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Derivation of an infinite-dilution activity coefficient model and application to two-component vapor-liquid equilibria data

Roper, Vaughan Phillip, Ph.D.

Rice University, 1988
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DERIVATION OF AN INFINITE-DILUTION ACTIVITY
COEFFICIENT MODEL AND APPLICATION TO
TWO-COMPONENT VAPOR-LIQUID EQUILIBRIA DATA

by

VAUGHAN PHILLIP ROPER

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

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Houston, Texas
May, 1988
Abstract

"DERIVATION OF AN INFINITE-DILUTION ACTIVITY COEFFICIENT MODEL AND APPLICATION TO TWO-COMPONENT VAPOR-LIQUID EQUILIBRIA DATA" by Vaughan Phillip Roper

Infinite-dilution fugacity coefficients were obtained for the binary system fluorene/phenanthrene at thirteen temperatures by fitting total pressure across the entire mole fraction range by a computer routine. A thermodynamically consistent routine, that allowed for both positive and negative pressure deviations from the ideal values, was used to correlate data over the full mole fraction range from 0 to 1. The four-suffix Margules activity coefficient model without modification essentially served this purpose since total pressures and total pressure derivatives with respect to mole fraction were negligible compared to pressure measurement precision.

The water/ethanol system studied by Kolbe and Gmehling and binary systems studied by Maher, Srivastava and Smith comprised of aniline, chlorobenzene, acetonitrile and other polar compounds were fit for total pressure across the entire mole fraction range for binary Vapor-Liquid-Equilibria (VLE) using the rigorous, thermodynamically consistent expression derived by Ibl and Dodge from the Gibbs-Duhem Relation. Data correlation was performed using a computer least squares procedure. Infinite-dilution fugacity coefficients
were obtained using a modified Margules activity coefficient model which gives residual values of \( x_1 \, d\ln \gamma_1 + x_2 \, d\ln \gamma_2 \) across the mole fraction range that lie between the value of \( \tilde{v}d\Pi/dx_1/RT \) at \( x_1 = 0 \) and \( x_1 = 1 \). \( x_1 \) and \( \gamma_1 \) and \( x_2 \) and \( \gamma_2 \) are the mole fraction and activity coefficient of components 1 and 2 respectively. \( \tilde{v} \) is the mixture liquid molar volume, \( \Pi \) is total pressure, \( R \) is the ideal gas constant, and \( T \) is temperature in absolute units.

This correlational procedure, a modified Margules model, yielded infinite-dilution fugacity coefficients differing from the non-rigorous Margules model (derived for a binary at constant pressure) by a few percent but in some cases by as much as ten percent. The modified version is necessary in fitting binary total pressure versus mole fraction data to an expression totally consistent with Gibb's Phase Rule. Its application implies that the derivative of pressure with respect to mole fraction may affect the values of activity coefficients determined, especially at either infinite-dilution axis where the absolute value of this derivative is greatest.
Acknowledgements

The author wishes to thank the Department of Energy for financially supporting him during this project as well as funding this research.

He also wishes to express deep gratitude to Riki Kobayashi for his advise and direction concerning this complicated research problem, as well as being a very good friend.

Ray Martin also gave the author very good support in terms of his abilities as a scientific machinist and as a good friend and associate.
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ii.) **Greek Letters**
Δ .......................... Change in Property Upon Mixing
γ .......................... Liquid Phase Activity Coefficient
μ .............................. Chemical Potential
Π .............................. Total Pressure
ϕ .............................. Vapor Phase Activity Coefficient

iii.) Superscripts
-
.......................... Partial Molar Property

~ .......................... Quantity per Mole in Liquid

^ .......................... Normalized Fugacity

* .......................... Reference Value

E .......................... Excess Property

L,liq .......................... Liquid Phase Property

s .......................... Saturation Property

V,vap .......................... Vapor Phase Property

2 .......................... Quantity Squared

∞ .......................... At Infinite-Dilution
iv.) **Subscripts**

- ........................................... Pure Component Property

F ............................................. Fluorene

ideal .................. Property as Determined by Ideal Mixing

inf-dil. ....................... At Infinite-Dilution

mix ................... Experimentally Determined Mixture Value

P ............................................. Phenanthrene

vap ............................... Vaporization Property

1 ................................. Refers to Component 1

2 ................................. Refers to Component 2

v.) **Mathematical Symbols**

d ....................................... Total Derivative

exp ....................................... Exponential Function

ln ....................................... Natural Logarithm Function
I. INTRODUCTION

i.) Purpose and Products of Research;

The objective of this project was to develop a method to accurately determine infinite-dilution fugacity coefficients from thermodynamic data on two-component Vapor-Liquid-Equilibria (VLE) systems using a rigorous, thermodynamically consistent relationship. The system fluorene/phenanthrene was investigated for total pressure versus mole fraction at several temperatures in a well-degassed, constant volume cylinder maintained at constant temperature in a thermostatted bath. The liquid volume in the sample cylinder was much larger than the vapor volume, allowing for the assumption of constant liquid mole fraction, being the same as that prepared initially regardless of temperature change between measurements.

These data, collected at thirteen temperatures from 160°C to 280°C in ten degree intervals, were correlated by a four-suffix Margules activity coefficient model, Wohl (1946), to determine infinite-dilution fugacity coefficients for fluorene in phenanthrene and phenanthrene in fluorene. A thermodynamically consistent total pressure fit over the entire mole fraction range was used in the common form of \( x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2 = 0 \). The derivative of pressure with respect to mole fraction was not considered for the
adjustment of infinite-dilution activity coefficients because the total pressure was relatively low (below atmospheric at all temperatures investigated) in this system. The precision of two-component, total pressure measurements, \( \Pi \), at these low pressures did not warrant the inclusion of the infinite-dilution values of \( d\Pi/dx_1 \) into consistency fitting. Also, even though liquid molar volume versus temperature data for pure phenanthrene have been correlated by Gurevich and Bednov (1972), comparable data for fluorene are unavailable.

Other data collected by Kolbe and Ghmeling (1985a, 1985b) on water/ethanol, and Smith and Maher (1979a, 1979b, 1980) and Smith and Srivastava (1986) on total pressure of binaries, were correlated by a modified Margules activity coefficient model. This modification of the Margules model allowed for the inclusion of pressure derivative effects at infinite-dilution in the determination of infinite-dilution fugacity coefficients. These total pressure versus mole fraction data were correlated for thermodynamic consistency as described by Ibl and Dodge (1953) by a computer least squares fitting routine developed by this author, Roper (1988). The results show that although most infinite-dilution fugacity coefficients were changed by only a few percent or less, some were altered by a considerable
amount by using the modified four-suffix Margules expression which takes into account the pressure derivative effects at infinite-dilution.

ii.) **Evaluation of Infinite-Dilution Coefficients:**

The solution across the entire mole fraction range of the rigorous thermodynamic relation due to Ibl and Dodge (1953);

\[
\frac{\text{dln} f_1}{\text{dx}_1} + x_2 \frac{\text{dln} f_2}{\text{dx}_1} = \frac{\tilde{v}}{RT} \frac{\text{d} \Pi}{\text{dx}_1},
\]  

(1)

is very nonlinear with respect to the definition of total pressure as;

\[
\Pi = x_1 \gamma_1 P_1^S + x_2 \gamma_2 P_2^S = f_1 + f_2.
\]  

(2)

\( x_1, f_1, \gamma_1, P_1^S \) and \( x_2, f_2, \gamma_2, P_2^S \) are the mole fractions, component fugacities, activity coefficients, and saturation pressures of components 1 and 2 respectively. \( R \) is the ideal gas constant, \( T \) is temperature and \( \tilde{v} \) is the mixture liquid molar volume.

Equation 2 is, however, very acceptable as a data correlating working relationship, especially by computer routine. The usual form of Margules' activity coefficient
expressions were modified to solve the thermodynamically exact, according to Ibl and Dodge, two-component VLE differential equation, \( \text{I} \). The additional terms in equations \( 5a \) and \( 5b \) add the contribution of the pressure derivative at infinite-dilution to each nonideality coefficient of the trace component at the other component pure axis, without violating Henry's law.

Although this differential equation has been presumed to be exact, Ibl and Dodge (1953), its application is not, because complete mixture liquid molar volume data are generally not available. The linear approximation in the mid-mole fraction range to a true solution becomes exact, however, at each infinite-dilution axis.

Henry's law states that at infinite-dilution the partial pressure of the trace component in the vapor phase at constant temperature is proportional to the liquid mole fraction of that component times its Henry's law constant, Henry (1803);

\[
y_i \Pi = H_i x_i |_{x_i \to 0}, \tag{3}
\]

\( H_i \) is the Henry's law constant of component \( i \) in the mixture liquid and is an infinite-dilution property. If the vapor phase is considered ideal, as it is in all correlational
work done for this report, the component fugacity can be presented as;

\[ f_i = y_i \Pi = P_i^S x_i \gamma_i \]  \hspace{1cm} (4a)

Combining equations 3 and 4a leads to;

\[ \gamma_i^\infty = \frac{H_i}{P_i^S} \]  \hspace{1cm} (4b)

The activity coefficient, \( \gamma_i \), will have a constant slope with respect to mole fraction at infinite-dilution of component \( i \), Malone (1987). Note that \( \gamma_i \) is referenced to the saturation pressure and not to the fugacity of pure \( i \).

It is usually advantageous to consider a pure component activity coefficient equal to one when its mole fraction is at or very near to one and the other component occurs in a trace amount. The classical expressions of Margules illustrate these principles and most two-component VLE data can be fit with his model. It is necessary to use a four-suffix form when the system total pressure assumes both positive and negative deviations from the ideal value as calculated by Raoult's law.

The activity coefficient expressions used to achieve the inclusion of pressure derivative effects, especially at infinite-dilution, are
\[ \gamma_1 = \exp \left( x_2^2 (a x_1 + k l x_1 x_2 + b x_2) + p x_2 \right) \tag{5a}, \]

and

\[ \gamma_2 = \exp \left( x_1^2 (c x_2 + k 2 x_1 x_2 + d x_1) + q x_1 \right) \tag{5b}, \]

where the terms added in modification of the fundamental Margules four-suffix expressions are underlined. The terms with parameters \( a, k_1, b, c, k_2, \) and \( d \) satisfy

\[ x_1 \, d \ln \gamma_1 + x_2 \, d \ln \gamma_2 = 0. \]

Equations 5a and 5b are consistent with Henry's law for each infinitely dilute component. They generate a linear solution to equation 1 with boundary values given by

\[ v_2 \frac{d \Pi}{dx_1} \big|_{x_1=0} \text{ at } x_1 = 0 \text{ and } v_1 \frac{d \Pi}{dx_1} \big|_{x_1=1} \text{ at } x_1 = 1. \]

\( v_1 \) and \( v_2 \) are pure component 1 and 2 saturation pressures. Even though \( x_1 \, d \ln \gamma_1 / dx_1 + x_2 \, d \ln \gamma_2 / dx_1 \) has a value by equations 5 that is linear between \( q \) and \( -p \), azeotropes, where equation 1 should be exactly zero, are well predicted if systems correlated displays this behavior.
II. PERSPECTIVES

i.) Purpose of Infinite-Dilution Correlations:

Continuum fluids as heterogeneous as coal liquefaction products cannot be fully resolved by conventional on-line or batch distillation, regardless of the number of theoretical stages employed. Such a mixture with most components present in only trace amounts, or containing a near infinite number of species, is not separable into individual components by analytical batch distillation. Any cut from a true-boiling-point (TBP) distillation of a coal liquid will contain chemical individuals that boil as pure components, at the same pressure at which the fraction was collected, at temperatures both considerably above and below the boiling point of the fraction itself.

These fractional cuts have been separated by chromatography and the components assigned by mass spectroscopy by the Phillips Petroleum Company. Each cut contains a collection of components whose boiling points as pure components will span almost the same range as the boiling points of the components found in the entire mixture, see figure 55. Thus, as shown by Phillips, analytical distillation cannot
be used to resolve the continuum mixture into an orderly subset of continuum mixtures, much less pure components.

The concept of infinite-dilution fugacity coefficients has been developed to characterize the affinities of the individual components for the near-continuum liquid in which they are present in trace concentrations. Expressions for the individual component activities at infinite-dilution can be integrated into functions describing the thermodynamic properties and VLE behavior of these very many component mixtures, such as has been done by Gualtieri, Kincaid, and Morrison (1982) as well as Cotterman, Bender, and Prausnitz (1985).

ii.) Continuum Thermodynamics;

Several approaches have been taken in expressing thermodynamic properties of these polydispersed mixtures. All methods involve a continuous chemical potential function times a continuous probability-density-function (pdf) integrated over an interval, either over a complete number of species or a fraction treated as a continuum mixture plus the property evaluated for a number of discrete components. The independent index of integration, usually denoted I, may be any of a number of properties such as aromaticity, TBP of
a differential fraction, molecular weight, etc. Expressed mathematically this is;

\[ \int_{I} F(I) dI = 1 \quad \text{or} \quad \sum_{i}^{j} x_{i} + \int_{I} n_{j} F(I) dI = 1; \]  
\[ \text{where} \sum_{i}^{j} x_{i} + n_{j} = 1, \]  

(6a)

(6b)

where there are \( j \) discrete components, separately identifiable species. \( F(I) \), the pdf is continuous in the non-discrete species interval or sum of intervals (several pdf's possibly with different definitions of \( I \)).

These models have been expanded to perform flash calculations, determine phase equilibria, evaluate infinite-dilution fugacity coefficients, and express thermodynamic properties, e.g., for a hard sphere van der Waals molecule, Cotterman, Bender, and Prausnitz (1985) and Gaultieri, Kincaid, and Morrison (1982). To predict \( \gamma^{\infty}_{i} \)'s for arbitrary polyaromatic continuum liquids is to predict the VLE relationships of coal liquids. The objective of this work is to explore these relationships and develop an experimental procedure to accomplish the measurements needed.

Examples of continuum fluids are fatty acids and esters in vegetable oils, colloidal dispersions, polymer soups, coal hydrogenation products, shale oils, and crude oil heavy
fractions. Fluids of interest to the petroleum and synthetic crude industries often include both discrete and infinite-dilution components, Cotterman, Bender, and Prausnitz (1985).

iii.) Infinite-Dilution Behavior of Coal Liquid Components;

Nasir and Kobayashi (1981) have shown incurrence of large VLE measurement errors for large boiling point cuts from relatively ideal continuum mixtures. These errors in 90°C fractions are a direct result of cut-component vapor pressure variations. In cooperation with the Phillips Petroleum Company's analytical division they have shown that for coal liquids each narrow boiling cut produced by laboratory distillation contained compounds having a broad range of pure component boiling points. The occurrence of compounds with a wide range of pure component boiling points in the vapor of each narrow boiling fraction was traced to the large number-of-theoretical-trays in the analytical column and to high nonideality in the liquid phase. Although the resolution of mixtures by analytical distillation into cuts of a meaningful boiling point sequence is impossible, they recommend that narrow boiling range cuts should be taken for best VLE measurements.
Kragas and Kobayashi (1983) proposed methods for measuring infinite-dilution fugacity coefficients from data for binary systems of dilute compounds in a common solvent. Vapor pressure data were to be taken in the range of solute mole fraction from 0.025 to 0.150. The slope of the binary vapor pressure curve dΠ/dx₁ at x₁ = 0 is used in the following expression, which is thermodynamically exact at constant temperature as x₁ → 0;

\[
γ₁^{∞} = \frac{\phi_L}{f_1^L} \left[ 1 + \frac{(\partial Π/\partial x_1)_T (v_2^V - v_2^L)}{RT} \right] x₁ \to 0',
\]

developed by Gautreaux and Coates (1955) and adapted by Kragas (1982). φ is the vapor phase nonideality coefficient of component 1, \( v_2^V \) and \( v_2^L \) are the molar volumes of pure component 2 vapor and liquid phases respectively. \( f_1^L \) is the pure component 1 reference fugacity (saturation pressure) at the temperature of the mixture.

iv.) Experimental;

Vapor pressures of binary mixtures formed from components found in coal liquids are measured by the static equilibrium method, assuming constant mole fractions in the liquid. Vapor pressures of the pure components are also measured. Since there is no liquid-vapor mixing by either
refluxing or vapor recycling, equilibrium is established by component transfer across the large liquid volume / small vapor volume interface. The liquid is mixed and the interface is agitated by mechanical-magnetic coupling to maintain a closed system. The cell was initially charged with liquid, almost to its total capacity, to ensure that the vapor space would be small and the liquid mole fractions would be very close to the mole fractions of the total charge, see Appendix I.

This method insures that a true two-component VLE and not a steady-state is established in the preliminarily degassed cell. An example of VLE data measured by a steady-state method is a distillation still, with a monos-tatic blanket gas, where constant reflux at constant temperature is assumed to be an equilibrium condition between the liquid and vapor in the still. The blanket gas is in reality an intrinsic third component.

Vapor pressure versus temperature dependence was also established in this equipment for each pure component used in this study, the results being used in subsequent determinations of mixture nonideality. All compounds used in this infinite-dilution fugacity study of coal liquid components have been purified to better than 99.95 percent
in a zone purification unit, developed in this laboratory, Martin and Martin et al. (1984).

The binary mixture studied shows both positive and negative deviations from ideal pressure over the two-component mole fraction range. Although the total pressure, \( \Pi \), at constant temperature has a monotonically increasing value across the mole fraction range of fluorene in phenanthrene, it shows a negative excess pressure near pure phenanthrene and a positive excess pressure for the remainder of the mole fraction range.

The experiments were performed at constant volume and the results were correlated at constant temperature, i.e. pressure versus mole fraction, therefore:

\[
\text{d}E_{\text{vap}} = T \, \text{d}S_{\text{vap}} - \Pi \, \text{d}V_{\text{vap}} \quad \text{(8)}
\]
\[
\text{d}H_{\text{vap}} = T \, \text{d}S_{\text{vap}} \quad \text{(9)}
\]
\[
\text{d}G = n v \, \text{d}\Pi, \quad \text{(10)}
\]
\[
\text{and} \quad \text{d}G^E = \tilde{V}^E \, \text{d}\Pi \quad \text{(11)}
\]

also, in the liquid

\[
\text{d}E_{\text{mix}} = T \, \text{d}S_{\text{mix}} + \Pi \, \text{d}\Delta V_{\text{mix}} \quad \text{(12)}
\]
\[
\Delta V_{\text{mix}} = \tilde{v}^E = n \, \tilde{v} - n \, x_1 \, v_1 - n \, x_2 \, v_2.
\]

\( \tilde{v} \) is the mixture liquid molar volume, \( n \) is the number of moles of mixture, \( v_1 \) and \( v_2 \) are the pure component liquid
molar volumes. \( V \) is phase total volume, \( S \) is entropy, \( E \) is internal energy, \( G \) is Gibbs free energy, and \( H \) is enthalpy. The superscript \( E \) indicates an excess property and \( \Delta \) refers to a property change upon mixing.

If \( V^E \) is assumed to be very nearly equal to zero, thermodynamic property calculations are quite simple as \( dG^E \) would then equal zero and \( G^E \) would equal a constant. But \( V^E \) has a nonzero value (no matter how small) for every mixture, except when adding volumes of isotropic molecules, so that a nonzero \( dG^E \) model in conjunction with an expression for \( dH \), van Ness (1964), gives rise to a formula for \( V^E \):

\[
V^E = nRT \frac{d(x_1 \ln \gamma_1)/dx_1 - d(x_2 \ln \gamma_2)/dx_2}{\gamma_1 P_1 \ln(x_1 \gamma_1)/\ln x_1 - \gamma_2 P_2 \ln(x_2 \gamma_2)/\ln x_2}
\]

Vapor pressure versus temperature dependence has been established for pure phenanthrene and pure fluorene as well as 0.05, 0.15, 0.25, 0.50, and 0.75 mole fractions of fluorene in phenanthrene. A model is proposed to better define the system and accurately determine the infinite-dilution fugacity coefficients by including terms in their expressions accounting for pressure derivative with respect to mole fraction effects at infinite-dilution. Although these data were not correlated with these
additional terms representing pressure derivative effects for reasons mentioned above, the infinite-dilution coefficients of fluorene in phenanthrene and phenanthrene in fluorene have been well determined. Also, data obtained by a total pressure method for binary systems from other sources have been well correlated with this model using the rigorous thermodynamic consistency expression including the pressure derivatives at infinite-dilution.
III. MATHEMATICAL FORMULATION

1.) Relations and Assumptions:

If pressure as well as temperature could be fixed at a given mole fraction in two-component VLE, data for these systems could be correlated by thermodynamic consistency using the familiar form of the Gibbs-Duhem as expressed by Margules, \( x_1 \, d\ln \gamma_1 + x_2 \, d\ln \gamma_2 = 0 \). By Gibbs' Phase Rule we know this is not possible at two phase equilibrium for two and only two components, i.e., a well degassed sample in a constant volume equilibrium cell with total pressure set by temperature and mole fraction.

In these systems pressure effects contribute to nonideality throughout the entire mole fraction range, particularly at infinite-dilution. This requires the addition of terms to the activity coefficient expressions of Margules which will at least give exact solutions at infinite-dilution to the above differential thermodynamic consistency relation, equation \( \) \( 1 \). In the absence of mixture liquid volume data, this will be only an approximate solution away from the pure component axes in the two-component pressure versus mole fraction diagram although infinite-dilution activity coefficients are precisely
determined. When there is a scarcity of the needed mixture liquid volume data, infinite-dilution behaviors are determined by using pure component volumes versus temperature data in a linear solution to equation 1.

In this solution scheme the mixture molar volume is assumed to be very nearly equal to the mole fraction weighted sum of the individual saturated pure component liquid volumes, i.e., excess volume of mixing close to zero. Therefore, away from infinite-dilution the activity coefficients will only be very good approximations to what their true values really are (assuming ideal vapor), although they will be as exact as the accuracy of the data allows at infinite-dilution.

ii.) Modified Margules Nonideality Coefficients Model;

The objective, to develop a thermodynamically consistent method of obtaining precise infinite-dilution activity coefficients, is accomplished very simply by adding linear terms to the polynomials of the four-suffix Margules activity coefficient expressions. They appear as;

$$\gamma_1 = \exp \left[ x_2 \left( a x_1 + k x_1 x_2 + b x_2 \right) + px_2 \right] \quad (5a),$$

and
\[ \gamma_2 = \exp \left[ \frac{c}{b} x_1^2 (cx_2 + k2x_1x_2 + dx_1) + gx_1 \right] \]  

(5b),

where the terms added have been underlined. Note that these additional terms will not change the Henry's law constant nor violate the argument that the majority component has an activity coefficient of one at its pure component axis.

The parameters a, c, k1, k2, b, and d (or the equivalent set a, b, d, and k) are determined by a complete system, mole fraction versus isothermal pressure, least squares, computer fitting routine. Following Margules, the equivalent consistency restrictions are made in the second order and higher terms of the polynomials in the expressions for \( \gamma_1 \) and \( \gamma_2 \). Then \( k1 = k2 = k \), \( k = 1.5(b + d - a - c) \), and \( c = a + 3(b - d) \). These constraints are programmed into the least squares fitting routine, see Appendix II.

\( p \) and \( q \) are set by the end point (pure component axis) solutions to the differential consistency expression, equation 1. Then at \( x_1 = 1 \),

\[ p = -1 \frac{d \ln \gamma_1}{dx_1} \bigg|_{x_2=0} = - \frac{v_1}{RT} \frac{d \Pi}{dx_1} \bigg|_{x_2=0} \]  

(13a)

and at \( x_1 = 0 \),
\[ q = \left. \frac{d \ln \gamma_2}{dx_1} \right|_{x_2=1} = \frac{\nu_2}{RT} \left. \frac{d \Pi}{dx_1} \right|_{x_2=1} \]  \hspace{1cm} (13b) \\

\( \nu_1 \) and \( \nu_2 \) are the molar volumes of pure components 1 and 2 respectively.

The addition of the \( p \) and \( q \) terms may have a relatively large affect on the fitting parameters \( a, b, d, \) and \( k \) although these will still obey the restrictions stated above and will in themselves give terms in the integral of \( \ln \gamma_1 - \ln \gamma_2 \) from \( x_1 = 0 \) to \( x_1 = 1 \) which sum to zero. The presence of the \( p \) and \( q \) terms will give a small remainder in the \( \ln \gamma_1 - \ln \gamma_2 \) integration. Because liquid compressibility is very small, \( \tilde{\nu}_\text{liq} \Pi \ll RT, p \) and \( q \) are also relatively small although \( d \Pi / dx_1 \) can be considerable.
IV. PROCEDURE

i.) Sample-Cell Preparation;

Approximately sixty gram samples were weighed as solid into a small beaker to the nearest milligram on a Seederer-Kolhbusch pan balance, the relative amounts being determined by the mole fraction desired. The solids in the covered beaker were melted to homogeneity at 120 °Celsius by stirring well with a heated spatula. The solution was carefully poured into the hot sample-cell until it was almost completely filled. The cell cap was secured tightly while the sample was still liquid. The cell was then installed in the degassing oven, the reflux column was attached and a vacuum was gently pulled at the top of the condenser.

ii.) Degassing Sample;

Considerable trouble was initially encountered in eliminating associated gases from the sample before acceptable vapor pressure values were obtained, especially after an increase in temperature for higher temperature measurements. This problem was essentially solved by constructing and operating a primary reflux apparatus. That equipment
was also used to degas mixtures of coal liquefaction components and it is designed to condense and freeze the mixtures with total conservation of the samples. This procedure preserves the mole fractions initially prepared.

In the vapor pressure apparatus, the vapor space, which is small compared to the liquid volume, is evacuated gently several times to achieve consistent pressures at a given temperature, but not nearly as often as needed without the primary refluxing / degassing of the compound or mixture. Consequently much less mixture vapor is lost during this 'gas pumping' process. The repeatability of vapor pressures as the temperature was raised and lowered indicated that not enough of the mixture was lost by 'pumping' to change the mole fractions in the liquid by an amount that can be detected from the experimental results.

The primary degassing apparatus consisted of a cylindrical oven that surrounded the sample-cell, a glass condenser 400 mm in length, and a strong vacuum system to pull gas from the top of the condenser. The condenser was of sufficient length to allow the rising vapors to both liquefy and solidify before they could exit at the condenser top. This insured that essentially no compound or mixture vapor was lost from the system through the condenser. Solid
condensation in the upper portions of the inner condenser sleeve was intermittently heated by a heat gun and melted down to recombine with the liquid in the cell.

The degassing oven, mounted concentrically around the stationary sample-cell, was powered by a variable voltage rheostat to control boil-up temperature. The oven was mounted on a laboratory jack so that it might be lowered for cell cooling, then raised again and the oven temperature increased above the previous setting. This allowed the associated light gases to be removed in packets instead of by violent boil-up.

The vacuum system was complete with a Leybold-Hearus (L-H) thermocouple gauge which indicated pressures at the condenser head of around 10 millitorr absolute. A compound trap was included to monitor mixture loss if any, and another trap close to the vacuum pump insured that no vacuum pump oil escaped into the system. The sample-cell cap was especially designed and built by Mr. Ray Martin of our laboratory to accommodate counter current vapor ascent and liquid reflux descent, and to allow for complete cell-to-condenser shut-off. The rest of the degassing apparatus was designed and assembled by this author.
The charge in the cell was adjudged to be degassed to the capability of the auxiliary degassing apparatus when the temperature program was completed, solid melting was no longer eruptive as a result of the evolution of trapped gases, and solid deposition of degassed vapor was very smooth. All solid sample was run back down into the cell by wrapping the condenser with heating tape and heating just enough to liquefy any remaining condensed mixture. The cell-to-condenser valves were then shut-off tightly with the sample in the cell under vacuum. The sample-cell and cap were then disconnected from the degassing apparatus vacuum and connected to the vapor pressure apparatus. A vacuum was again drawn and the cap vapor-valve opened to the vapor pressure apparatus vacuum at room temperature.

Because the degasser could not reach temperatures as high as the maximum salt bath temperature, an additional milder degassing operation was performed at these higher temperatures in the apparatus. This also allowed excess liquid due to thermal expansion to flow out of the sample-cell vapor space and be caught in the trap of the vapor pressure apparatus. The mole fraction of the liquid remaining in the sample-cell was unchanged since only well mixed liquid was lost by expansion.
iii.) **Data Acquisition Equipment**;

Vapor pressures of pure compounds and mixtures of compounds purified from coal liquefaction products were measured by the static pressure, constant mole fraction method. The sample and reference gas are separated by a differential pressure cell which is electrically coupled by a linear transformer to a Differential Pressure Null Indicator (Ruska DPI) and is coupled by nitrogen gas pressure to a spiraled quartz Bourdon tube. Actual pressures were measured by the Bourdon tube balanced in a magnetic field inside a Ruska Digital Quartz Gauge (DDR 6000). The DDR was calibrated frequently by a (L-H) thermocouple gauge at pressures below 100 microns of Mercury and by a Ruska Dead Weight Gauge at the high and midpoint calibration points recommended by the manufacturer. The DDR was found to be accurate to one part in fifty thousand at 1032.71 mm Hg, the recommended high pressure calibration point.

Voltage from the DDR is measured by a programmable Kiethley Digital Volt Meter which is interfaced to a Commodore 2001 CBM computer. Pressure is displayed in units of millimeters of Mercury on the computer screen every four minutes along with other converted inputs of temperature,
computer cycle time, set point temperature, and fine temperature control heater slope and intercept.

Temperature is measured by a Platinum Resistance Thermometer coupled to the same Kiethley DVM in the Ohms measurement mode. The computer controls the measurement mode of the DVM through IEEE interface command and maintains the DVM Ohms mode for all but two seconds of the four minute program cycle to maintain a constant current in the PRT and eliminate PRT warm-up resistance drift. The PRT resistance signal from the DVM is processed in the computer with the IPTS conversion using the Callendar Equation. The computer operates a fine control heater which maintained the thermostatic salt bath temperature within plus and minus five one-thousandths of a degree Celsius at an accuracy of plus or minus one one-hundredth of a degree from the set point.

The potassium / sodium - nitrate / nitrite salt thermostat caused stress corrosion cracking and frequent failure of the torsion bolts in the DPI-cell. This problem has been rectified by replacing the salt thermostat with Multitherm IG-2. The control equipment was installed and interfaced by the author for this project and is now in use to measure vapor pressures of pure component C10+ long-chain paraffins.
iv.) Data Collection:

Although the Commodore CBM 2001 series professional computer has the capacity to store all of the data for a run during the course of the experiment, and even though the experimental parameters were well maintained automatically, manipulation of machine controls was necessary. The valves controlling the DPI-cell evacuation, sample-cell shut-off, and reference gas inlet nitrogen supply and exhaust to vacuum pump were all operated manually. Data were recorded manually from the computer display into a notebook.

The pressure null electrical balance in the Differential Pressure Indicator (DPI) was manually set after over-night DPI-cell evacuation at the desired set-point temperature. The DPI-cell would be evacuated to less than ten microns of Mercury during the over-night DPI-cell nulling process.

Multiple data readings were taken at every temperature for every experiment to insure consistency at that temperature. The data were plotted as the natural logarithm of pressure versus inverse temperature. Temperatures of data collected were decreased/increased by ten degree Celsius intervals successively to insure repeatable values at any
particular temperature. When the pressure no longer achieved a static value, over seventy two hours at a fixed temperature, the sample was assumed to be decomposing and the experiment terminated.

Data were smoothed over the temperature range investigated (160 to 280° Celsius in most cases, pure fluorene and pure phenanthrene to 320° Celsius) by second order Chebychev polynomials computed on the Rice University, Chemical Engineering Department's VAX Computer. When deviations between actual and calculated vapor pressure values across the temperature range were within one part in three hundred that experiment was deemed acceptable and terminated. The salt bath was lowered, and the equipment purged and cleaned. A new, recently degassed sample was then connected to the DPI-cell and the bath raised and sealed for a new experiment.
V. DATA

Infinite-dilution fugacity coefficients were obtained for the binary system fluorene/phenanthrene at thirteen temperatures by fitting total pressure across the entire mole fraction range by a thermodynamically consistent computer routine. Infinite-dilution activity coefficients as listed were calculated by the four-suffix Margules model, which allows for both positive and negative pressure deviations from the ideal values. Data plotted are the logarithm pressure versus inverse temperature and the excess enthalpy, excess pressure, activity coefficients, logarithm activity coefficient ratio, vapor mole fractions, excess in Gibb's free energy change upon mixing, and excess molar entropy; versus liquid mole fraction fluorene. Also shown are liquid model parameters and infinite-dilution activity coefficients, both versus temperature.

The water/ethanol system data are shown as total and excess pressure, activity coefficients, vapor mole fractions, excess in Gibb's free energy change upon mixing, logarithm activity coefficient ratio, and the Gibbs-Duhem function; all versus liquid mole fraction ethanol. Infinite-dilution fugacity coefficients as calculated by computer least squares data fitting using a modified
four-suffix Margules model, including $d\Pi/dx$ effects, and pure component properties are listed.

The binary VLE systems ethanol/aniline, acetone/aniline, chlorobenzene/aniline, methanol/aniline, 1-pentene/aniline, acetone/chlorobenzene, ethyl acetate/chlorobenzene, methanol/chlorobenzene, 1-pentene/chlorobenzene, acetonitrile/aniline, acetonitrile/chlorobenzene, and benzene/acetonitrile were computer fit for excess pressure across the entire mole fraction range using the modified Margules model. Infinite-dilution fugacity coefficients and pure component properties are listed. Excess pressure, activity coefficients, vapor mole fractions, excess in Gibbs's free energy change upon mixing, logarithm activity coefficient ratio, and the Gibbs-Duhem function are shown for each binary.

A plot of a coal liquefaction fractional-cut pure components boiling point distribution superimposed on the true boiling point curve versus amount distilled data from Phillips Petroleum Company is included. The projected trace components continuous activity coefficient distribution in a model continuum liquid is also shown.
### Table I

**Total Pressure Measurements for Phenanthrene/Fluorene**

**Pressure Smoothed by Second Order Chebychev Polynomials**

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<th>Mole Fraction Fluorene</th>
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<th>0.1500</th>
<th>0.2500</th>
<th>0.5000</th>
<th>0.7500</th>
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42.70 45.06 52.48 62.51 83.71 97.65 104.67 110.97

230.00
58.43 61.17 70.15 83.27 110.63 128.51 138.52 148.41
58.08 61.08 70.67 83.31 110.64 128.96 138.32 146.59

240.00
78.11 81.55 94.01 109.68 144.55 168.17 180.37 192.48
77.97 81.79 94.05 109.80 144.64 168.48 180.81 191.69

250.00
104.12 108.64 124.64 143.21 187.30 218.33 233.22 250.74
103.40 108.25 123.83 143.21 187.16 217.87 233.96 248.30

260.00
135.56 141.25 161.78 184.92 239.67 278.66 298.87 318.54
135.55 141.72 161.36 184.97 239.84 279.05 299.84 318.76

270.00
175.31 183.72 207.49 236.60 304.50 354.24 381.46 407.48
175.74 183.63 208.23 236.68 304.54 354.17 380.80 405.76

280.00
224.96 235.57 267.36 300.36 383.48 445.85 480.60 507.70
225.50 235.61 266.24 300.20 383.35 445.65 479.50 512.39
Table II

**Pure Component Properties**

Pressure is given in units of millibars, pure component volumes are in cubic centimeters per gram-mole, R equals 83140.0 mbar per gram-mole per degree Kelvin. $Z_i^0 = \frac{P_i^S V_i^S}{K/R}$.

<table>
<thead>
<tr>
<th>$T, ^\circ$C</th>
<th>$P_1^S$</th>
<th>$V_1^S$</th>
<th>$Z_1^0$</th>
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</table>

Pressure is given in units of kilo-Pascals, pure component volumes are in cubic centimeters per gram-mole, R equals 8314.0 kPa per gram-mole per degree Kelvin. $Z_i^0 = \frac{P_i^S V_i^S}{K/R}$.

<table>
<thead>
<tr>
<th>$T, ^\circ$C</th>
<th>$P_1^S$</th>
<th>$V_1^S$</th>
<th>$Z_1^0$</th>
<th>$P_2^S$</th>
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<td>Ethanol (1) / Aniline (2)</td>
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Table III

Infinite-Dilution Coefficients

Infinite-dilution activity coefficients listed have a computational accuracy of approximately 0.0001.

**Fluorene / Phenanthrene by Roper and Kobayashi:**

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**Ethanol / Water by Kolbe and Gmehling:**

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Infinite-dilution activity coefficients listed have a computational accuracy of approximately 0.0001. Note; * implies vapor phase nonideality calculations were included in data fitting.
**Systems investigated by Mayer and Smith:**

**Ethanol / Aniline**

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**Acetone / Aniline**

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### Methanol / Aniline

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### Acetone / Chlorobenzene

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### Ethyl Acetate / Chlorobenzene

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### Methanol / Chlorobenzene

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### 1-Pentene / Chlorobenzene

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### Acetonitrile / Aniline

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### Acetonitrile / Chlorobenzene

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<th>$\gamma^\infty$ Acetonitrile</th>
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<td></td>
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### Benzene / Acetonitrile System by Srivastava and Smith:

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<th>$\gamma^\infty$ Benzene</th>
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Table IV

Phenanthrene / Fluorene System

Activity Coefficient Model Parameters:

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<th>Temperature, °C</th>
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<th>b</th>
<th>c</th>
<th>d</th>
<th>k</th>
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<td>-2.984</td>
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<tr>
<td>180.00</td>
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Table V

**Excess Enthalpy per Mole as Determined by lnΠ versus 1/T**

*Assuming Constant Liquid Mole Fraction from 170 - 270 °C*

\[ h^E [kJ/g-mole] = \Delta h_{vap,mix} - \Delta h_{vap,ideal} \]

\[ \Delta h_{vap,ideal} = x_P \Delta h_{vap,P} + x_F \Delta h_{vap,F} \]

\[ \Delta h_{vap,Phenanthrene} = 63.64 [kJ/g-mole] \]

\[ \Delta h_{vap,Fluorene} = 57.31 [kJ/g-mole] \]

<table>
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<th>Mole Fraction Fluorene</th>
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<td>0.0000 0.0500 0.1500 0.2500 0.5000 0.7500 0.9000 1.0000</td>
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\[ \Delta h_{vap,mix} \]

63.668 62.836 61.356 59.231 57.548 58.876 57.484 57.279

\[ \Delta h_{vap,ideal} \]

63.668 63.349 62.710 62.071 60.474 57.423 57.918 57.279

**Excess Enthalpy per Mole of Mixture, h^E**

0.000 -0.513 -1.354 -2.840 -2.926 -1.453 -0.434 0.000
Figure 1. Plots of the natural log of the vapor pressure versus 1000/temperature in degrees Kelvin for pure phenanthrene and pure fluorene and binary mixtures of 0.05, 0.15, 0.25, 0.50, 0.75, and 0.90 mole fractions fluorene in phenanthrene.
Figure 2. Experimental excess enthalpy calculated from 160 to 280°C versus mole fraction fluorene for mixtures of 0.05, 0.15, 0.25, 0.50, 0.75 and 0.90 mole fraction fluorene in phenanthrene, by sixth order polynomial fit.
Figure 3a. A plot of excess pressure in mm Hg versus mole fraction fluorene (1) for mixtures with phenanthrene (2). Curve drawn from four suffix Margules activity coefficients model, actual reduced data at 160.00°C represented by points.
Figure 3b. A plot of component fugacity coefficients at 160.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model, gamma inf-dil. (1) = 0.612, gamma inf-dil. (2) = 1.225.
Figure 3c. A plot at 160.0°C of the logarithm of the gamma ratio, $\ln \left( \frac{\gamma_1}{\gamma_2} \right)$, versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 4a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2). curve drawn from four suffix Margules activity coefficients model, actual reduced data at 170.00C represented by points.
Figure 4b. A plot of component fugacity coefficients at 170.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. Gamma inf-dil. (1) = 0.635, gamma inf-dil. (2) = 1.274.
Figure 4c. A plot at 170.0C of the logarithm of the gamma ratio, ln (gamma 1 / gamma 2), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 5a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2). curve drawn from four suffix Margules activity coefficients model, actual reduced data at 180.00°C represented by points.
Figure 5b. A plot of component fugacity coefficients at 180.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2). From activity coefficients model, gamma inf-dil. (1) = 0.646, gamma inf-dil. (2) = 1.286.
Figure 5c. A plot at 180.0°C of the logarithm of the gamma ratio, \( \ln(\text{gamma}_1 / \text{gamma}_2) \), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 6a. A plot of excess pressure in mm Hg versus mole fraction fluorene (1) for mixtures with phenanthrene (2). Curve drawn from four suffix Margules activity coefficients model, actual reduced data at 190.0°C represented by points.
Figure 6b. A plot of component fugacity coefficients at 190.0°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. gamma inf-dil. (1) = 0.654, gamma inf-dil. (2) = 1.286.
Figure 6c. A plot at 190.0°C of the logarithm of the gamma ratio, ln (gamma_1 / gamma_2), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 7a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2). curve drawn from four suffix Margules activity coefficients model, actual reduced data at 200.00°C represented by points.
Figure 7b. A plot of component fugacity coefficients at 200.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. gamma inf-dil. (1) = 0.662, gamma inf-dil. (2) = 1.277.
Figure 7c. A plot at 200.0°C of the logarithm of the gamma ratio, ln (gamma 1 / gamma 2), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 8a. A plot of excess pressure in mm Hg versus mole fraction fluorene (1) for mixtures with phenanthrene (2), curve drawn from four suffix Margules activity coefficients model, actual reduced data at 210.00°C represented by points.
Figure 8b. A plot of component fugacity coefficients at 210.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. Gamma inf-dil. (1) = 0.669, gamma inf-dil. (2) = 1.259.
Figure 8c. A plot at 210.0°C of the logarithm of the gamma ratio, $\ln(\gamma_1 / \gamma_2)$, versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 9a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2), curve drawn from four suffix Margules activity coefficients model, actual reduced data at 220.00°C represented by points.
Figure 9b. A plot of component fugacity coefficients at 220.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model, gamma inf-dil. (1) = 0.676, gamma inf-dil. (2) = 1.235.
Figure 9c. A plot at 220.0°C of the logarithm of the gamma ratio, ln (gamma 1 / gamma 2), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 10a. A plot of excess pressure in mm Hg versus mole fraction fluorene (1) for mixtures with phenanthrene (2). Curve drawn from four suffix Margules activity coefficients model, actual reduced data at 230.00°C represented by points.
Figure 10b. A plot of component fugacity coefficients at 230.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. Gamma inf-dil. (1) = 0.683, gamma inf-dil. (2) = 1.203.
Figure 10c. A plot at 230.0°C of the logarithm of the gamma ratio, \( \ln(\text{gamma } 1 / \text{gamma } 2) \), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
P sat phenanthrene is 77.97 mmHg

P sat fluorene is 191.69 mmHg

\[
\ln(\text{gamma}_1) = x_2^{\times 2}(a x_1 + k x_1 x_2 + b x_2)
\]
\[
\ln(\text{gamma}_2) = x_1^{\times 2}(c x_2 + k x_1 x_2 + d x_1)
\]

\[a = -0.417, \ b = -0.370, \ c = -1.989, \ d = 0.154, \ k = 3.285\]

Figure 11a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2). Curve drawn from four suffix Margules activity coefficients model, actual reduced data at 240.00°C represented by points.
Figure 11b. A plot of component fugacity coefficients at 240.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. gamma inf-dil. (1) = 0.691, gamma inf-dil. (2) = 1.166.
Figure 11c. A plot at 240.0°C of the logarithm of the gamma ratio, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 12a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2), curve drawn from four suffix Margules activity coefficients model, actual reduced data at 250.00°C represented by points.
Figure 12b. A plot of component fugacity coefficients at 250.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model, gamma inf-dil. (1) = 0.699, gamma inf-dil. (2) = 1.124.
Figure 12c. A plot at 250.0°C of the logarithm of the gamma ratio, \( \ln (\text{gamma } 1 / \text{gamma } 2) \), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 13a. A plot of excess pressure in mm Hg versus mole fraction fluorene (1) for mixtures with phenanthrene (2). Curve drawn from four suffix Margules activity coefficients model, actual reduced data at 260.00°C represented by points.
Figure 13b. A plot of component fugacity coefficients at 260.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. Gamma inf-dil. (1) = 0.708, gamma inf-dil. (2) = 1.078.
Figure 13c. A plot at 260.0°C of the logarithm of the gamma ratio, \( \ln \left( \frac{\gamma_1}{\gamma_2} \right) \), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 14a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2). Curve drawn from four suffix Margules activity coefficients model, actual reduced data at 270.00°C represented by points.
Figure 14b. A plot of component fugacity coefficients at 270.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model, gamma inf-dil. (1) = 0.718, gamma inf-dil. (2) = 1.029.
Figure 14c. A plot at 270.0°C of the logarithm of the gamma ratio, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 15a. A plot of excess pressure in mm Hg versus mole mole fraction fluorene (1) for mixtures with phenanthrene (2). curve drawn from four suffix Margules activity coefficients model, actual reduced data at 280.00°C represented by points.
Figure 15b. A plot of component fugacity coefficients at 280.00°C versus mole fraction fluorene (1) for mixtures with phenanthrene (2), from activity coefficients model. 
\( \gamma_{\text{inf-dil. (1)}} = 0.731 \), \( \gamma_{\text{inf-dil. (2)}} = 0.977 \).
Figure 15c. A plot at 280.0°C of the logarithm of the gamma ratio, \( \ln(\text{gamma } 1/\text{gamma } 2) \), versus liquid mole fraction fluorene (1) for mixtures with phenanthrene (2).
Figure 16. A plot of the vapor mole fractions of fluorene and phenanthrene versus liquid mole fraction fluorene for mixtures of fluorene and phenanthrene from 160.0 to 280.0 degrees Celsius. Curves drawn by activity coefficient model.
Figure 17. A plot of the Change in Gibbs excess molar free energy, $\Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal})$ versus mole fraction fluorene for mixtures of fluorene in phenanthrene from 160.0 to 280.0 degrees Celsius.
Figure 18. A plot of the excess molar entropy \((\text{hex} - \text{gex})/T\) from 160.0 to 280.0 degrees Celsius versus liquid mole fraction fluorene in mixtures with phenanthrene, by coefficient model.
Figure 19. A plot of component fugacity coefficient model parameters determined by data fitting of the total pressure of mixtures of fluorene with phenanthrene across the entire composition range versus temperature from 160 to 280 Celsius.
Figure 20. A plot of component infinite-dilution fugacity coefficients as determined by parameters b for fluorene and d for phenanthrene versus temperature from 160 to 280 Celsius.
Fig. 21a. Total and excess pressure versus mole fraction ethanol for mixtures with water from theoretical activity model and actual reduced data at 90.1°C represented by points.
Fig. 21b. Component fugacity coefficients at 90.1°C versus mole fraction ethanol (1) for mixtures with water (2), gamma inf-dil. (1) = 5.815, gamma inf-dil. (2) = 2.703.
Fig. 21c. Vapor mole fractions of ethanol (1) and water (2) versus liquid mole fraction ethanol for mixtures with water at 90.1°C, by coefficient model.
Fig. 21d. Change in Gibbs excess molar free energy, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction ethanol for mixtures with water at 90.1°C.
Fig. 21e. Logarithm of the gamma ratio at 90.1°C, \( \ln(\gamma_1/\gamma_2) \), versus liquid mole fraction ethanol (1) for mixtures with water (2).
Fig. 21f. Gibbs-Duhem function at 90.1°C, $dP/dx_1 \times \text{Liqvol/RT}$ = $x_1 \times d(\ln(g_1))/dx_1 - x_2 \times d(\ln(g_2))/dx_2$, versus liquid mole fraction ethanol (1) for mixtures with water (2). Data indicate $dP/dx_1 = 0$ at approximately $x_1 = 0.89$. 
Fig. 22a. Total and excess pressure versus mole fraction ethanol (1) for mixtures with water (2) from theoretical activity model and actual reduced data at 108.2°C represented by points.
Fig. 22b. Component fugacity coefficients at 108.2°C versus mole fraction ethanol (1) for mixtures with water (2). gamma inf-dil. (1) = 5.684, gamma inf-dil. (2) = 2.684.
Fig. 22c. Vapor mole fractions of ethanol (1) and water (2) versus liquid mole fraction ethanol for mixtures with water at 108.2°C, by coefficient model.
Fig. 22d. Change in Gibbs excess molar free energy, 
\[ \Delta g^{(\text{excess})} = \Delta g - \Delta g^{(\text{ideal})} \], versus liquid mole fraction ethanol for mixtures with water at 108.2°C.
Fig. 22e. Logarithm of the gamma ratio at 108.2°C, \( \ln (\gamma_1 / \gamma_2) \), versus liquid mole fraction ethanol (1) for mixtures with water (2).
Fig. 22f. Gibbs-Duhem function at 108.2°C, $dP/dx_1 \times \text{Liqvol}/RT = x_1 \times d(ln(g_1))/dx_1 - x_2 \times d(ln(g_2))/dx_2$, versus liquid mole fraction ethanol ($x_1$) for mixtures with water ($x_2$). Data indicate $dP/dx_1 = 0$ at approximately $x_1 = 0.88$. 
Fig. 23a. Total and excess pressure versus mole fraction ethanol (1) for mixtures with water (2) from theoretical activity model and actual reduced data at 130.3°C represented by points.
Fig. 23b. Component fugacity coefficients at 130.3°C versus mole fraction ethanol (1) for mixtures with water (2). gamma inf-dil. (1) = 5.546, gamma inf-dil. (2) = 2.627.
Fig. 23c. Vapor mole fractions of ethanol (1) and water (2) versus liquid mole fraction ethanol for mixtures with water at 130.3°C, by coefficient model.
Fig. 23d. Change in Gibbs excess molar free energy, 
\( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction ethanol for mixtures with water at 130.3°C.
Fig. 23e. Logarithm of the gamma ratio at 130.3°C, ln (gamma 1 / gamma 2), versus liquid mole fraction ethanol (1) for mixtures with water (2).
Fig. 23f. Gibbs-Duhem function at 130.3°C, $dP/dx1\times L_{iqvol}/RT = x1\times d(ln(g1))/dx1 - x2\times d(ln(g2))/dx2$, versus liquid mole fraction ethanol (1) for mixtures with water (2).

Data indicate $dP/dx1 = 0$ at approximately $x1 = 0.88$. 
Fig. 24a. Total and excess pressure versus mole fraction ethanol (1) for mixtures with water (2) from theoretical activity model and actual reduced data at 150.5°C represented by points.
Fig. 24b. Component fugacity coefficients at 150.5°C versus mole fraction ethanol (1) for mixtures with water (2), gamma inf-dil. (1) = 5.191, gamma inf-dil. (2) = 2.530.
Fig. 24c. Vapor mole fractions of ethanol (1) and water (2) versus liquid mole fraction ethanol for mixtures with water at 150.5°C, by coefficient model.
Fig. 24d. Change in Gibbs excess molar free energy, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction ethanol for mixtures with water at 150.5°C.
Fig. 24e. Logarithm of the gamma ratio at 150.5°C, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction ethanol (1) for mixtures with water (2).
Fig. 24f. Gibbs-Duhem function at 150.5°C, \( \frac{dP}{dx_1} \approx \frac{\text{Liqvol}}{RT} \)
= \( x_1 \frac{d(\ln(g_1))}{dx_1} - x_2 \frac{d(\ln(g_2))}{dx_2} \), versus liquid mole fraction ethanol (1) for mixtures with water (2).
Data indicate \( \frac{dP}{dx_1} = 0 \) at approximately \( x_1 = 0.87 \).
Fig. 25a. Excess pressure versus mole fraction ethanol (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 313.15K represented by points.
Fig. 25b. Component fugacity coefficients at 313.15K versus mole fraction ethanol (1) for mixtures with aniline (2). Gamma inf-dil. (1) = 2.5262, gamma inf-dil. (2) = 3.0046.
Fig. 25c. Vapor mole fractions of ethanol (1) and aniline (2) versus liquid mole fraction ethanol for mixtures with aniline at 313.15K, by coefficient model.
Fig. 25d. Change in Gibbs excess molar free energy.
\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \]
versus liquid mole fraction ethanol for mixtures with aniline at 313.15K.
Fig. 25e. Logarithm of the gamma ratio at 313.15K, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction ethanol (1) for mixtures with aniline (2).
Fig. 25f. Gibbs-Duhem function at 313.15K, \( \frac{dP}{dx_i} \times \text{Liqvol}/RT = x_1 \frac{d(\ln g_1)}{dx_1} - x_2 \frac{d(\ln g_2)}{dx_2} \) versus liquid mole fraction ethanol (1) for mixtures with aniline (2).
Fig. 26a. Excess pressure versus mole fraction ethanol for mixtures with aniline (2) from theoretical activity model and actual reduced data at 350.81K represented by points.
Fig. 26b. Component fugacity coefficients at 350.81K versus mole fraction ethanol (1) for mixtures with aniline (2). 
gamma \text{ inf-dil.} \ (1) = 2.1148, \quad \gamma \text{ inf-dil.} \ (2) = 2.6389.
Fig. 26c. Vapor mole fractions of ethanol (1) and aniline (2) versus liquid mole fraction ethanol for mixtures with aniline at 350.81K, by coefficient model.
Fig. 26d. Change in Gibbs excess molar free energy. 
\[ \Delta g^{(excess)} = \Delta g - \Delta g^{(ideal)} \] versus liquid mole fraction ethanol for mixtures with aniline at 350.81K.
Fig. 26e. Logarithm of the gamma ratio at 350.81K, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction ethanol (1) for mixtures with aniline (2).
Fig. 26f. Gibbs-Duhem function at 350.81K, $dP/dx_1 \times \text{Liqvol}/RT$ = $x_1 \times d(\ln (g_1))/dx_1 - x_2 \times d(\ln (g_2))/dx_2$, versus liquid mole fraction ethanol (1) for mixtures with aniline (2).
Fig. 27a. Excess pressure versus mole fraction ethanol (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 386.67K represented by points.

Data collected by Maher and Smith

Curve by modified four suffix Margules

\[ a = 0.9567, \quad k_1 = -0.1299, \quad b = 0.5658, \quad p = -0.000672 \]
\[ c = 0.4353, \quad k_2 = -0.1299, \quad d = 0.7396, \quad q = 0.01855 \]
\[ c = a + 3(b - d), \quad k_2 = k_1 = 1.5(b + d - a - c) \]

integral test = -0.0126
Fig. 27b. Component fugacity coefficients at 386.67K versus mole fraction ethanol (1) for mixtures with aniline (2). gamma inf-dil. (1) = 1.7491, gamma inf-dil. (2) = 2.1344.
Fig. 27c. Vapor mole fractions of ethanol (1) and aniline (2) versus liquid mole fraction ethanol for mixtures with aniline at 386.67K, by coefficient model.
Fig. 27d. Change in Gibbs excess molar free energy,\[ \Delta g(\text{excess}) - \Delta g - \Delta g(\text{ideal}), \] versus liquid mole fraction ethanol for mixtures with aniline at 386.67K.
Fig. 27e. Logarithm of the gamma ratio at 386.67K, $\ln (\text{gamma 1} / \text{gamma 2})$, versus liquid mole fraction ethanol (1) for mixtures with aniline (2).
Fig. 27f. Gibbs-Duhem function at 386.67K, dP/dx1*Liqvol/RT = x1*d(ln(g1))/dx1 - x2*d(ln(g2))/dx2, versus liquid mole fraction ethanol (1) for mixtures with aniline (2).
Data collected by Maher and Smith
Curve by modified four suffix Margules

\[ a = -0.4876, \, k_1 = -0.5160, \, b = -0.2847, \, p = -0.00164 \]
\[ c = 0.0747, \, k_2 = -0.5160, \, d = -0.4722, \, q = 0.00150 \]
\[ c = a + 3(b - d), \, k_2 = k_1 = 1.5(b + d - a - c) \]
\[ \text{integral test} = -0.0016 \]

\[ P_{\text{sat acetone}} \]
\[ P_{\text{sat aniline}} \]

Fig. 28a. Excess pressure versus mole fraction acetone
(1) for mixtures with aniline (2) from theoretical activity model
and actual reduced data at 313.15K represented by points.
Fig. 28b. Component fugacity coefficients at 313.15K versus mole fraction acetone (1) for mixtures with aniline (2), \( \gamma_{\text{inf-dil. (1)}} = 0.7510 \), \( \gamma_{\text{inf-dil. (2)}} = 0.6246 \).
Fig. 28c. Vapor mole fractions of acetone (1) and aniline (2) versus liquid mole fraction acetone for mixtures with aniline at 313.15K, by coefficient model.
Fig. 28d. Change in Gibbs excess molar free energy, 
$\Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal})$, versus liquid mole fraction acetone for mixtures with aniline at 313.15K.
Fig. 28e. Logarithm of the gamma ratio at 313.15K, $\ln(\gamma_1 / \gamma_2)$, versus liquid mole fraction acetone (1) for mixtures with aniline (2).
Fig. 28f. Gibbs-Duhem function at 313.15K, \( \frac{dP}{dx_1} \frac{\text{Liqvol}}{RT} = x_1 \times \frac{d\ln(g_1)}{dx_1} - x_2 \times \frac{d\ln(g_2)}{dx_2} \), versus liquid mole fraction acetone (1) for mixtures with aniline (2).
Fig. 29a. Excess pressure versus mole fraction chlorobenzene (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 293.15K represented by points.
Fig. 29b. Component fugacity coefficients at 293.15K versus mole fraction chlorobenzene (1) for mixtures with aniline (2). gamma inf-dil. (1) = 2.1511, gamma inf-dil. (2) = 3.0616.
Fig. 29c. Vapor mole fractions of chlorobenzene (1) and aniline (2) versus liquid mole fraction chlorobenzene for mixtures with aniline at 293.15K, by coefficient model.
Fig. 29d. Change in Gibbs excess molar free energy, 
\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \], versus liquid mole fraction chlorobenzene for mixtures with aniline at 293.15K.
Fig. 29e. Logarithm of the gamma ratio at 293.15K, $\ln(\gamma_1/\gamma_2)$, versus liquid mole fraction chlorobenzene (1) for mixtures with aniline (2).
Fig. 29f. Gibbs-Duhem function at 293.15K, \( \frac{dP}{dx_1}\text{Liqvol}/RT = x_1\frac{d(ln(g_1))}{dx_1} - x_2\frac{d(ln(g_2))}{dx_2} \), versus liquid mole fraction chlorobenzene (1) for mixtures with aniline (2).
Fig. 30a. Excess pressure versus mole fraction chlorobenzene (I) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 343.15K represented by points.
Fig. 30b. Component fugacity coefficients at 343.15K versus mole fraction chlorobenzene (1) for mixtures with aniline (2). Gamma inf-dil. (1) = 2.1189, gamma inf-dil. (2) = 2.2391.
Fig. 30c. Vapor mole fractions of chlorobenzene (1) and aniline (2) versus liquid mole fraction chlorobenzene for mixtures with aniline at 343.15K, by coefficient model.
Fig. 30d. Change in Gibbs excess molar free energy.
\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \], versus liquid mole fraction chlorobenzene for mixtures with aniline at 343.15K.
Fig. 30e. Logarithm of the gamma ratio at 343.15K, ln (gamma 1 / gamma 2), versus liquid mole fraction chlorobenzene (1) for mixtures with aniline (2).
Fig. 30f. Gibbs-Duhem function at 343.15K, \( \frac{dP}{dx_1} \times \text{Liqvol}/RT \) = \( x_1 \times \frac{d(\ln(g_1))}{dx_1} - x_2 \times \frac{d(\ln(g_2))}{dx_2} \), versus liquid mole fraction chlorobenzene (1) for mixtures with aniline (2).
Data collected by Maher and Smith
Curve by modified four suffix Margules

\[ a = 0.7138, \quad k_1 = -0.3340, \quad b = 0.5923, \quad p = -0.00169 \]
\[ c = 0.6986, \quad k_2 = -0.3340, \quad d = 0.5974, \quad q = 0.00362 \]
\[ c = a + 3(b - d), \quad k_2 = k_1 = 1.5(b + d - a - c) \]
\[ \text{integral test} = -0.0027 \]

Fig. 31a. Excess pressure versus mole fraction chlorobenzene (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 393.15K represented by points.
Fig. 31b. Component fugacity coefficients at 393.15K versus mole fraction chlorobenzene (1) for mixtures with aniline (2). gamma inf-dil. (1) = 1.8052, gamma inf-dil. (2) = 1.8240.
Fig. 31c. Vapor mole fractions of chlorobenzene (1) and aniline (2) versus liquid mole fraction chlorobenzene for mixtures with aniline at 393.15K, by coefficient model.
Fig. 31d. Change in Gibbs excess molar free energy, 
$\Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal})$, versus liquid 
mole fraction chlorobenzene for mixtures with aniline at 393.15K.
Fig. 31e. Logarithm of the gamma ratio at 393.15K, \( \ln (\gamma_1 / \gamma_2) \), versus liquid mole fraction chlorobenzene (1) for mixtures with aniline (2).
Fig. 31f. Gibbs-Duhem function at 393.15K, $\frac{dP}{dx_1} \times \text{Liqvol}/RT = x_1 \frac{d(\ln g_1)}{dx_1} - x_2 \frac{d(\ln g_2)}{dx_2}$, versus liquid mole fraction chlorobenzene (1) for mixtures with aniline (2).
Fig. 32a. Excess pressure versus mole fraction methanol (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 293.15K represented by points.
Fig. 32b. Component fugacity coefficients at 293.15K versus mole fraction methanol (1) for mixtures with aniline (2). Gamma inf-dil. (1) = 2.2700, gamma inf-dil. (2) = 2.5362.
Fig. 32c. Vapor mole fractions of methanol (1) and aniline (2) versus liquid mole fraction methanol for mixtures with aniline at 293.15K, by coefficient model.
Fig. 32d. Change in Gibbs excess molar free energy, 
$\Delta g^{\text{excess}} = \Delta g - \Delta g^{\text{ideal}}$, versus liquid mole fraction methanol for mixtures with aniline at 293.15K.
Fig. 32e. Logarithm of the gamma ratio at 293.15K, $\ln(\gamma_1/\gamma_2)$, versus liquid mole fraction methanol (1) for mixtures with aniline (2).
Fig. 32f. Gibbs-Duhem function at 293.15K, \( \frac{dP}{d \xi_1} \cdot \text{Liqvol/RT} - \frac{x_1 \cdot d(\ln(g_1))}{dx_1} - \frac{x_2 \cdot d(\ln(g_2))}{dx_2} \), versus liquid mole fraction methanol (1) for mixtures with aniline (2).
Fig. 33a. Excess pressure versus mole fraction methanol (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 338.15K represented by points.

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\[ a = 1.3593, \; k_1 = -0.6139, \; b = 0.7415, \; p = -0.00153 \]
\[ c = 0.7396, \; k_2 = -0.6139, \; d = 0.9181, \; q = 0.00724 \]
\[ c = a + 3 \; (b - d), \; k_2 = k_1 = 1.5 \; (b + d - a - c) \]
\[ \text{integral test} = -0.0044 \]
Fig. 33b. Component fugacity coefficients at 338.15K versus mole fraction methanol (1) for mixtures with aniline (2), gamma \( \text{inf-dil.} \) (1) = 2.0959, gamma \( \text{inf-dil.} \) (2) = 2.5995.
Fig. 33c. Vapor mole fractions of methanol (1) and aniline (2) versus liquid mole fraction methanol for mixtures with aniline at 338.15K, by coefficient model.
Fig. 33d. Change in Gibbs excess molar free energy, 
\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \], versus liquid mole fraction methanol for mixtures with aniline at 338.15K.
Fig. 33e. Logarithm of the gamma ratio at 338.15K, \( \ln(\gamma_1/\gamma_2) \), versus liquid mole fraction methanol (1) for mixtures with aniline (2).
Fig. 33f. Gibbs-Duhem function at 338.15K, $dP/dx_1 \times \text{Liqvol/RT}$ $= x_1 \times d(\ln(g_1))/dx_1 - x_2 \times d(\ln(g_2))/dx_2$, versus liquid mole fraction methanol (1) for mixtures with aniline (2).
Fig. 34a. Excess pressure versus mole fraction methanol (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 385.15K represented by points.
Fig. 34b. Component fugacity coefficients at 385.15K versus mole fraction methanol (1) for mixtures with aniline (2). gamma inf-dil. (1) = 1.7391, gamma inf-dil. (2) = 2.2518.
Fig. 34c. Vapor mole fractions of methanol (1) and aniline (2) versus liquid mole fraction methanol for mixtures with aniline at 385.15K, by coefficient model.
Fig. 34d. Change in Gibbs excess molar free energy.  
\[ \Delta g^{(excess)} = \Delta g - \Delta g^{(ideal)} \], versus liquid mole fraction methanol for mixtures with aniline at 385.15K.
Fig. 34e. Logarithm of the gamma ratio at 385.15K, ln (gamma 1 / gamma 2), versus liquid mole fraction methanol (1) for mixtures with aniline (2).
Fig. 34f. Gibbs-Duhem function at 385.15K, $\frac{dP}{dx_1} \times \text{Liqvol/RT}$ = $x_1 \frac{d(ln(g_1))}{dx_1} - x_2 \frac{d(ln(g_2))}{dx_2}$, versus liquid mole fraction methanol (1) for mixtures with aniline (2).
Fig. 35a. Excess pressure versus mole fraction 1-pentene (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 277.35K represented by points.
Fig. 35b. Component fugacity coefficients at 277.35K versus mole fraction 1-pentene (1) for mixtures with aniline (2). gamma inf-dil. (1) = 13.800 gamma inf-dil. (2) = 18.468.
Fig. 35c. Vapor mole fractions of 1-pentene (1) and aniline (2) versus liquid mole fraction 1-pentene for mixtures with aniline at 277.35K, by coefficient model.
Fig. 35d. Change in Gibbs excess molar free energy.
\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \]
versus liquid mole fraction 1-pentene for mixtures with aniline at 277.35K.
Fig. 35e. Logarithm of the gamma ratio at 277.35K, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction 1-pentene (1) for mixtures with aniline (2).
Fig. 35f. Gibbs-Duhem function at 277.35K, $\frac{dP}{dx_1} \times \text{Liqvol}/RT = x_1 \frac{d(\ln(g_1))}{dx_1} - x_2 \frac{d(\ln(g_2))}{dx_2}$, versus liquid mole fraction i-pentene (1) for mixtures with aniline (2).
Fig. 36a. Excess pressure versus mole fraction 1-pentene (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 313.15K represented by points.
Fig. 36b. Component fugacity coefficients at 313.15K versus mole fraction 1-pentene (1) for mixtures with aniline (2), gamma inf-dil. (1) = 8.5479 gamma inf-dil. (2) = 11.953.
Fig. 36c. Vapor mole fractions of 1-pentene (1) and aniline (2) versus liquid mole fraction 1-pentene for mixtures with aniline at 313.15K, by coefficient model.
Fig. 36d. Change in Gibbs excess molar free energy,
\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \], versus liquid mole fraction 1-pentene for mixtures with aniline at 313.15K.
Fig. 36e. Logarithm of the gamma ratio at 313.15K, $\ln(\text{gamma 1} / \text{gamma 2})$, versus liquid mole fraction of 1-pentene (1) for mixtures with aniline (2).
Fig. 36f. Gibbs-Duhem function at 313.15K, $\frac{dP}{dx_1} \cdot \text{Liqvol}/RT$ = $x_1 \cdot \frac{d(ln(g_1))}{dx_1} - x_2 \cdot \frac{d(ln(g_2))}{dx_2}$, versus liquid mole fraction 1-pentene (1) for mixtures with aniline (2).
Fig. 37a. Excess pressure versus mole fraction 1-pentene (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 350.81K represented by points.
Fig. 37b. Component fugacity coefficients at 350.81K versus mole fraction 1-pentene (1) for mixtures with aniline (2). gamma inf-dil. (1) = 5.9630 gamma inf-dil. (2) = 7.8065.
Fig. 37c. Vapor mole fractions of 1-pentene (1) and aniline (2) versus liquid mole fraction 1-pentene for mixtures with aniline at 350.81K, by coefficient model.
Fig. 37d. Change in Gibbs excess molar free energy. 
Delta g(excess) = Delta g - Delta g(ideal), versus liquid mole fraction 1-pentene for mixtures with aniline at 350.81K.
Fig. 37e. Logarithm of the gamma ratio at 350.81K, \( \ln \left( \frac{\gamma_1}{\gamma_2} \right) \), versus liquid mole fraction of 1-pentene (1) for mixtures with aniline (2).
Fig. 37f. Gibbs-Duhem function at 350.81K, \( \frac{dP}{dx_1 \cdot \text{Liq vol}/RT} = x_1 \cdot \frac{d\ln(g_1)}{dx_1} - x_2 \cdot \frac{d\ln(g_2)}{dx_2} \), versus liquid mole fraction 1-pentene (1) for mixtures with aniline (2).
P sat acetone is 56.60 kPa

P sat chlorobenzene is 3.563 kPa

Data collected by Maher and Smith Curve by modified four suffix Margules

\[
a = 0.4035, \quad k_1 = -0.1387, \quad b = 0.4373, \quad p = -0.00149 \\
c = 0.5235, \quad k_2 = -0.1387, \quad d = 0.3973, \quad q = 0.00335 \\
c = a + 3(b - d), \quad k_2 = k_1 = 1.5(b + d - a - c) \\
\text{integral test} = -0.0024
\]

Fig. 38a. Excess pressure versus mole fraction acetone (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 313.15K represented by points.
Fig. 38b. Component fugacity coefficients at 313.15K versus mole fraction acetone (1) for mixtures with chlorobenzene (2).

\[ \gamma_{\text{inf-dil}} \text{(1)} = 1.5461 \]

\[ \gamma_{\text{inf-dil}} \text{(2)} = 1.4927 \]
Fig. 38c. Vapor mole fractions of acetone (1) and chlorobenzene (2) versus liquid mole fraction acetone for mixtures with chlorobenzene at 313.15K, by coefficient model.
Fig. 38d. Change in Gibbs excess molar free energy. 
\( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction acetone for mixtures with chlorobenzene at 313.15K.
Fig. 38e. Logarithm of the gamma ratio at 313.15K, $\ln (\gamma_1 / \gamma_2)$, versus liquid mole fraction acetone (1) for mixtures with chlorobenzene (2).
Fig. 38f. Gibbs-Duhem function at 313.15K, $dP/dx_1 \times \text{Liqvol/RT} = x_1 \times d(\ln(g_1))/dx_1 - x_2 \times d(\ln(g_2))/dx_2$, versus liquid mole fraction acetone (1) for mixtures with chlorobenzene (2).
Fig. 39a. Excess pressure versus mole fraction acetone (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 353.00K represented by points.
Fig. 39b. Component fugacity coefficients at 353.00K versus mole fraction acetone (1) for mixtures with chlorobenzene (2), gamma inf-dil. (1) = 1.4040 gamma inf-dil. (2) = 1.3596.
Fig. 39c. Vapor mole fractions of acetone (1) and chlorobenzene (2) versus liquid mole fraction acetone for mixtures with chlorobenzene at 353.00K, by coefficient model.
Fig. 39d. Change in Gibbs excess molar free energy, $\Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal})$, versus liquid mole fraction acetone for mixtures with chlorobenzene at 353.00K.
Fig. 39e. Logarithm of the gamma ratio at 353.00K, \( \ln(\text{gamma 1} / \text{gamma 2}) \), versus liquid mole fraction acetone (1) for mixtures with chlorobenzene (2).
Fig. 39f. Gibbs-Duhem function at 353.00K, \( \frac{dP}{dx_1*\text{Liqvol}/RT} = x_1 \frac{d(\ln(g_1))}{dx_1} - x_2 \frac{d(\ln(g_2))}{dx_2} \), versus liquid mole fraction acetone (1) for mixtures with chlorobenzene (2).
Fig. 40a. Excess pressure versus mole fraction acetone (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 386.66K represented by points.
Fig. 40b. Component fugacity coefficients at 386.66K versus mole fraction acetone (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 1.3176 gamma inf-dil. (2) = 1.2649.
Fig. 40c. Vapor mole fractions of acetone (1) and chlorobenzene (2) versus liquid mole fraction acetone for mixtures with chlorobenzene at 386.66K, by coefficient model.
Fig. 40d. Change in Gibbs excess molar free energy, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction acetone for mixtures with chlorobenzene at 386.66K.
Fig. 40e. Logarithm of the gamma ratio at 386.66K, \( \ln(\gamma_1/\gamma_2) \), versus liquid mole fraction acetone (1) for mixtures with chlorobenzene (2).
Fig. 40f. Gibbs-Duhem function at 386.66K, $dP/dx_1\times Liqvol/RT = x_1 \times d(ln(g_1))/dx_1 - x_2 \times d(ln(g_2))/dx_2$, versus liquid mole fraction acetone (1) for mixtures with chlorobenzene (2).
Fig. 41a. Excess pressure versus mole fraction ethyl acetate (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 313.15K represented by points.
Fig. 41b. Component fugacity coefficients at 313.15K versus mole fraction ethyl acetate (1) for mixtures with chlorobenzene (2).

\[ \gamma_{\text{inf-dil.}} (1) = 1.0694 \] \[ \gamma_{\text{inf-dil.}} (2) = 1.0626. \]
Fig. 41c. Vapor mole fractions of ethyl acetate (1) and chlorobenzene (2) versus liquid mole fraction ethyl acetate for mixtures with chlorobenzene at 313.15K, by coefficient model.
Fig. 41d. Change in Gibbs excess molar free energy at 313.15K,
\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \], versus liquid
mole fraction ethyl acetate for mixtures with chlorobenzene.
Fig. 41e. Logarithm of the gamma ratio at 313.15K. 
\[ \ln \left( \frac{\gamma_1}{\gamma_2} \right) \] versus liquid mole fraction ethyl acetate (1) for mixtures with chlorobenzene (2).
Fig. 41f. Gibbs-Duhem function at 313.15K, $dP/dx_1 = x_1^* d\ln(g_1)/dx_1 - x_2^* d\ln(g_2)/dx_2$, versus liquid mole fraction ethyl acetate (1) for mixtures with chlorobenzene (2).
Fig. 42a. Excess pressure versus mole fraction methanol (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 338.15K represented by points.
Fig. 42b. Component fugacity coefficients at 338.15K versus mole fraction methanol (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 10.908 gamma inf-dil. (2) = 8.6645.
Fig. 42c. Vapor mole fractions of methanol (1) and chlorobenzene (2) versus liquid mole fraction methanol for mixtures with chlorobenzene at 338.15K, by coefficient model.
Fig. 42d. Change in Gibbs excess molar free energy at 338.15K, 
$\Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal})$, versus liquid 
mole fraction methanol for mixtures with chlorobenzene.
Fig. 42e. Logarithm of the gamma ratio at 338.15K, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction methanol (1) for mixtures with chlorobenzene (2).
Fig. 42f. Gibbs-Duhem function at 338.15K, \( \frac{dP}{dx_1}\cdot \text{Liqvol}/RT = x_1\frac{d(\ln g_1)}{dx_1} - x_2\frac{d(\ln g_2)}{dx_2} \), versus liquid mole fraction methanol (1) for mixtures with chlorobenzene (2).
Data collected by Maher and Smith
Curve by modified four suffix Margules

\[ a = 2.3379, \quad k_1 = -1.5800, \quad b = 1.7728, \quad p = -0.00178 \]
\[ c = 2.2803, \quad k_2 = -1.5800, \quad d = 1.7920, \quad q = 0.10219 \]
\[ c = a + 3 \cdot (b - d), \quad k_2 = k_1 = 1.5 \cdot (b + d - a - c) \]
\[ \text{integral test} = -0.0520 \]

Fig. 43a. Excess pressure versus mole fraction methanol (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 385.15K represented by points.
Fig. 43b. Component fugacity coefficients at 385.15K versus mole fraction methanol (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 5.8768 gamma inf-dil. (2) = 6.6470.
Fig. 43c. Vapor mole fractions of methanol (1) and chlorobenzene (2) versus liquid mole fraction methanol for mixtures with chlorobenzene at 385.15K, by coefficient model.
Fig. 43d. Change in Gibbs excess molar free energy at 385.15K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction methanol for mixtures with chlorobenzene.
Fig. 43e. Logarithm of the gamma ratio at 385.15K, \( \ln(\text{gamma 1} / \text{gamma 2}) \), versus liquid mole fraction methanol (1) for mixtures with chlorobenzene (2).
Fig. 43f. Gibbs-Duhem function at 385.15K, $dP/dx_1 = x_1 \cdot d(\ln(g_1))/dx_1 - x_2 \cdot d(\ln(g_2))/dx_2$, versus liquid mole fraction methanol (1) for mixtures with chlorobenzene (2).
Fig. 44a. Excess pressure versus mole fraction 1-pentene (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 280.00K represented by points.
Fig. 44b. Component fugacity coefficients at 280.00K versus mole fraction 1-pentene (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 1.7468 gamma inf-dil. (2) = 1.9172.
Fig. 44c. Vapor mole fractions of 1-pentene (1) and chlorobenzene (2) versus liquid mole fraction 1-pentene for mixtures with chlorobenzene at 280.00K, by coefficient model.
Fig. 44d. Change in Gibbs excess molar free energy at 280.00K, 
$\Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal})$, versus liquid 
mole fraction 1-pentene for mixtures with chlorobenzene.
Fig. 44e. Logarithm of the gamma ratio at 280.00K, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction 1-pentene (1) for mixtures with chlorobenzene (2).
Fig. 44f. Gibbs-Duhem function at 280.00K, \( \frac{dP}{dx} \cdot \text{Liqvol}/RT \)
\[ = x_1 \cdot \frac{d \ln(g_1)}{dx_1} - x_2 \cdot \frac{d \ln(g_2)}{dx_2} \]
versus liquid mole fraction 1-pentene (1) for mixtures with chlorobenzene (2).
Fig. 45a. Excess pressure versus mole fraction 1-pentene (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 320.00K represented by points.
Fig. 45b. Component fugacity coefficients at 320.00K versus mole fraction 1-pentene (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 1.5433 gamma inf-dil. (2) = 1.6077.
Fig. 45c. Vapor mole fractions of 1-pentene (1) and chlorobenzene (2) versus liquid mole fraction 1-pentene for mixtures with chlorobenzene at 320.00K, by coefficient model.
Fig. 45d. Change in Gibbs excess molar free energy at 320.00K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction 1-pentene for mixtures with chlorobenzene.
Fig. 45e. Logarithm of the gamma ratio at 320.00K, \( \ln (\text{gamma } 1 / \text{gamma } 2) \), versus liquid mole fraction 1-pentene (1) for mixtures with chlorobenzene (2).
Fig. 45f. Gibbs-Duhem function at 320.00K, $dP/dx1*\text{Liqvol/RT}$

$= x1*d(ln(g1))/dx1 - x2*d(ln(g2))/dx2$, versus liquid mole fraction 1-pentene (1) for mixtures with chlorobenzene (2).
Fig. 46a. Excess pressure versus mole fraction 1-pentene (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 360.00K represented by points.
Fig. 46b. Component fugacity coefficients at 360.00K versus mole fraction 1-penten (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 1.3955 gamma inf-dil. (2) = 1.3796.
Fig. 46c. Vapor mole fractions of 1-pentene (1) and chlorobenzene (2) versus liquid mole fraction 1-pentene for mixtures with chlorobenzene at 360.00K, by coefficient model.
Fig. 46d. Change in Gibbs excess molar free energy at 360.00K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction 1-pentene for mixtures with chlorobenzene.
Fig. 46e. Logarithm of the gamma ratio at 360.00K, \( \ln (\gamma_1 / \gamma_2) \), versus liquid mole fraction 1-pentene (1) for mixtures with chlorobenzene (2).
Fig. 46f. Gibbs-Duhem function at 360.00K, $dP/dx_1 \cdot \text{Liqvol}/RT = x_1 \cdot d(\ln(g_1))/dx_1 − x_2 \cdot d(\ln(g_2))/dx_2$, versus liquid mole fraction 1-pentene (1) for mixtures with chlorobenzene (2).
Data collected by Maher and Smith
Curve by modified four suffix Margules

\[ a = 0.0888, \ k_1 = -0.6513, \ b = -0.2185, \ p = -0.00020 \]
\[ c = -0.4465, \ k_2 = -0.6513, \ d = 0.2266, \ q = 0.00028 \]
\[ c = a + 3(b - d), \ k_2 = k_1 = 1.5(b + d - a - c) \]
\[ \text{integral test} = -0.0002 \]

Fig. 47a. Excess pressure versus mole fraction acetonitrile (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 293.15K represented by points.
Fig. 47b. Component fugacity coefficients at 293.15K versus mole fraction acetonitrile (1) for mixtures with aniline (2). gamma inf-dil. (1) = 0.8036 gamma inf-dil. (2) = 1.2547.
Fig. 47c. Vapor mole fractions of acetonitrile (1) and aniline (2) versus liquid mole fraction acetonitrile for mixtures with aniline at 293.15K, by coefficient model.
Fig. 47d. Change in Gibbs excess molar free energy, 

\[ \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \]

versus liquid mole fraction acetonitrile for mixtures with aniline at 293.15K.
Fig. 47e. Logarithm of the gamma ratio at 293.15K, \( \ln(\gamma_1/\gamma_2) \), versus liquid mole fraction acetonitrile (1) for mixtures with aniline (2).
Fig. 47f. Gibbs-Duhem function at 293.15K, $dP/dx_1 \times \text{Liqvol}/RT = x_1 \times d(\ln(g_1))/dx_1 - x_2 \times d(\ln(g_2))/dx_2$, versus liquid mole fraction acetonitrile (1) for mixtures with aniline (2).
P sat acetonitrile is 69.59 kPa

P sat aniline is 1.42 kPa

Data collected by Maher and Smith
Curve by modified four suffix Margules

\[ a = 0.3939, k_1 = -0.0850, b = -0.1718, p = -0.00134 \]
\[ c = -0.4121, k_2 = -0.0850, d = 0.0969, q = 0.00190 \]
\[ c = a + 3(b - d), k_2 = k_1 = 1.5(b + d - a - c) \]
integral test = -0.0016

Fig. 48a. Excess pressure versus mole fraction acetonitrile (1) for mixtures with aniline (2) from theoretical activity model and actual reduced data at 343.15K represented by points.
Fig. 48b. Component fugacity coefficients at 343.15K versus mole fraction acetonitrile (1) for mixtures with aniline (2), gamma inf-dil. (1) = 0.8411 gamma inf-dil. (2) = 1.1038.
Fig. 48c. Vapor mole fractions of acetonitrile (1) and aniline (2) versus liquid mole fraction acetonitrile for mixtures with aniline at 343.15K, by coefficient model.
Fig. 48d. Change in Gibbs excess molar free energy, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction acetonitrile for mixtures with aniline at 343.15K.
Fig. 48e. Logarithm of the gamma ratio at 343.15K, \( \ln(\text{gamma } 1 / \text{gamma } 2) \), versus liquid mole fraction acetonitrile (1) for mixtures with aniline (2).
Fig. 48f. Gibbs-Duhem function at 343.15K, \( \frac{dP}{dx1} \cdot Liqvol/RT = x1 \cdot d(ln(g1))/dx1 - x2 \cdot d(ln(g2))/dx2 \), versus liquid mole fraction acetonitrile (1) for mixtures with aniline (2).
Fig. 49a. Excess pressure versus mole fraction acetonitrile (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 293.15K represented by points.
Fig. 49b. Component fugacity coefficients at 293.15K versus mole fraction acetonitrile (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 3.6106, gamma inf-dil. (2) = 4.2457.
Fig. 49c. Vapor mole fractions of acetonitrile (1) and chlorobenzene (2) versus liquid mole fraction acetonitrile for mixtures with chlorobenzene at 293.15K, by coefficient model.
Fig. 49d. Change in Gibbs excess molar free energy at 293.15K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction acetonitrile for mixtures with chlorobenzene.
Fig. 49e. Logarithm of the gamma ratio at 293.15K, 
ln (gamma 1 / gamma 2), versus liquid mole fraction 
acetonitrile (1) for mixtures with chlorobenzene (2).
Fig. 49f. Gibbs-Duhem function at 293.15K, \( \frac{dP}{dx_1 \cdot \text{Liqvol}/RT} = x_1 \cdot \frac{d(\ln g_1)}{dx_1} - x_2 \cdot \frac{d(\ln g_2)}{dx_2} \), versus liquid mole fraction acetonitrile (1) for mixtures with chlorobenzene (2).
**Fig. 50a.** Excess pressure versus mole fraction acetonitrile (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 343.15K represented by points.
Fig. 50b. Component fugacity coefficients at 343.15K versus mole fraction acetonitrile (1) for mixtures with chlorobenzene (2).
gamma inf-dil. (1) = 3.0013, gamma inf-dil. (2) = 3.4619.
Fig. 50c. Vapor mole fractions of acetonitrile (1) and chlorobenzene (2) versus liquid mole fraction acetonitrile for mixtures with chlorobenzene at 343.15K, by coefficient model.
Fig. 50d. Change in Gibbs excess molar free energy at 343.15K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction acetonitrile for mixtures with chlorobenzene.
Fig. 50e. Logarithm of the gamma ratio at 343.15K, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction acetonitrile (1) for mixtures with chlorobenzene (2).
Fig. 50f. Gibbs-Duhem function at 343.15K, \( \frac{dP}{dx_i} \times \text{Liqvol}/RT = x_1 \frac{d(\ln(g_1))}{dx_1} - x_2 \frac{d(\ln(g_2))}{dx_2} \), versus liquid mole fraction acetonitrile (1) for mixtures with chlorobenzene (2).
Fig. 51a. Excess pressure versus mole fraction acetonitrile (1) for mixtures with chlorobenzene (2) from theoretical activity model and actual reduced data at 393.15K represented by points.
Fig. 51b. Component fugacity coefficients at 393.15K versus mole fraction acetonitrile (1) for mixtures with chlorobenzene (2). gamma inf-dil. (1) = 2.4749, gamma inf-dil. (2) = 2.8392.
Fig. 51c. Vapor mole fractions of acetonitrile (1) and chlorobenzene (2) versus liquid mole fraction acetonitrile for mixtures with chlorobenzene at 393.15K, by coefficient model.
Fig. 51d. Change in Gibbs excess molar free energy at 393.15K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction acetonitrile for mixtures with chlorobenzene.
Fig. 51e. Logarithm of the gamma ratio at 393.15K, ln (gamma 1 / gamma 2), versus liquid mole fraction acetonitrile (1) for mixtures with chlorobenzene (2).
Fig. 51f. Gibbs-Duhem function at 393.15K, \( \frac{dP}{d\chi_1} \cdot \text{Liqvol}/RT \)
\[ = \chi_1 \frac{d}{d\chi_1} \ln(g_1) - \chi_2 \frac{d}{d\chi_2} \ln(g_2) \]
versus liquid mole fraction acetonitrile (1) for mixtures with chlorobenzene (2).
Fig. 52a. Excess pressure versus mole fraction benzene (1) for mixtures with acetonitrile (2) from theoretical activity model and actual reduced data at 298.16K represented by points.
Fig. 52b. Component fugacity coefficients at 298.16K versus mole fraction benzene (1) for mixtures with acetonitrile (2). gamma_{inf-dil.} (1) = 3.2624, gamma_{inf-dil.} (2) = 3.2062.
Fig. 52c. Vapor mole fractions of benzene (1) and acetonitrile (2) versus liquid mole fraction benzene for mixtures with acetonitrile at 298.16K, by coefficient model.
Fig. 52d. Change in Gibbs excess molar free energy at 298.16K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction benzene for mixtures with acetonitrile.
Fig. 52e. Logarithm of the gamma ratio at 298.16K, ln (gamma 1 / gamma 2), versus liquid mole fraction benzene (1) for mixtures with acetonitrile (2).
Fig. 52f. Gibbs-Duhem function at 298.16K, \( \frac{dP}{dx_1} \times \text{LiqVol}/RT \) = \( x_1 \times d(\ln(\text{g}_1))/dx_1 - x_2 \times d(\ln(\text{g}_2))/dx_2 \) versus liquid mole fraction benzene (1) for mixtures with acetonitrile (2). Data indicate an azeotrope at 0.54 mole fraction benzene.
Fig. 53a. Excess pressure versus mole fraction benzene (1) for mixtures with acetonitrile (2) from theoretical activity model and actual reduced data at 348.03K represented by points.
Fig. 53b. Component fugacity coefficients at 348.03K versus mole fraction benzene (1) for mixtures with acetonitrile (2). gamma inf-dil. (1) = 2.7772, gamma inf-dil. (2) = 2.8600.
Fig. 53c. Vapor mole fractions of benzene (1) and acetonitrile (2) versus liquid mole fraction benzene for mixtures with acetonitrile at 348.03K, by coefficient model.
Fig. 53d. Change in Gibbs excess molar free energy at 348.03K, \( \Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal}) \), versus liquid mole fraction benzene for mixtures with acetonitrile.
Fig. 53e. Logarithm of the gamma ratio at 348.03K, \( \ln(\text{gamma}_1 / \text{gamma}_2) \), versus liquid mole fraction benzene (1) for mixtures with acetonitrile (2).
Fig. 53f. Gibbs-Duhem function at 348.03K, $\frac{dP}{dx1} \times \text{Liqvol/RT} = x1 \times \frac{d(\ln g1)}{dx1} - x2 \times \frac{d(\ln g2)}{dx2}$, versus liquid mole fraction benzene (1) for mixtures with acetonitrile (2). Data indicate an azeotrope at 0.54 mole fraction benzene.
Fig. 54a. Excess pressure versus mole fraction benzene (1) for mixtures with acetonitrile (2) from theoretical activity model and actual reduced data at 397.86K represented by points.
Fig. 54b. Component fugacity coefficients at 397.86K versus mole fraction benzene (1) for mixtures with acetonitrile (2). gamma inf-dil. (1) = 2.4449, gamma inf-dil. (2) = 2.5546.
Fig. 54c. Vapor mole fractions of benzene (1) and acetonitrile (2) versus liquid mole fraction benzene for mixtures with acetonitrile at 397.86K, by coefficient model.
Fig. 54d. Change in Gibbs excess molar free energy at 397.86K, $\Delta g(\text{excess}) = \Delta g - \Delta g(\text{ideal})$, versus liquid mole fraction benzene for mixtures with acetonitrile.
Fig. 54e. Logarithm of the gamma ratio at 397.86K, \( \ln(\gamma_1 / \gamma_2) \), versus liquid mole fraction benzene (1) for mixtures with acetonitrile (2).
Fig. 54f. Gibbs-Duhem function at 397.86K, $dP/dxi \cdot \text{Liqvol}/RT = x_1 \cdot d(\ln(g_1))/dx_1 - x_2 \cdot d(\ln(g_2))/dx_2$, versus liquid mole fraction benzene ($x_i$) for mixtures with acetonitrile ($x_i$). Data indicate an azeotrope at 0.51 mole fraction benzene.
Figure 55. Coal Liquefaction Fractional-Cut Pure Components Boiling Point Distribution Superimposed on TBP Curve Versus Amount Distilled.
Figure 56. Projection of Trace Components Continuous Activity Coefficient Distribution in Model Continuum Liquid.
VI. DISCUSSION AND CONCLUSIONS

i.) Experimental Purpose and Design;

The purpose of this study was to present a general method for the determination of the infinite-dilution behavior of individual molecular species in a representative pure component environment characteristic of coal liquefaction processes. In this work the coal derived compound chosen was phenanthrene as the "central" specie to be investigated as a possible distillation diluent. Fortuitously, the generality of the method also implies that the other component fluorene as well as all mixtures of fluorene and phenanthrene can be labelled as the central component. The behavior of other components of coal derived liquids at trace concentrations, such as those existing in the liquefaction product, in phenanthrene would represent only one central specie in binary thermodynamic VLE with each of the other many, very dilute species.

Since phenanthrene has a low melting point, a high boiling point, and a low vapor pressure with respect to viscosity for a coal liquefaction component, it has the proper thermal-properties to be investigated. It is certainly one of the most abundant of coal components. The behavior of the coal liquefaction derived compound fluorene was investigated at six mole fractions in mixture with
phenanthrene. Enough data were collected for consistency correlation by a four-suffix Margules activity coefficient model. The data at fluorene mole fraction of 0.90 were not used in the total pressure correlations since DPI diaphragm problems were suspected in that experimental run, see Appendix II.

The fact that the liquid mole fraction was fixed at or very near the total mole fraction by the charging technique used, allowed the experiments to be conducted under the constraints of fixed temperature and fixed liquid mole fraction. These constraints fixed all other intensive and mixture extensive variables; the system pressure, excess volume of mixing and the vapor mole fractions.

ii.) Research Accomplished in this Project;

A nonideality liquid activity coefficient model is derived rigorously from the Gibbs and the Gibbs-Duhem equations for two-component, two-phase systems. Gibbs' Phase Rule gives the number of degrees of freedom as 2 for a two-component system at vapor-liquid equilibrium. Fixing both the mixture temperature and the two-component liquid mole fraction invariably sets the system total pressure. This fortuitous property allows for an almost exact solution
to the differential relation, equation 1, for thermodynamic consistency. The concise fugacity coefficient relations that form this solution are modifications of those given by Margules, and correlate well total pressure, binary data from this work as well as from other researchers.

This thesis presents a new, generalized approach to obtaining infinite-dilution fugacity coefficients. An attempt is made to better define thermodynamic consistency and working functions, free energy etc., for two-component mixtures at vapor-liquid coexistence with possible generalization to multicomponent vapor-liquid equilibrium at low to moderate total pressures. This approach also produces activity coefficients for each of the two components across the entire mole fraction range for binary VLE as well as at both infinite-dilution axes. The model is self-consistent thermodynamically and generates functions for total and excess pressure, excess free energy, and excess entropy for binary system VLE data collected by the total pressure method. It can be used as a thermodynamically exact model for binary, liquid miscible VLE systems including polar mixtures.

iii.) Problem Solution;
Because $x_1 + x_2 = 1$, $\gamma_1$ and $\gamma_2$ are not independent in the expression for pressure as;

$$\Pi = P_1^S x_1 \gamma_1 + P_2^S x_2 \gamma_2,$$  \hspace{1cm} (2)

at fixed temperature and fixed mole fraction. Since $\gamma_1$ and $\gamma_2$ are interrelated through total pressure, the problem is to match $\gamma_1$ and $\gamma_2$ as nonideality expressions across the mole fraction range.

A solution to the differential equation representing two-component thermodynamic consistency was sought by correlating total pressure as a weighted sum of $\gamma_1$ and $\gamma_2$, so that;

$$\gamma_1 = e^{a x_1 x_2^2} e^{k x_1 x_2^3} e^{b x_2^3} e^{p x_2},$$  \hspace{1cm} (14a)

and and

$$\gamma_2 = e^{c x_1 x_2^2} e^{k x_1 x_2^3} e^{d x_1^3} e^{q x_1}.$$  \hspace{1cm} (14b)

This model appears to be applicable if the two-component VLE data are collected in the proper experimental fashion; being a well degassed, closed system with only two components and pressure measured above a static vapor-liquid interface, i.e., membrane to reference gas or directly by a pressure transducer.
Since $x_1$ and $x_2$ are always positive the signs of $a$, $k$, $b$, and $p$ and $c$, $k$, $d$, and $q$ will respectively determine whether $\gamma_1$ and $\gamma_2$ are greater or less than one. All that can really be said about the form of the nonideality expressions is that the $b$ and $p$ and the $d$ and $q$ term exponentials are increasingly significant over the $a$ and $k$ and the $c$ and $k$ term exponentials respectively as the mole fraction distribution approaches dilute to infinitely dilute solutions in component 1 and component 2 respectively. Therefore $b$ and $p$ and $d$ and $q$ are considered the infinite-dilution parameters, and $\gamma_1^\infty = e^{b+p}$ for infinitely dilute component 1 in component 2 and $\gamma_2^\infty = e^{d+q}$ for infinitely dilute component 2 in component 1. The fluorene/phenanthrene system was fit with $p, q = 0$ because of the low total pressure measurements involved. Since this was not the case for the other systems fitted, $p$ and $q$ were not set equal to zero but were set by equations 13.

iv.) Mathematical Aspects;

Equation 1 will have values between $p$ and $q$, as given by equations 13, across the mole fraction range and will equal zero at the predicted mole fraction of the azeotrope if such exist in the system being fitted for thermodynamic consistency. This linear interpolation of the value of
equation 1 is admittedly an approximation between \( x_1 = 0 \) and \( x_1 = 1 \) although the end point values \( p \) and \( q \) are as determinable as pure component data and \( \frac{d\Pi}{dx_1} \) values at \( x_1 = 0 \) and \( x_1 = 1 \) will allow.

Excess volumes which have been measured under one atmosphere (not a true two-component system and certainly not a total pressure apparatus) are usually rather small compared to liquid mixture molar volumes. Although \( \frac{d\Pi}{dx_1} \) is nonlinear across the mole fraction range it is always monotonically increasing or decreasing and has its largest value at either \( x_1 = 0 \) or \( x_1 = 1 \). This fact and that of the relative smallness of excess volumes along with the very small magnitude of liquid compressibility, \( \sim \Pi/RT \), make the approximation solution to equation 1 suffice.

In is seen in the above activity coefficient expressions, equations 5, that the terms containing \( b \) and \( d \) are the primary contributors to the infinite-dilution activity coefficients of components 1 and 2 respectively. \( b \) and \( d \) are determined by complete system data fitting, being restricted in the parametric set \((a,b,d,k)\) by the expression

\[
x_1 \frac{d\ln\gamma_1}{dx_1} + x_2 \frac{d\ln\gamma_2}{dx_2} = 0.
\]

\( p \) and \( q \) are determined by pure component molar volumes, which are usually readily available data, and \( \frac{d\Pi}{dx_1} \) at both infinite-dilution axes, which are
determined by system data fitting with \( p, q = 0 \) and then used to calculate the \( p \) and \( q \) used in data refitting. Even though in comparison \( p \) and \( q \) are usually small with respect to \( b \) and \( d \) their addition into the polynomials of the individual coefficient expressions is thermodynamically justifiable. Their inclusion usually changes the infinite-dilution coefficients by only a few percent although cases are listed in the Table III where they affect those values by as much as ten percent or more.

Another advantage to the inclusion of the \( p \) and \( q \) terms in the expressions of the activity coefficients is a prediction of the approximate azeotropic mole fraction if the particular system correlated shows such behavior. At this approximate mole fraction value the differential consistency relation, equation 1, will equal zero as \( d \Pi / dx_1 |_{azeo} = 0 \). This is reflected on a plot of the function \( x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} \) as determined by the modified Margules activity coefficient model. Agreement between the azeotropic mole fraction predicted and the azeotropic mole fraction as evaluated by \( d \Pi / dx_1 \) equal to zero from \( d \Pi / dx_1 \) data will be an indication of the solution approximation.

The importance of the \( p \) and \( q \) terms in the modified model will increase with temperature. Vapor pressure rises
exponentially with temperature and, although by theory the two-component mixture will be less nonideal at higher temperatures, the difference in pure component vapor pressures will increase as will $d\Pi/dx_1$.

v.) Experimental and Correlational Results;

The data show some interesting VLE behavior in exhibiting both positive deviation from ideal pressure in the mid-mole to pure fluorene mole fraction range and also negative deviation from ideal pressure toward the fluorene infinite-dilution axis. Raoult's law determines ideal pressure as the weighted sum of the pure component saturation pressures at that temperature. Any deviations of the real system pressure from ideal is indication of nonideal component behavior in mixing theory. The four-suffix Margules (unmodified) was used to explain this peculiar behavior in the fluorene/phenanthrene binary system by correlating nonideality coefficients at not only infinite-dilution but everywhere else in the mole fraction range.

Activity coefficient parameters where calculated by a least squares computer fitting routine, Roper (1988), applied to total pressure versus mole fraction data at each of the ten degree interval temperatures investigated for
fluorene/phenanthrene system VLE. No effort was made to smooth nonideality fits between successive temperatures and, as can be seen in Figure 18, all coefficient parameters seem to relate well to temperature and imply that mixture nonideality decreases as temperature increases. This is in agreement with the thermodynamic theory that entropy increases with temperature.

It can be seen in Figure 18, the plot of the excess entropy versus mole fraction, that the single phase liquid in equilibrium with a vapor phase is the most thermodynamically stable state for any mixture of fluorene with phenanthrene in the temperature range investigated. These values of excess entropy were evaluated from the Heat of Vaporization curve, shown in Figure 2, and the molar excess Gibbs free energy change upon mixing, expressed as $\Delta g^E = RT \left[ x_1 \ln y_1 + x_2 \ln y_2 \right]$ and shown in Figure 17. Theoretical consistency is preserved in obtaining negative values of $\Delta s_{\text{mix}}$ as independent investigations were performed to determine the liquid phase miscibility of these two compounds.

Excess enthalpy was calculated from logarithm total pressure versus inverse temperature data and assumed to be constant in the reduced temperature range in which data were taken (approximately from 0.45 to 0.60 by the critical
point estimation method of Lydersen (1955)). Because the vapor space was small compared to the liquid volume, the liquid mole fraction was very near to being constant throughout this temperature range. Data for each mixture were taken at all temperatures investigated during each experimental run.

vi.) **Recommendations for Future Research:**

The derived fugacity coefficient model applies to all mixtures of two components at vapor-liquid equilibria. It yields infinite-dilution fugacity coefficients of any mixture as a matter of course, since the parameters for such are incorporated in the coefficient expressions. All four infinite-dilution parameters, two per coefficient expressed, are determined by fitting isothermal data across the entire mole fraction range, at least five precise intermediate mixture pressures as well as both pure component vapor pressures. This amount of information as well as liquid molar volume data should be collected on any new two-component systems investigated by the total pressure versus mole fraction method.

If the application of thermodynamic consistency in nonideality model data fitting is to be improved in the
future, the assumption of ideal vapor should be removed through the use of either a virial expansion or an appropriate equation of state. Also, the relation between the coefficient parameters and the partial molar volumes, $\bar{v}_1$ and $\bar{v}_2$, needs to be established. This will give rise, upon application of the differential equation to two-component VLE, a complete nonideality model containing parameters $a$, $b$, $c$, $d$, $k_1$, $k_2$, $p$, and $q$ with the restrictions of Margules substituted by liquid molar volume correlation. It is recommended that in the future liquid molar volume versus mole fraction data be collected from the equilibrium cell during measurement of binary VLE by the total pressure method. This data can be used to correlate data for thermodynamic consistency through partial molar volumes.

A sufficient number of binary infinite-dilution values should be determined to enable the development of an estimation procedure for infinite-dilution activity coefficients of trace components in arbitrary central polyaromatic molecules, figure 56. The amount of data required should be reduced materially by full utilization of group contribution methods such as UNIQUAC or UNIFAC, Reid and Prausnitz (1977).
VI. REFERENCES


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APPENDIX I

Error Analysis;

Assume ideal vapor so that at a particular temperature:
\[ \Pi = \gamma_1 x_1 P^s_1 + \gamma_2 x_2 P^s_2 \]
\( \gamma_1 \) and \( \gamma_2 \) are the fugacity coefficients in the liquid phase. Let \( \Delta x_1 \) and \( \Delta x_2 \) be the change in the mole fractions in the liquid of components 1 and 2 upon vaporization into vapor volume \( V^{vap} \) from liquid volume \( V^{liq} \), assuming that \( V^{liq} \) does not change appreciably. Let
\[ \Delta x_1 = \frac{\Delta \text{moles 1 in liquid}}{(\text{moles 1 + moles 2}) \text{ in liquid}} \]
and
\[ \Delta x_2 = \frac{\Delta \text{moles 2 in liquid}}{(\text{moles 1 + moles 2}) \text{ in liquid}} \]
where of course \( \Delta x_1 = -\Delta x_2 \).

Then \( \Delta x_1 - \Delta x_2 = 2\Delta x_1 \) and
\[ \Delta x_1 = \frac{1}{2} \frac{(\Delta \text{moles 1} - \Delta \text{mole 2}) \text{ in liquid}}{(\text{moles 1 + moles 2}) \text{ in liquid}} \]

For an ideal vapor,
\[ \Delta \text{moles 1 in liquid} = \text{moles 1 vaporized} = \]
\[ y_1 \frac{V^{vap}}{V_1^{vap}} = \frac{\gamma_1 x_1 P^s_1}{\Pi} \frac{V^{vap}}{V_1^{vap}} \]
and \( \Delta \text{moles 2 in liquid} = \text{moles 2 vaporized} = \)
\[ y_2 \frac{V^{vap}}{V_2^{vap}} = \frac{\gamma_2 x_2 P^s_2}{\Pi} \frac{V^{vap}}{V_2^{vap}} \]

Since \( (\text{moles 1 + moles 2}) \text{ in liquid} = V^{liq}/(x_1 V_1^{liq} + x_2 V_2^{liq}) \)
for \( V^E = 0 \) then
\[ \Delta x_1 = \frac{v_{\text{vap}} \left[ \frac{\gamma_1 x_1 P_1^s}{v_{\text{vap}}^1} - \frac{\gamma_2 x_2 P_2^s}{v_{\text{vap}}^2} \right]}{2\Pi N v_{\text{liq}}} \left[ x_{1v_{\text{liq}}} + x_{2v_{\text{liq}}} \right]. \]

\( v_{\text{liq}}, v_{1v_{\text{liq}}}, v_{2v_{\text{liq}}} \) and \( v_{\text{vap}} \) are pure component molar volumes.

At pressures below atmosphere the vapor can be considered ideal so that \( v_{\text{vap}}^1 \approx RT/P_1^s \) and \( v_{\text{vap}}^2 \approx RT/P_2^s \), then

\[ \Delta x_1 = \frac{v_{\text{vap}}}{2\Pi N v_{\text{liq}}} \left[ \gamma_1 x_1 (P_1^s)^2 - \gamma_2 x_2 (P_2^s)^2 \right] \left[ x_{1v_{\text{liq}}} + x_{2v_{\text{liq}}} \right]. \]

Let \( v_{\text{vap}}/v_{\text{liq}} \) be kept as small as possible. At \( T = 553.15, RT \approx 34.5(10)^6 \) and at \( T = 433.15, RT \approx 27.0(10)^6 \) cc mm-Hg/g-mole. Examples show for the phenanthrene(1)-fluorene(2) system:

At \( T = 553.15; \ a = c = 0.61, b = 0.49, d = 0.21, P_1^s = 225.50, P_2^s = 512.39, v_{1v_{\text{liq}}} = 189.8, v_{2v_{\text{liq}}} = 177.0; \)
\[ x_1 = 0.95, \Pi = 235.61, \Delta x_1 = 0.00043v_{\text{vap}}/v_{\text{liq}} \]
\[ x_1 = 0.50, \Pi = 383.35, \Delta x_1 = -0.00078v_{\text{vap}}/v_{\text{liq}} \]
\[ x_1 = 0.10, \Pi = 479.50, \Delta x_1 = -0.00126v_{\text{vap}}/v_{\text{liq}}. \]

At \( T = 433.15; \ a = c = 1.41, b = 0.91, d = 0.25, P_1^s = 4.87, P_2^s = 16.26, v_{1v_{\text{liq}}} = 173.8, v_{2v_{\text{liq}}} = 162.1; \)
\[ x_1 = 0.95, \Pi = 5.35, \Delta x_1 = 0.0000007v_{\text{vap}}/v_{\text{liq}} \]
\[ x_1 = 0.50, \Pi = 11.97, \Delta x_1 = -0.0000036v_{\text{vap}}/v_{\text{liq}} \]
\[ x_1 = 0.10, \Pi = 15.03, \Delta x_1 = -0.0000001v_{\text{vap}}/v_{\text{liq}}. \]
APPENDIX II
Least Squares Data Fitting Routine

C* DATA I/O AND MAIN PROGRAM
Implicit real*8 (A-H, P-Z)
Dimension c(5), x(8), y(8), Fvec(8), Wa(400), Iwa(6)
Dimension xl(41), x2(41), g1(41)
Dimension g2(41), dlnge(41), dlnge2(41)
Dimension dp(41), totpress(41), pnormal(8), pex(41)
Dimension vl(41), v2(41), vliq(41), extra(41)
Common x, y, ps1, ps2, p, q, R, TK
External Fcn
N = 6
Read(17,*) M, TC
Do i=1, M
   Read(17,*) x(i), y(i)
End do
ps1 = y(M)
ps2 = y(1)
Do i=1, M
   pid = x(i)*y(M) + (1.0D00 - x(i))*y(1)
   pnormal(i) = y(i) - pid
   Write(18, 103) x(i), pnormal(i)
End do
xl(1) = 0.0D00
x2(1) = 1.0D00
Do i=2, 41
   xl(i) = xl(i-1) + 0.025D00
   x2(i) = 1.0D00 - xl(i)
End do
xl(41) = 1.0D00
x2(41) = 0.0D00
TK = TC + 273.15D00
R = appropriate value
C(1) = 1.0D00
C(2) = 1.0D00
C(3) = 1.0D00
C(4) = 1.0D00
C(5) = 1.0D00
C(6) = 1.0D00
p = 0.0D00
q = 0.0D00
Lwa = 400
To1 = Dsqrt(Dpmpar(1))
Call Lmdl1(Fcn, M, N, c, Fvec, To1, Info, Iwa, Wa, Lwa)
Fnorm = Enorm(M, Fvec)
Write(6, 1000) Fnorm, Info, p, c(1), c(5), c(2),
* q, c(3), c(6), c(4)
Write(23, 102) c(1), c(5), c(2), p
Write(23, 102) c(3), c(6), c(4), q
glinf = exp(c(2) + p)
g2inf = exp(c(4) + q)
Write(6, 2000) glinf, g2inf
Write(6, 100)
Call Gammas (c,x1,x2,g1,g2,dlnl1,dlnl2)
Call Derpress (x1,x2,g1,g2,dlnl1,dlnl2,totpress,dp,pex)
Do i=1,41
  Write(29,101) x1(i),g1(i),g2(i),dlnl1(i),dlnl2(i)
  extra(i) = x1(i)*dlnl1(i) + x2(i)*dlnl2(i)
  Write(27,103) x1(i),extra(i)
  Write(31,103) x1(i),pex(i)
  Write(32,103) x1(i),totpress(i)
  Write(26,104) x1(i),x2(i),dp(i)
End do
Do i=1,41
  v1(i) = x1(i)*g1(i)*R*TK*dlnl1(i)
  v2(i) = x2(i)*g2(i)*R*TK*dlnl2(i)
  vliq(i) = (v1(i) + v2(i))/dp(i)
  Write(33,105) x1(i),v1(i),v2(i),vliq(i)
End do
Stop

2000 Format('inf-dil. gamma (1) = ',F8.5,
  *5X,'inf-dil. gamma (2) = ',F8.5)
100 Format(/)
1000 Format (5X,31H FINAL L2 NORM OF THE RESIDUALS,D15.7 //
  *5X,15H EXIT PARAMETER,16X,110 //
  *5X,27H FINAL APPROXIMATE SOLUTION // (2X,4(F15.8,2X)/))
101 Format(5(D22.16,2X))
102 Format(5(D22.16,2X))
103 Format(2(D22.16,2X))
104 Format(3(D22.16,2X))
105 Format(4(F15.4,2X))
END

C* LEAST SQUARES SUBROUTINE
Subroutine Fcn(M,N,c,Fvec,Iflag)
Implicit real*8 (A-H,P-Z)
Dimension c(6),x(8),y(8),Fvec(8),w(8),z(8),u(8),v(8)
Common x,y,ps1,ps2,p,q,R,TK
Do i=1,M
  c(3) = c(1) + 3.0D00*(c(2) - c(4))
  c(5) = -1.5D00*(c(1) - c(2) + c(3) - c(4))
  c(6) = c(5)
  u(i) = x(i)
  v(i) = 1.0D00 - x(i)
  w(i) = c(1)*u(i) + c(5)*u(i)*v(i) + c(2)*v(i)
  z(i) = c(3)*v(i) + c(6)*u(i)*v(i) + c(4)*u(i)
  w(i) = exp(w(i)*v(i)**2 + p*v(i))
  z(i) = exp(z(i)*u(i)**2 + q*u(i))
  Fvec(i) = y(i) - u(i)*w(i)*ps1 - v(i)*z(i)*ps2
End do
Return
END
C* PRESSURE AND PRESSURE DERIVATIVE SUBROUTINE

Subroutine Derpress (x1,x2,g1,g2,d1ng1,d1ng2,
&totpress,dp,pex)
Implicit real*8(A-H,P-Z)
Dimension x1(4l),x2(4l),g1(4l)
Dimension g2(4l),d1ng1(4l),d1ng2(4l)
Dimension dp(4l),totpress(4l),pex(4l),x(8),y(8)
Common x,y,ps1,ps2,p,q,R,TK
Do i=1,4l
  totpress(i) = x1(i)*g1(i)*ps1 + x2(i)*g2(i)*ps2
  pex(i) = totpress(i) - x1(i)*ps1 - x2(i)*ps2
  dp(i) = ps1*g1(i)*(1.0D00 + x1(i)*d1ng1(i))
  dp(i) = dp(i) + ps2*g2(i)*(-1.0D00 + x2(i)*d1ng2(i))
End do
Return
END

C* ACTIVITY COEFFICIENT CALCULATION SUBROUTINE

Subroutine Gammas (c,x1,x2,g1,g2,d1ng1,d1ng2)
Implicit real*8(A-H,P-Z)
Dimension c(6),extra(4l),d1ng1(4l),d1ng2(4l)
Dimension x1(4l),x2(4l),g1(4l),g2(4l),x(8),y(8)
Common x,y,ps1,ps2,p,q,R,TK
Do i=1,4l
  g1(i) = c(1)*x1(i) + c(5)*x1(i)*x2(i) + c(2)*x2(i)
  g2(i) = c(3)*x2(i) + c(6)*x1(i)*x2(i) + c(4)*x1(i)
  d1ng1(i) = c(1) - c(2) + c(5)*(x2(i) - x1(i))
  d1ng1(i) = d1ng1(i)*x2(i)**2 - 2.0D00*x2(i)**2*g1(i)
  d1ng1(i) = d1ng1(i) - p
  d1ng2(i) = c(4) - c(3) + c(6)*(x2(i) - x1(i))
  d1ng2(i) = d1ng2(i)*x1(i)**2 + 2.0D00*x1(i)**2*g2(i)
  d1ng2(i) = d1ng2(i) + q
  g1(i) = g1(i)*x2(i)**2 + p*x2(i)
  g2(i) = g2(i)*x1(i)**2 + q*x1(i)
  g1(i) = exp(g1(i))
  g2(i) = exp(g2(i))
End do
Return
END