.4960    -3.79      1.5350      1.5545     1.27
0.4260   60.00        1.5020      1.4466    -3.69      1.5660      1.5924     1.69
0.4895   60.00        1.4060      1.3011    -7.46      1.6910      1.7410     2.96
0.5660   60.00        1.3600      1.1839   -12.95      1.7520      1.9336    10.37
0.7050   60.00        1.1330      1.0659    -5.93      2.1860      2.3161     5.85
0.7350   60.00        1.0830      1.0506    -2.99      2.4000      2.4033     0.14
0.7960   60.00        1.0670      1.0273    -3.72      2.5400      2.5851     1.78
0.8800   60.00        1.0400      1.0084    -3.04      2.6120      2.8439     8.88
0.8940   60.00        1.0170      1.0064    -1.04      2.5790      2.8879    11.98
0.9250   60.00        1.0380      1.0031    -3.36      3.4990      2.9860   -14.66
0.9500   60.00        1.0170      1.0013    -1.54      3.4010      3.0658    -9.86
```

```
LEMF EQUATION
1-PROPANOL(1), WATER(2) AT 60 C
REFFERENCE, MURTI ET AL.,IND.ENG.CHEM.,CHEM,ENG.DATA SER.,3,72(1958)



A21ST =      0.0          A12ST =      0.0
A21 =     137.09          A12 =     639.51
ALFA21 = -1.000           ALFA12 = -1.000
18 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0544



   X       TEMP       G1OBS       G1CAL  %ERROR      G2OBS       G2CAL  %ERROR

0.0390    60.00      9.7320      9.6440   -0.90     1.0140      1.0093   -0.47
0.0650    60.00      8.1400      7.3886   -9.23     1.0240      1.0241    0.00
0.1545    60.00      3.6000      3.7263    3.51     1.1400      1.1117   -2.48
0.1790    60.00      3.1900      3.2391    1.54     1.1730      1.1433   -2.53
0.1960    60.00      2.9000      2.9660    2.28     1.1840      1.1667   -1.46
0.2620    60.00      2.3090      2.2346   -3.22     1.2710      1.2684   -0.21
0.3000    60.00      2.0000      1.9648   -1.76     1.3280      1.3337    0.43
0.4090    60.00      1.5550      1.4983   -3.65     1.5350      1.5451    0.66
0.4260    60.00      1.5020      1.4509   -3.40     1.5660      1.5811    0.96
0.4895    60.00      1.4060      1.3104   -6.80     1.6910      1.7226    1.87
0.5660    60.00      1.3600      1.1952  -12.12     1.7520      1.9083    8.92
0.7050    60.00      1.1330      1.0745   -5.17     2.1880      2.2928    4.79
0.7350    60.00      1.0830      1.0581   -2.30     2.4000      2.3848   -0.63
0.7960    60.00      1.0670      1.0325   -3.24     2.5400      2.5834    1.71
0.8800    60.00      1.0400      1.0105   -2.84     2.6120      2.8856   10.48
0.8940    60.00      1.0170      1.0081   -0.87     2.5790      2.9397   13.99
0.9250    60.00      1.0380      1.0040   -3.28     3.4990      3.0635  -12.45
0.9500    60.00      1.0170      1.0017   -1.50     3.4010      3.1678   -6.86
```

```
ORIGINAL NRTL EQUATION
2-PROPANOL (1), ETHYL ACETATE (2) AT 60 C
REFFERENCE, MURTI ET AL.,IND.ENG.CHEM.,CHEM,ENG.DATA SER.,3,72(1958)



A21ST =      0.0          A12ST =      0.0
A21 =     512.96          A12 =       1.78
ALFA21 =  0.300           ALFA12 =  0.300
19 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0245



   X       TEMP       G1OBS       G1CAL   %ERROR       G2OBS       G2CAL   %ERROR

0.0775    60.00      2.0170      1.8883    -6.38      1.0130      1.0057    -0.72
0.0805    60.00      1.8450      1.3787     1.83      1.0190      1.0061    -1.26
0.1650    60.00      1.6120      1.6459     2.10      1.0190      1.0248     0.57
0.2475    60.00      1.5420      1.4748    -4.36      1.0340      1.0544     1.97
0.3200    60.00      1.4040      1.3584    -3.25      1.0680      1.0893     1.99
0.4095    60.00      1.2940      1.2477    -3.58      1.1280      1.1436     1.38
0.5085    60.00      1.1860      1.1577    -2.39      1.1990      1.2184     1.62
0.5680    60.00      1.1500      1.1164    -2.92      1.2460      1.2711     2.02
0.5725    60.00      1.1470      1.1136    -2.91      1.2440      1.2754     2.52
0.6400    60.00      1.1150      1.0768    -3.42      1.3190      1.3429     1.82
0.6865    60.00      1.0660      1.0565    -0.89      1.3940      1.3942     0.02
0.7335    60.00      1.0490      1.0397    -0.89      1.4620      1.4501    -0.81
0.8245    60.00      1.0220      1.0164    -0.55      1.5710      1.5705    -0.03
0.8410    60.00      1.0240      1.0133    -1.04      1.5960      1.5942    -0.11
0.8705    60.00      1.0040      1.0087     0.47      1.6680      1.6379    -1.80
0.9065    60.00      1.0120      1.0045    -0.75      1.6720      1.6938     1.31
0.9145    60.00      1.0100      1.0037    -0.62      1.7540      1.7066    -2.70
0.9260    60.00      1.0110      1.0028    -0.81      1.6440      1.7253     4.95
0.9545    60.00      1.0170      1.0010    -1.57      1.6920      1.7729     4.78
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```
LEMF EQUATION
2-PROPANOL (1), ETHYL ACETATE (2) AT 60 C
REFFERENCE, MURTI ET AL.,IND.ENG.CHEM.,CHEM,ENG.DATA SER.,3,72(1958)


A21ST =      0.0          A12ST =      0.0
A21 =    120.44           A12 =    268.19
ALFA21 = -1.000           ALFA12 = -1.000
19 DATA POINTS
STD. DEV. OF CALCULATED GAMMAS =   0.0249


   X      TEMP       G1OBS      G1CAL  %ERROR      G2OBS      G2CAL  %ERROR

0.0775   60.00      2.0170     1.8926   -6.17     1.0130     1.0060   -0.69
0.0805   60.00      1.8450     1.8825    2.03     1.0190     1.0065   -1.23
0.1650   60.00      1.6120     1.6414    1.82     1.0190     1.0259    0.67
0.2475   60.00      1.5420     1.4688   -4.74     1.0340     1.0558    2.11
0.3200   60.00      1.4040     1.3534   -3.60     1.0680     1.0905    2.11
0.4095   60.00      1.2940     1.2449   -3.80     1.1280     1.1440    1.42
0.5085   60.00      1.1860     1.1569   -2.45     1.1990     1.2172    1.52
0.5680   60.00      1.1500     1.1165   -2.91     1.2460     1.2687    1.82
0.5725   60.00      1.1470     1.1138   -2.90     1.2440     1.2728    2.32
0.6400   60.00      1.1150     1.0776   -3.35     1.3190     1.3391    1.53
0.6865   60.00      1.0660     1.0575   -0.80     1.3940     1.3897   -0.31
0.7335   60.00      1.0490     1.0407   -0.79     1.4620     1.4453   -1.14
0.8245   60.00      1.0220     1.0171   -0.48     1.5710     1.5669   -0.26
0.8410   60.00      1.0240     1.0139   -0.98     1.5960     1.5911   -0.31
0.8705   60.00      1.0040     1.0092    0.51     1.6680     1.6362   -1.91
0.9065   60.00      1.0120     1.0047   -0.72     1.6720     1.6946    1.35
0.9145   60.00      1.0100     1.0039   -0.60     1.7540     1.7080   -2.62
0.9260   60.00      1.0110     1.0030   -0.80     1.6440     1.7278    5.10
0.9545   60.00      1.0170     1.0011   -1.56     1.6920     1.7785    5.11
```

APPENDIX D

DATA SOURCES

DATA SOURCES

BINARY MISCIBLE SYSTEMS	REF.
Acetone-carbon tetrachloride at 50°C.	34
Acetone-chloroform at 35.17°C.	10
Acetone-chloroform at 50°C.	34
Acetone-methanol at 50°C.	34
Acetone-methanol at 100°C.	8
Acetone-methyl acetate at 50°C.	34
Acetone-toluene at 45°C.	20
Acetone-water at 25°C.	10
Acetone-water at 100°C.	8
Acetone-water at 150°C.	8
Acetone-water at 200°C.	8
Acetonitrile-toluene at 45°C.	20
Benzene-n-heptane at 400 mm. Hg.	19
Butanol-water at 760 mm. Hg.	21
Carbon tetrachloride-benzene at 49.99°C.	10
Carbon tetrachloride-benzene at 760 mm. Hg.	21
Chloroform-benzene at 760 mm. Hg.	10
Chloroform-ethyl acetate at 760 mm. Hg.	10
Chloroform-methanol at 50°C.	34
Chloroform-methanol at 760 mm. Hg.	10
Cyclohexane-n-heptane at 25°C.	14
Ethanol-benzene at 400 mm. Hg.	19
Ethanol-benzene at 40°C.	10
Ethanol-ethyl acetate at 760 mm. Hg.	6
Ethanol-n-heptane at 400 mm. Hg.	15
Ethanol-water at 50 mm. Hg.	10
Ethanol-water at 380 mm. Hg.	10
Ethanol-water at 760 mm. Hg.	10
Ethanol-water at 760 mm. Hg.	21
n-Heptane-toluene at 760 mm. Hg.	35

DATA SOURCES (continued)

Methanol-benzene at 55°C.	31
Methanol-benzene at 35°C.	10
Methanol-carbon tetrachloride at 55°C.	10
Methanol-carbon tetrachloride at 55°C.	31
Methanol-ethanol at 760 mm. Hg.	10
Methanol-ethyl acetate at 760 mm. Hg.	10
Methanol-n-heptane at 760 mm. Hg.	1
Methanol-toluene at 760 mm. Hg.	1
Methanol-toluene at 760 mm. Hg.	10
Methanol-water at 760 mm. Hg.	21
Methanol-water at 100°C.	8
Methyl acetate-benzene at 760 mm. Hg.	10
Methyl acetate-chloroform at 760 mm. Hg.	10
Methyl acetate-methanol at 50°C.	34
Methylethylketone-n-heptane at 760 mm. Hg.	35
Methylethylketone-toluene at 760 mm. Hg.	35
Nitroethane-toluene at 45°C.	20
Nitromethane-carbon tetrachloride at 45°C.	10
1-Propanol-benzene at 45°C.	10
1-Propanol-ethyl acetate at 60°C.	18
1-Propanol-water at 40°C.	10
1-Propanol-water at 60°C.	18
2-Propanol-ethyl acetate at 60°C.	18

BINARY PARTIALLY MISCIBLE SYSTEMS

Aniline-water	7
1-Butanol-water	36
Cyclohexane-furfural	46
Ethyl acetate-water	6
Furfural-water	47
n-Heptane-furfural	46
n-Hexane-furfural	46

DATA SOURCES (continued)

Isobutanol-water	36
Nitroethane-n-octane	48
Nitroethane-2,2,4,trimethyl pentane	48
Propylene oxide-water	42

TERNARY MISCIBLE SYSTEMS

Acetone-methanol-chloroform at 50°C	34
Acetone-methanol-water at 100°C.	8
Acetone-methyl acetate-methanol at 50°C.	34
Chloroform-methanol-ethyl acetate at 760 mm. Hg.	10
Ethanol-benzene-n-heptane at 400 mm. Hg.	19
Ethanol-ethyl acetate-water at 760 mm. Hg.	6
Methanol-carbon tetrachloride-benzene at 55°C.	31
Methanol-ethanol-water at 760 mm. Hg.	3
Methanol-n-heptane-toluene at 760 mm. Hg.	1
Methyl acetate-chloroform-benzene at 760 mm. Hg.	10
Methylethylketone-n-heptane-toluene at 760 mm. Hg.	35

TERNARY IMMISCIBLE SYSTEMS

Acetone-water-chloroform at 25°C.	51
Acetone-water-methyl acetate at 30°C.	49
Ethanol-water-benzene at 25°C.	51
Ethanol-water-ethyl acetate at 70°C.	49
n-Heptane-cyclohexane-furfural at 30°C.	46
Isooctane-n-hexane-furfural at 30°C.	46
1-Propanol-water-benzene at 37.7°C.	50

NOMENCLATURE

A - Empirical constant
a - Activity
a - Empirical constant
b - Empirical constant
B - Second virial coefficient
c - Empirical constant
C - Third virial coefficient
C - Cohesive energy (Eq. III-8)
D - Fourth virial coefficient
E - Error (Eq. V-7)
f - Fugacity
F - Number of degrees of Freedom in the system
$\bar{G}$ - Partial molal value of G
G - Any property of the system
G - Gibbs free energy
g - Residual Gibbs energy
H - Enthalpy
$\bar{M}$ - Partial molal value of M
M - Any property of the system
n - Number of moles
n - Number of components
N - Number of data points
Pi - Partial pressure of component i
P - Pressure of the system
q - Effective molal volume (Eq. III-1)
R - Gas law constant
T - Temperature of the system
U - Energy of vaporization
V - Molar volume
W - Accentric factor
WH - Accentric factor of Polar component's homomorph

X - Liquid phase mole fraction
Y - Vapor phase mole fraction
Z - Compressibility factor
Z - Effective volume fraction (Eq. III-1)

GREEK LETTERS

α - Empirical constant in NRTL equation
β - Non-polar solubility parameter
γ - Activity coefficient
δ - Combination of virial coefficients. See Eq. (II-42).
Φ - Volume fraction
ϕ - Fugacity coefficient
μ - Dipole moment
η - Vapor phase association constant
λ - Energy of interaction
θ - Number of phases in the system
τ - Polar solubility parameter
ψ - Energy term in Eq. (III-10)

SUBSCRIPTS

i, j, k - Pertaining to components i, j, k
$*$ - Identifies ideal state
c - Identifies critical property
r - Identifies reduced property

SUPERSCRIPTS

' - Pertaining to phase 1
" - Pertaining to phase II
$-$ - Identifies partial molal properties
$\wedge$ - Identifies component in solution
° - Identifies reference state
L - Pertaining to the liquid phase
v - Pertaining to the vapor phase
E - Identifies Excess property
M - Identifies mixing property
s - Identifies saturated property
$*$ - Identifies ideal state

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VITA

Jose Mario Marina, a naturalized U. S. citizen, was born in , . He attended a private school, run by his parents, through the seventh grade and continued his education at the Instituto de Segunda Enseñanza de Marianao, where he graduated Bachiller en Ciencias in 1953.

In 1954 he won a scholarship, sponsored by Café Pilón, to study Chemical Engineering at the Universidad de Santo Tomas de Villanueva. While going to school he worked repairing electronic equipment at first and later as a part time employee for a switchgear manufacturing plant owned by General Electric Co. He received the degree of Chemical Engineer in 1959 and shortly thereafter married Carmen Novoa from Havana, Cuba. He continued to work for General Electric for a brief period and then came to the U. S. in a training program sponsored by G.E.

He continued his studies at New York University, where in 1964 he graduated Master of Chemical Engineering. In September 1964 he was admitted to the doctoral program at Newark College of Engineering.

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He is most grateful to Merck & Co. for a leave of absence with pay, for a period of 18 month, to conduct this research at Newark College of Engineering.

The names and ages of his children are: Jacqueline, 10; Jose Mario Jr., 8; and Annette, 6.