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Prediction of Binary Azeotropes.

Harry Douglas Pruett III

*Louisiana State University and Agricultural & Mechanical College*

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in

The Department of Chemical Engineering

by

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ABSTRACT

The qualitative aspects of azeotropy are well known. The quantitative prediction of binary azeotropes has been the subject of study here. The state of the art was reviewed and a selected bibliography compiled. It was observed that existing methods were usually based on a homologous series approach; however, a fundamental objective of research efforts in this field has been prediction from pure component properties only. The regular solution model has made possible a priori vapor liquid equilibrium prediction for certain nonpolar-nonpolar mixtures within the limits of engineering accuracy. The emphasis of this investigation has been to extend regular solution theory so that systems involving nonpolar, polar, or hydrogen bonded molecules might be placed on a firm quantitative basis.

In general, two independent parameters are required to describe vapor liquid equilibrium data. These are frequently equivalent to infinite dilution coefficients. For the regular solution model, it is convenient to define the parameters as the symmetry between and inherent magnitude of infinite dilution coefficients. The symmetry factor is described by a volume ratio where the precise volume concept is to be selected. Here, the effective volume was taken as a function of molecular size, shape, and polarity. The relative magnitude for systems containing polar or hydrogen bonded molecules was assumed to be controlled by a polar solubility parameter which was evaluated through a homomorphic model. Associated liquids were successfully treated as simple polar compounds. It was found that a Flory-Huggins size correction was necessary to stabilize the apparent polar solubility parameter so that it could be modeled. For nonpolar
systems, the inherent magnitude can be adjusted through a geometric mean deviation factor; however, only one parameter is required for entirely nonpolar systems.

Certain combinations of the following were studied here: alcohols, ketones, esters, ethers, hydrocarbons, halogenated hydrocarbons, pyridine, and carbon disulfide. Conclusions are based on literature as well as experimental data. A total of 191 binary cases were used in the analysis. Eight new azeotropic points at atmospheric pressure were established: binaries involving heptane or 24 dimethyl pentane with 12 dichloroethane, dibromomethane, and ethyl iodide, also benzene or carbon tetrachloride with ethyl iodide.
CHAPTER I
INTRODUCTION

The term azeotrope (a = not, zeo = to boil, trope = with change) was first suggested by Wade and Merriman in 1911, "it is proposed, in order to avoid the cumbrous periphas' mixtures having a minimum (or maximum) boiling point' to designate them as azeotropic mixtures... An azeotropic mixture resembles a chemical individual in boiling without undergoing change of composition, but differs from it in losing this fixed characteristic as soon as the pressure is altered." In 191 , Lecat proved that azeotropy could not be regarded as a rare phenomenon. The early history of azeotropy has been reviewed by Swietoslawski and Malesinski. During and immediately following World War II, a host of azeotropic correlation and prediction techniques appeared. The state of the art is reviewed in chapter III. Eight new azeotropes are reported in chapter IV. A selected bibliography emphasizing binary azeotropic prediction is presented.

Quantitative azeotropic prediction is usually based on a homologous series approach. However, the goal of prediction from pure component properties only should always be kept in mind. Perhaps the greatest advance made thus far in this direction is the theory of regular solutions which is considered in chapter II. A method based in part on the regular solution model is presented in chapter V. Separate correlations are offered for nonpolar, simple polar, and alcohol-inert systems. The results obtained should encourage further research.
CHAPTER I REFERENCES


CHAPTER II

THEORY

A. DEFINITIONS

Raoult's law is often taken as the definition of an ideal solution. In reality, it is a necessary rather than a sufficient condition. Raoult's law will be used as the standard of ideality in this report. It can be expressed as follows:

\[ P_i = x_i p_i^* \]  

where \( p_i \) = partial pressure of component \( i \)
\( x_i \) = liquid phase mole fraction of \( i \)
\( p_i^* \) = vapor pressure of pure component \( i \)

for a real solution,

\[ y_i \pi = y_i x_i p_i^* \]  

where \( y_i \) = vapor phase mole fraction of \( i \)
\( \pi \) = total pressure
\( y_i \) = liquid phase activity coefficient of \( i \)
\( p_i^* \) = adjusted vapor pressure of \( i \)

The adjusted vapor pressure is defined in Appendix A. As the vapor phase approaches ideality, \( p_i^* \) and \( p_i^\# \) become essentially identical. It is assumed that vapor phase nonideality can be estimated with reasonable accuracy for low pressure systems so that the problem of vapor liquid equilibrium prediction is simply the calculation of liquid phase activity coefficients from pure component data only. In general, this will require a model of the excess free energy.

The concept of an excess function is fundamental to a description
of nonideal solutions. The excess value of a particular thermodynamic property is the difference between actual and ideal solution behavior of that property at the same conditions of temperature, pressure, and composition. For example, the excess free energy is defined by:

\[ G^E = (G_{Actual} - G_{Ideal}) \text{ at } T, p, x \]

The following symbols will be used to represent the indicated thermodynamic property: \( G \) = Gibbs free energy, \( H \) = enthalpy, \( S \) = entropy, \( U \) = energy, \( V \) = volume, \( A \) = Helmholtz free energy. Molal properties will be the corresponding lower case symbol: \( g, h, s, u, v, a \). The excess functions of different thermodynamic properties are simply related:

\[ g^E = h^E - T s^E \]  
\[ g^E = u^E + pv^E - T s^E \]  
\[ a^E = u^E - T s^E \]

Obviously, all excess functions are zero for an ideal solution. The relationship between excess free energy and liquid phase activity coefficient is usually expressed as follows:

\[ RT \ln \gamma_1 = \frac{\partial G^E}{\partial n_1} \]  

where \( R \) = gas constant
\( T \) = absolute temperature
\( n_1 \) = moles of component 1

Equation (6) can be restated in a more convenient form:

for a binary mixture,

\[ RT \ln \gamma_1 = g^E + (1-x_1) \frac{\partial a^E}{\partial x_1} \]  

Positive deviations from Raoult's law exist when \( \gamma_1 > 1 \); negative deviations, when \( \gamma_1 < 1 \). Ideal behavior corresponds to \( \gamma_1 = 1 \). In general,
the direction of departure from Raoult's law is known a priori, but the magnitude is not.

B. SOLUTION MODELS

There are two classical approaches to modeling nonideal solutions. The chemical approach seeks to explain all deviations by postulating the formation of new chemical species in the mixture. The physical approach describes all deviations to be the result of differences in intermolecular forces of mixture components. Each point of view has its own area of application and these areas overlap. However, the physical approach seems to be more useful when equilibrium prediction from pure component properties only is desired. Therefore, the plan of this investigation will be to apply a physically oriented model to those systems where it is most appropriate and extend such a model to more complex cases as is feasible.

A physical approach requires a picture of the liquid state and a knowledge of intermolecular phenomena. Unfortunately, there is no simple ideal liquid model comparable to the ideal gas or crystal. In simple solids the marked regularity of the arrangement of molecules leads to the assumption of perfect order. Each molecule is confined to a particular site and the only motion it can have is vibration about that point; moreover, the motion of each molecule can be regarded as independent of the motion of all other molecules. On the other hand, the theory of perfect gases is based on the assumptions of random motion and a complete absence of cohesive forces. The liquid state is neither completely ordered as in the solid nor completely random as in the gas. The molecules are sufficiently close together so that their motions must be influenced strongly by their interactions with each other but are not
sufficiently localized that simple vibration about a fixed point can be
assumed. "... (the liquid state is) like a central party in politics or
a moderate denomination in religion, it is less rigorously defined and
more difficult to understand than either of the extremes that flank
it." Often, liquids are described as gas-like or solid-like, that is,
as either a dense gas or a partially disordered crystal. Although the
latter has been more widely used in solution theory, these approaches
do not necessarily lead to different expressions.

1. Regular Solutions

Regular solution theory was developed simultaneously by Hilde­
brand,3,4 Scatchard,5 and Guggenheim6 around 1930. This approach dif­
fered from an ideal solution in that a nonvanishing, positive energy of
mixing was postulated. Except for this difference, the regular and
ideal solution models are similar. The following concepts are shared:

(a) random mixing
(b) \( V^E = 0 \)
(c) ideal entropy of mixing
(d) no chemical effects

Applying assumptions (b) and (c), to equation (4), the excess molal
free energy is simply:

\[
g^E = u^E
\]

(8)

An expression for the excess energy can be derived if it is assumed
that the solution environment can be considered a quasi-lattice. A
lattice model can be constructed from the following characteristics:

(a) lattice is uniform and rigid
(b) a lattice site is occupied by a single molecule
(c) all sites are occupied
(d) each site has \( Z \) nearest neighbors

This number \( Z \) is usually referred to as the coordination number; it is
an integer which falls in the range, \( 1 \leq z \leq 12 \). A lattice with \( z = 12 \) is called close-packed because no higher value is geometrically possible. 7

The mixture process can be represented as follows:

\[
\text{liquid (1) + liquid (2) } \rightarrow \text{mixture (1+2)}
\]

The excess energy is identical to the energy of mixing, therefore:

\[
U^E = (N_{11} \epsilon_{11} + N_{12} \epsilon_{12} + N_{22} \epsilon_{22}) - (N_{11}^o \epsilon_{11} + N_{22}^o \epsilon_{22}) \quad (9)
\]

where \( N_{1j} \) = total number of nearest neighbor \( ij \) pairs,

\( N_{11}^o = N_{11} \) for pure component \( i \)

\( \epsilon_{ij} \) = \( ij \) potential energy (cal/pair)

The quantity \( \epsilon_{ij} \) represents the increase in potential energy when an \( ij \) pair of molecules are brought together from infinite distance to their equilibrium separation in the pure or mixed lattice. The definition of \( N_{1j} \) implies that only nearest neighbor interactions will be considered;

\( N_{11} \) and \( N_{11}^o \) are simply related:

\[
N_{11} = N_{11}^o - \frac{N_{11}}{2} \quad (10)
\]

combining equations (9) and (10),

\[
U^E = N_{12} (\epsilon_{12} - \frac{1}{2} \epsilon_{11} - \frac{1}{2} \epsilon_{22}) \quad (11)
\]

by definition,

\[
\bar{A}_{12} = (2\epsilon_{12} - \epsilon_{11} - \epsilon_{22}) \quad (12)
\]

where \( \bar{A}_{12} \) = exchange energy (cal/pair)

The exchange (or interchange) energy is the change in potential energy when 2 \( ij \) molecular pairs are formed in solution from single pairs of \( ii \) and \( ij \) molecules.
combining equations (11) and (12),

\[ U^E = N_{12} \frac{\Delta A_{12}}{2} \]  \hspace{1cm} (13)

An expression for \( N_{12} \) can be derived through the assumption of random mixing. If adjacent lattice sites are labelled a and b, then the probability that component 1 occupies site a is equal to its mole fraction \( x_1 \) for random mixing. Similarly, the probability that component 2 occupies site b is \( x_2 \). Then, the probability that component 1 is on site a and simultaneously component 2 is on site b is simply \( x_1 x_2 \). Because the combinations 1-2 and 2-1 are distinguishable, the probability that a particular pair of sites is occupied by an ij pair is \( 2 x_1 x_2 \); or, \( 2 N_1 N_2 / (N_1 + N_2)^2 \), where \( N_i \) = number of molecules of component i. There are a total of \( \frac{1}{2} N (N_1 + N_2) \) pairs of neighboring sites in the mixture, therefore:

\[ N_{12} = \frac{1}{2} \sum (N_1 + N_2) \cdot \frac{2 N_1 N_2}{(N_1 + N_2)^2} \]

or,

\[ N_{12} = \sum \frac{N_1 N_2}{N_1 + N_2} \]  \hspace{1cm} (14)

combining equations (13) and (14),

\[ U^E = \frac{N_1 N_2}{N_1 + N_2} \frac{\sum \Delta A_{12}}{2} \]  \hspace{1cm} (15)

which can be restated,

\[ U^E = (n_1 + n_2) x_1 x_2 \frac{\sum N_0 \Delta A_{12}}{2} \]  \hspace{1cm} (16)
where \( n_i \) = moles of component \( i \)

\[ N_0 = \text{Avogadro's number} \]

in terms of the energy per mole of solution,

\[ u = x_1 x_2 \frac{E N_0 A_{12}}{2} \] \hspace{1cm} (17)

combining equations (8) and (17), and then differentiating according to equation (7),

\[ \ln \gamma_1 = \frac{E N_0 A_{12}}{2 RT} x_1^2 \]\hspace{1cm} (18)

Derivations thus far have led to the important equations (17) and (18). It should be recognized that these expressions differ from those usually associated with the regular solution model. The treatment given thus far has been referred to as the "strictly regular solution model". These approaches are related. The regular solution approach is macroscopic rather than molecular in nature and defines the basic probabilities in terms of volumetric rather than mole fractions.

let \( c_{ij} \) = \( ij \) cohesive energy density (cal/cc)

\[ A_{12} = \text{exchange energy (cal/cc)} \]

\[ M_{12} = \text{total 1-2 interaction} \]

\[ \phi_i = \text{volumetric fraction of component } i \]

reforming equation (11),

\[ U^E = M_{12} (\hat{c}_{11} + \hat{c}_{22} - c_{12}) \] \hspace{1cm} (19)

For random mixing, the probability of \( ij \) interaction is equal to \( 2 \phi_1 \phi_2 \) or \( 2 V_1 V_2 / (V_1 + V_2)^2 \). If \( v^E = 0 \), the total solution
environment is simply \((V_1 + V_2)\), therefore:

\[
M_{12} = \frac{2 \frac{V_1}{V_1 + V_2} \frac{V_2}{V_1 + V_2}}{V_1 + V_2}
\]

(20)

by definition,

\[
A_{12} = (c_{11} + c_{22} - 2 c_{12})
\]

(21)

combining equations (19), (20), and (21),

\[
Y^E = \frac{V_1}{V_1 + V_2} \frac{V_2}{V_1 + V_2} A_{12}
\]

(22)

which can be rearranged,

\[
Y^E = (V_1 n_1 + V_2 n_2) \phi_1 \phi_2 A_{12}
\]

(23)

finally, in terms of the molal energy,

\[
\phi^E = (V_1 x_1 + V_2 x_2) \phi_1 \phi_2 A_{12}
\]

(24)

As before, it is assumed that \(g^E = \phi^E\).

differentiating according to equation (7),

\[
\ln \gamma_i = \frac{V_i A_{12}}{RT} \phi_j^2
\]

(25)

Equations (24) and (25) are the familiar regular solution expressions.

The interaction energies, \(c_{ii}\) and \(c_{12}\), differ but are related:

\[
c_{ii} = -\frac{2 N_0}{Z v_i} \epsilon_{ii}
\]

(26)

implicitly,

\[
c_{12} = -\frac{2 N_0}{2 \sqrt{v_1 v_2}} \epsilon_{12}
\]

(27)
Whereas $c_{ii}$ is a pure component property, $c_{12}$ is not known a priori.

$$c_{ii} = \frac{u_i}{v_i}$$

(28)

where $u_i$ = energy of complete vaporization

If adjustment were made for the differences in interaction energies, it could be shown that equation (25) degenerates into (18), equation (24) into (17), when $v_1 = v_2$. Therefore, the strictly regular solution approach should be considered a special case of the more general regular solution model. The appropriateness of using either approach depends on the similarity of the molal volumes.

The regular solution is defined by its underlying assumptions:

random ordering, $g^E - u^E > 0$, $s^E = 0$, $v^E = 0$. Unfortunately, none of these assumptions are valid. Nevertheless, the regular solution equations predict equilibrium with reasonable accuracy for many nonpolar-nonpolar systems. A proper theoretical justification for their use requires that the assumptions be reexamined.

at constant pressure,

$$g_p^E = u_p^E + p v_p^E - T s_p^E$$

(29)

According to the approach taken here, $g_p^E \approx u_v^E$. The properties $u_p^E$ and $u_v^E$ also $s_p^E$ and $s_v^E$ are related:

$$u_p^E = u_v^E + \left[ T \frac{\partial p}{\partial T} \right] v_p^E + \ldots$$

(30)

$$s_p^E = s_v^E + \left( \frac{\partial p}{\partial T} \right) v_p^E + \ldots$$

(31)
combining equations (29), (30), and (31),

$$E_p = \frac{E^E}{E^E} - T s^E_v$$

Equation (32) means that \(E_p\) is simply equal to \(a^E_v\). In general, \(E_p = E^E_v\) however, \(E_p \neq E^E_v\). The excess energy depends not only on the changes in potential energy which result from the fact that a molecule in solution experiences a change in nearest neighbors, but also on the changes in rotational and vibrational characteristics from pure to mixed environment.

or,

$$E^E_v = u^E_v \text{ (potential)} + u^E_v \text{ (rotation, vibration)}$$

(33)

The term \(u^E_v\) (potential) depends on the change in potential energy and is precisely what has been derived as \(E^E\). The term \(u^E_v\) (rotation, vibration) reflects changes in molecular vibration and rotation and has not been considered.

if,

$$E_p = u^E_v \text{ (potential)}$$

(34)

then,

$$T s^E_v = u^E_v \text{ (rotation, vibration)}$$

(35)

Equation (35) represents the fundamental assumption that has been taken. In summary, \(E_p = u^E_v \text{ (potential)}\).

2. Regular Solution Related Models

The regular solution model is similar to expressions derived by van Leer,11 Langmuir,12,13 and Wohl.14 Each approach takes the physical interpretation of nonideal behavior and assumes that \(E = u^E\). Wohl's
A procedure is the most general and serves as a basis for all expressions of this type. Wohl considered the excess function ($u^E$ or $W^E$) to be a power series in the "effective" volume fractions of the components:

$$u^E = \sum_i q_i x_i \left( \sum_{ij} Z_i Z_j a_{ij} + \sum_{ijk} Z_i Z_j Z_k a_{ijk} + \ldots \right)$$  \hspace{1cm} (36)

where $q_i$ = effective volume of component $i$

$Z_i$ = effective volumetric fraction of $i$

$a_{ij}$ = interaction parameters

The previously defined parameter $A_{12}$ is equal to $2 a_{12}$. The probability that any pair of molecules consists of one molecule of component 1 and one of component 2 is assumed to be $2 Z_1 Z_2$; similarly, the probability that a triplet of nearest neighbor molecules consists of molecules 1, 1, 2 is assumed to be $3Z_1^2 Z_2$, etc. For a binary system, the simplest form is:

$$u^E = (q_1 x_1 + q_2 x_2) Z_1 Z_2 A_{12}$$  \hspace{1cm} (37)

differentiating,

$$\ln \gamma_i = \frac{q_i A_{12}}{RT} Z_j^2$$  \hspace{1cm} (38)

or

$$\ln \gamma_i = \frac{A_{ij}'}{RT} \frac{x_i^2}{(\alpha_{ij} x_i + x_j)^2}$$  \hspace{1cm} (39)

where $\alpha_{ij} = q_i / q_j$

$$A_{ij}' = (\alpha_{ii} + \alpha_{ij} \alpha_{jj} - 2 \sqrt{\alpha_{ij}} \alpha_{ij})$$
If \( \alpha = \alpha_{12} \), then obviously \( A_{21}' = A_{12}' / \alpha \) and \( \alpha_{21} = 1/\alpha \). It should be noted that only the ratio of the effective volumes rather than their individual values appears. In general, two independent parameters are required to describe vapor liquid equilibrium data. Frequently these parameters are equivalent to infinite dilution coefficients where \( A = \ln \gamma_1 \) and \( B = \ln \gamma_2 \). For ideal behavior, \( A = B = 0 \). For a nonideal solution \( A \) and \( B \) assume positive or negative values depending on the deviation from Raoult's law. The nonideality can also be defined in terms of the symmetry between and inherent magnitude of these parameters. According to the approach taken here, the symmetry effect is described by \( \alpha \), the effective volume ratio, where \( \alpha \equiv A/B \). The magnitude condition is simply the exchange energy \( A_{12}' \) (or \( A_{12} \)), where \( A_{12}' = \alpha_{12} \) BRT.

Equation (38) or (39) is appropriate for the Wohl, van Laar, Langmuir, Margules, or regular solution equations. The use of the term effective volume is simply one way to leave the question of volume open. It has no theoretical significance. Van Laar based his work on the van der Waals equation of state:

\[
(p + \frac{\alpha}{v^2})(v - b) = RT
\]

where \( a, b = \) van der Waals constants

The term \( b \) represents the finite volume occupied by the molecules, while the term \( a/b^2 \) is a measure of the cohesive energy density. Then according to van Laar, \( \alpha = b_1/b_2 \) and \( A_{12} \equiv (\sqrt{a_1/b_1} - \sqrt{a_2/b_2})^2 \). Langmuir's approach, which has also been followed by Erdos\(^1\), emphasizes the peripheral nature of forces between polyatomic molecules and defines \( \alpha = S_1/S_2 \).
where \( S_i \) = a measure of the surface of molecule \( i \). In terms of macroscopic properties, \( \sigma = ([P_i]/[P_2])^{2/3} \) where \([P_i]\) = parachor of component \( i \). For regular solutions, \( \sigma = v_1/v_2 \). In general, \( \sigma = q_1/q_2 \) where a volume concept must be developed.

3. Quasichemical Model

The assumption of random mixing was taken throughout the treatment of regular solutions. However, if \( A_{12} \neq 0 \), preferential rather than random ordering must exist. Guggenheim has avoided this assumption by offering without proof what has been called the quasi-chemical approximation. This concept can be represented as follows:

\[
(1 - 1) + (2 - 2) = 2 \ (1 - 2)
\]

where \((i-j)\) = an \( ij \) pair of molecules

at equilibrium,

\[
N_{11} \ + \ N_{22} \ = \ 2\left(\frac{1}{2} \ N_{12}\right)
\]

as in equation (10),

\[
N_{11} \ = \ N_{11}^{o} \ - \ \frac{N_{11}}{2}
\]

The quantity \( N_{11}^{o} \) is equal to the total number of nearest neighbor pairs in the pure component environment; that is, \( N_{11}^{o} = \frac{1}{2} \sum N_i \).

then,

\[
N_{11} \ = \ \frac{1}{2} \left(2N_{11} \ - \ N_{12}\right)
\]

defining \( K \), the equilibrium constant,

\[
K = \frac{(\frac{1}{2} \ N_{12})^2}{N_{11} \ N_{22}} \ = \ \exp \left( - \ \frac{A_{12}}{kT}\right)
\]

where \( k \) = Boltzmann constant (=E/N_o)
combining equations (44) and (45),

\[
\frac{N_{12}^2}{(Z N_1 - N_{12})(Z N_2 - N_{12})} = \eta_{12}^2
\]  

(46)

where \( \eta_{12} = \exp\left(-\bar{A}_{12}/2kT\right) \)  

(47)

solving equation (46) for \( N_{12} \),

\[
N_{12} = \frac{Z(N_1 + N_2)x_1 x_2}{\beta + 1} \frac{2}{\beta + 1}
\]  

(48)

where a new variable \( \beta \) is defined for convenience

\[
\beta = 1 + 4 x_1 x_2 (\eta_{12}^{-2} - 1)
\]  

(49)

as before,

\[
U^E = N_{12} \frac{\bar{A}_{12}}{2}
\]  

(50)

combining equations (48) and (50),

\[
U^E = (N_1 + N_2)x_1 x_2 \frac{Z \bar{A}_{12}}{\beta + 1}
\]  

(51)

in terms of the molal energy,

\[
u^E = x_1 x_2 \frac{Z N_0 \bar{A}_{12}}{\beta + 1}
\]  

(52)

Equation (17) is the special case of equation (52) where \( \beta = 1 \).

The functions \( u^E \) and \( a^E \) are related:

\[
-\frac{\bar{a}^E}{T} = \int \frac{u^E}{x^2} dT
\]  

(53)

combining equations (52) and (53), and assuming that \( \bar{A}_{12} \) is independent
of temperature,

\[ \frac{-aE}{T} = x_1 x_2 z N_o \bar{A}_{12} \int \frac{dT}{T^2(\beta + 1)} \]  \hspace{1cm} (54)

Guggenheim has shown that:

\[ \beta = 1 + 2 x_1 x_2 \frac{\bar{A}_{12}}{kT} \]  \hspace{1cm} (55)

substituting the approximate form of \( \beta \) into equation (54),

\[ \frac{-aE}{T} = x_1 x_2 z N_o \bar{A}_{12} \frac{1}{2} \int \frac{dT}{T(\frac{T}{T} + \frac{x_1 x_2 A_{12}}{k})} \]  \hspace{1cm} (56)

integrating,

\[ aE = \frac{z N_o kT}{2} \ln \left[ 1 + \frac{x_1 x_2 \bar{A}_{12}}{kT} \right] + C \]  \hspace{1cm} (57)

The constant of integration, C, is equal to the excess entropy for an athermal solution and will be taken as zero here.

expanding the logarithmic term as a series,

\[ aE = x_1 x_2 \frac{z N_o \bar{A}_{12}}{2} \left[ 1 - \frac{\bar{A}_{12}}{2kT} x_1 x_2 + \ldots \right] \]  \hspace{1cm} (58)

if \( v_1 = v_2 \),

\[ \bar{A}_{12} = \frac{z N_o \bar{A}_{12}}{2} \]  \hspace{1cm} (59)

then, assuming \( g = a \),

\[ g^E = A_{12} x_1 x_2 \left[ 1 - \frac{A_{12}}{2RT} x_1 x_2 + \ldots \right] \]  \hspace{1cm} (60)

or

\[ g^E = A_{12} x_1 x_2 - \frac{A_{12}^2}{2RT} x_1^2 x_2^2 \]  \hspace{1cm} (61)
The expressions derived according to the quasi-chemical approximation become identical to the strictly regular solution forms as $A_{12}$ or $A_{12}$ converges to zero, that is, for random mixing. The limit as $A_{12} \to 0$:

$$\gamma_{12} = 1, \quad \beta = 1, \quad N_{12} = 2 N_1 N_2 / (N_1 + N_2), \quad \text{and} \quad g^E = a^E = u^E = A_{12} x_1 x_2.$$

The term $A_{12} x_1 x_2$ is the correction for nonrandomness with respect to $g$. It should be noted that this correction is always negative.

4. Barker Model

Barker has taken an approach to nonideal behavior that is similar to Guggenheim's treatment of strictly regular and quasi-chemical solution models. The following concepts are shared:

(1) quasi-lattice liquid model

(2) quasi-chemical approximation

(3) $g^E > a^E$

Previously it was assumed that all lattice sites were occupied, each by a single molecule. Here, each molecule occupies a certain number of sites $\geq 1$. However, the molecules are not considered to be so flexible that a remote segment of a particular molecule can fold back and occupy a neighboring site. Again it is assumed that all sites are occupied. The surface of each molecule is described by a certain number of contact points $\geq 2$ and contact types $\geq 1$. Then, the exchange energies of neighboring molecules depend on the parts of the molecular surface which are in contact.

For each contact type $i$ at equilibrium,

$$N_{ii} - N_{ii}^0 = \sum_{j \neq i} \frac{N_{ij}}{2}$$  \hspace{1cm} (62)
or,

\[ N_{ii} = \frac{1}{2} (Q_i N_k - \sum_{j \neq i} N_{ij}) \quad (63) \]

where \( Q_i \) = number of contact points of type \( i \) per molecule \( k \); that is, each contact type \( i \) is associated with a particular molecule \( k \).

as before,

\[ \frac{\left( \frac{1}{2} N_{ij} \right)^2}{N_{ii} N_{jj}} = \eta_{ij}^2 \quad (64) \]

by definition,

\[ X_i = \sqrt{N_{ii}/N} \quad (65) \]

where \( N = \sum_k N_k \)

The term \( X_i \) is an arbitrary parameter which is analogous to but not equal to the probability factor, i.e. \( \Phi_k \).

combining equations (64) and (65),

\[ N_{ij} = 2 X_i X_j \eta_{ij} N \quad (66) \]

based on previous arguments,

\[ U^E = \sum_i \sum_{j < i} N_{ij} \frac{\bar{A}_{ii}}{2} = \sum' N_{ij} \frac{\bar{A}_{ij}}{2} \quad (67) \]

since \( \eta_{ij} = \exp(-\bar{A}_{ij}/2kT) \),

\[ U^E = -kT \sum' N_{ij} \ln \eta_{ij} \quad (68) \]
combining equations (66) and (68),

\[
\mu^E = -2N kT \sum x_i x_j \eta_{ij} \ln \eta_{ij}
\]

(69)
in terms of the molal energy,

\[
\mu^E = -2RT \sum x_i x_j \eta_{ij} \ln \eta_{ij}
\]

(70)

Equation (70) is valid only if all \(N^O_{ij} (i\neq j) = 0\). If \(i\) and \(j\) are associated with the same molecule \(k\), this is obviously not true. Equation (70) can be reformed in the following manner:

\[
\mu^E (corrected) = \mu^E - \sum_k x_k \mu^E_0
\]

(71)

where \(\mu^E_0 = \mu^E\) evaluated at \(x_k = 1\) then,

\[
\frac{-\mu^E}{2RT} = \sum' (x_i x_j - x_k x_i^0 x_j^0) \eta_{ij} \ln \eta_{ij}
\]

\[
+ \sum''' x_i x_j \eta_{ij} \ln \eta_{ij}
\]

(72)

where \(\sum'' = \sum \sum'\) for \(ij\) associated with molecule \(k\)

\(\sum''' = \sum '\) for \(ij\) associated with unlike molecules

As all values of \(A_{ij} \to 0\), all \(\eta_{ij} = 1\), \(\ln \eta_{ij} = 0\), hence \(\mu^E = 0\) as expected. Since \(h^E = \mu^E\), \(h^E\) is also zero in this case. It should be noted that equation (72) is independent of the coordination number \(Z\) despite its quasi-lattice origins. Equation (72) has been used to model both \(\mu^E\) and \(h^E\). If the exchange energies can be estimated from physical and/or chemical interpretations, the solution is reasonably straightforward.
rephrasing equation (63),

\[
\gamma = N_{11} + \sum_{j \neq 1} \frac{N_{1j}}{2} = \frac{Q_1 N_k}{2}
\]

in terms of \(X_i\),

\[
\sum_i X_i \sum_j X_j \eta_{ij} = \frac{Q_1 x_k}{2}
\]

Equation (74) is a set of simultaneous nonlinear algebraic equations that must be solved for \(X_i\) before equation (72) can be used to describe the excess functions. Since \(\eta_{ij} = \eta_{ji}\), the coefficient matrix associated with equation (74) is symmetrical; moreover, the elements of the main diagonal are unity as \(\eta_{ii} = 1\). The term \(X_i\) varies from zero at \(x_k = 0\) to the maximum value \(x_k^0\) at \(x_k = 1\); that is, \(x_k^0 > x_k > 0\). As \(X_i\) is not a true probability, it can exceed unity. Equation (74) must also be solved if the functions \(g^E\) or \(\ln \gamma_i\) are to be described.

Barker derived the following simple expression for \(\gamma_i\) from the concepts outlined thus far: 15,16,21

\[
\ln \gamma_i = \sum_i Q_i \ln \left( \frac{X_i}{X_i^0} \right) + r_k (\gamma - 1) \ln \left( \frac{r_1 x_1 + r_2 x_2}{r_k} \right)
\]

where \(\gamma = \sum_i\) for all \(i\) associated with \(k\)

\(r_k = \) number of sites occupied by molecule \(k\)

Unfortunately, equation (75) depends on \(\gamma\). If \(\gamma\) is assumed to be 4,
coordination is then consistent from both intra and intermolecular
groups of view for organic compounds:

\[
\ln \gamma_k = \sum_i Q_i \ln \left( \frac{X_i}{X_k} \frac{r_i}{X_i^0} \right) + r_k \ln \left[ \frac{r_1 x_1 + r_2 x_2}{r_k} \right] \tag{7b}
\]

The terms \(Q_i\) and \(r_k\) are of course pure component properties. The value
of \(r_k\) should be related to the volume occupied by component \(k\). In
general, \(r_1/r_2\) should be \(\approx v_1/v_2\). The methylene group acts as a con-
venient standard for a single site. The difference in molal volume
at the same reduced temperature between members of any homologous
family reflects the difference in alkyl radical. Accordingly, a
methylene group occupies \(\sim 20\) cc/gmole. The molal volume of a par-
affin at its normal boiling point is approximately equal to its hy-
drogen number multiplied by ten. Then, each hydrogen represents one
external contact point if a coordination number of four is assumed.
The external contact number for other basic units such as a halogen
or oxygen atom, etc., are given in table (1). In general, \(r_k = Q\)
Total/2, where \(Q\) Total = \(\sum_i Q_i\) for all values of \(i\) associated with \(k\).
The concept of \(Q_i\) as an integer is usually retained, whereas \(r_k\)
assumes values such as \(\frac{1}{2}, 1, 1\frac{1}{2}, 2\) etc.

If each component has only a single contact type, equation (76)
degenerates into a form similar to the regular solution model. In
this case,

\(k = 1, X^0_1 = \sqrt{\frac{Q_i}{2}}, \quad Q_1 = 2r_1\)
Table (1)

External Contact Numbers for Barker Model

<table>
<thead>
<tr>
<th>Unit</th>
<th>$Q_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>- H</td>
<td>1</td>
</tr>
<tr>
<td>- O -</td>
<td>1</td>
</tr>
<tr>
<td>ÿ N</td>
<td>1</td>
</tr>
<tr>
<td>-CL</td>
<td>2.5</td>
</tr>
<tr>
<td>-BR</td>
<td>3</td>
</tr>
<tr>
<td>- I</td>
<td>4</td>
</tr>
<tr>
<td>ÿ C=C &lt;&lt;</td>
<td>1</td>
</tr>
<tr>
<td>- C≡C -</td>
<td>2</td>
</tr>
<tr>
<td>ÿ C=O</td>
<td>2</td>
</tr>
<tr>
<td>benzene ring</td>
<td>10</td>
</tr>
</tbody>
</table>
then,

\[ x_k = \frac{2}{Q_i} x_i (x_i + \eta x_i) , \]

\[
\ln \gamma_i = -2r_i \ln (x_i + \eta x_j) + r_i \ln (r_i x_i + r_j x_j) \tag{77}
\]

at infinite dilution, \( x_i = 0, x_j = x_j^0 \),

\[
\ln \gamma_i^\infty = -2r_i \ln \left( \eta \sqrt{r_j} \right) + r_i \ln r_j \tag{78}
\]

or,

\[
\ln \gamma_i^\infty = -2 r_i \ln \eta \tag{79}
\]

finally,

\[
\ln \gamma_i^\infty = \frac{r_i A_{12}}{RT} \tag{80}
\]

for a regular solution,

\[
\ln \gamma_i^\infty = \frac{v_i A_{12}}{RT} \tag{81}
\]

In this case, the most important difference between the Barker and regular solution models is that of volume concept. The Barker model is one means of extending regular and related solution approaches to systems where association and/or solvation are significant.

C. INTERMOLECULAR PHENOMENA

In order to describe the potential energies which determine \( A_{12} \), it is useful to study the principles of intermolecular phenomena. The classical works of Mie, Keesom, Debye, Latimer and Rodebush, London, etc. have been reviewed. \(22,23,24,25,26,27\) For an isolated \( i j \) pair of molecules, \( \varepsilon_{ij} \) is the sum of attractive and repulsive energies.
As the molecules become infinitely separated, $\varepsilon_{ij}$ approaches zero.

When the molecules approach very close to each other, repulsion sets in suddenly and strongly due to the interaction of the electronic clouds; and $\varepsilon_{ij}$ approaches positive infinity. A gas condenses to a liquid or solid as a result of the attractive effects. The average intermolecular distance $r_{ij}$ in a dense phase is determined by a balance between attractive and repulsive tendencies. There are four types of attraction which are important in this investigation:

(a) orientation (dipole-dipole interaction)
(b) induction (dipole-induced dipole interaction)
(c) dispersion (induced dipole-induced dipole interaction)
(d) specific chemical interaction such as hydrogen bonding

Although convenient, it is an assumption to treat these effects as separate. What can be gained is not a quantitatively useful form for $\varepsilon_{ij}$, but a theoretical foundation for modelling $u_{ij}$; that is, the molecular concepts are helpful in macroscopic analysis.

1. Van der Waals Forces

The physical attractive effects (or van der Waals forces) include orientation, induction, and dispersion. The interaction energy between two permanent dipoles depends upon their relative orientation. The most favorable orientation exists when the dipoles are aligned head to tail along a common line:

$$\varepsilon_{ij} \text{ (orientation)} = \frac{-2 \mu_i \mu_j}{r_{ij}^3}$$  \hspace{1cm} (82)

where $\mu_i$ = dipole moment of component $i$

The average value of $\varepsilon_{ij}$ (orientation) can be represented as a fraction,
\( f_{ij} \), of the optimal value. Thermal agitation interferes with the orientation of equation (82); that is, as \( T \) increases, \( f_{ij} \) decreases.

When \( T \to \infty \), the molecules approach the state of free rotation hence there is no net attraction or \( f_{ij} = 0 \). The usual form associated with \( f_{ij} \) is:

\[
f_{ij} = \frac{\mu_i \mu_j}{3r_{ij}^3 kT}
\]

Equation (83) can be valid only when the obvious constraint on \( f_{ij} \) is satisfied: \( 0 \leq f_{ij} \leq 1 \). If equations (82) and (83) are combined, the expression first derived by Keesom is obtained:

\[
\varepsilon_{ij} \text{ (orientation)} = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{r_{ij}^6 kT}
\]

A permanent dipole induces a dipole in another molecule and an additional attractive effect results. The property which reflects the relative tendency toward change in charge distribution of a particular molecule is its polarizability, \( \alpha \). The optimal orientation for induction exists when the dipole coincides with a line passing through the center of the (spherical) nonpolar molecule. If both molecules are polar, this value is:

\[
\varepsilon_{ij} \text{ (induction)} = -\frac{2}{6} \frac{(\alpha_i \mu_j^2 + \alpha_j \mu_i^2)}{r_{ij}}
\]

Again the average value of \( \varepsilon_{ij} \) (induction) can be represented as a fraction, \( f_{ij} \), of the minimum value. For any orientation, \( \varepsilon_{ij} \) (induction) < 0; hence, the average value is non-zero even for infinitely
high temperatures. For free rotation, \( f_{ij} = \frac{3}{2} \) so that:

\[
\varepsilon_{ij} \text{ (induction)} = - \frac{1}{6} \frac{\alpha_i \mu_j^2 + \alpha_j \mu_i^2}{r_{ij}}
\]  

(86)

Attractive effects associated with polarity were established around 1920 through the work of Keesom (orientation), and Debye (induction). However, attraction between nonpolar molecules was not understood until 1930 when London proposed the dispersion effect. At any instant the electrons of a molecule are in some configuration with respect to the nuclei which results in instantaneous dipole moments. An instantaneous dipole tends to induce a dipole in a neighboring molecule regardless of its orientation. The instantaneous dipole-induced dipole interaction results in an attractive energy which exists whatever the nature of the molecules. London called this phenomena dispersion and was able to derive the following expression:

\[
\varepsilon_{ij} \text{ (dispersion)} = - \frac{3}{4} \frac{\alpha_i \alpha_j}{r_{ij}} \frac{I}{6}
\]  

(87)

The term \( I \) is the average ionization energy and is almost a universal constant for the systems considered in this dissertation.

The potential energy function \( \varepsilon_{ij} \) is the sum of all attractive and repulsive contributions. In 1903, Mie proposed that this function be expressed as:

\[
\varepsilon_{ij} = \left[ \frac{C}{r_{ij}} - \frac{D}{r_{ij}} \right] \quad \text{if } n > m
\]  

(88)
The terms $C$ and $D$ are parameters which represent repulsion and attraction respectively. If $n = 12$ and $m = 6$, equation (88) becomes the familiar Lennard-Jones potential. Equations (84), (86), and (87) are the simplest, nontrivial formulae for the van der Waals effects. These equations indicate that $m = 6$ as well as:

$$D = \left[ \frac{3}{4} \alpha_i \alpha_j \mu_i^2 + \alpha_i \mu_i^2 + \frac{2}{3} \frac{\mu_i^2 \mu_j^2}{kT} \right]$$

Equation (89)

In general, $C$ cannot be as simply stated; consequently, it is convenient to remove the repulsion dependency in analyzing $\epsilon_{ij}$. At equilibrium, the forces of attraction and repulsion are equal; that is, $\epsilon_{ij}$ is at its minimum state:

$$-\frac{\partial \epsilon_{ij}}{\partial r_{ij}} = 0$$

Equation (90)

differentiating equation (88) and solving for $C$,

$$C = \sigma_{ij}^{n-m} \frac{m}{n} D$$

Equation (91)

where $\sigma_{ij}$ = equilibrium intermolecular distance

combining equations (88) and (91),

$$\epsilon_{ij} = \frac{D}{\sigma_{ij}^m} \left[ \frac{m}{n} \left( \frac{\sigma_{ij}}{r_{ij}} \right)^n - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^m \right]$$

Equation (92)

assuming the Lennard-Jones potential,

$$\epsilon_{ij} = \frac{D}{2\sigma_{ij}^6}$$

Equation (93)
Equation (93) could be used to define the exchange energy $\tilde{A}_{12}$ in terms of attraction only. Such an expression would be approximately correct in the absence of specific chemical interactions.

2. Hydrogen Bonding

The most important chemical effect in nonelectrolytic solutions is hydrogen bonding. Latimer and Rodebush first proposed the hydrogen bond in 1920 in order to explain the unusual properties of water. Under certain conditions a hydrogen atom is attracted by two atoms instead of only one so that it may be considered to be acting as a bridge between two donor atoms or between a single donor atom and a carbon atom, provided that a sufficient number of negative groups are attached to the carbon atom. In general, hydrogen cannot coordinate between two carbon atoms. The requirements of a donor atom are small size and high electronegativity. Hence, the upper, right-hand corner of the periodic table contains these atoms: nitrogen, oxygen, and fluorine. The strength of the hydrogen bond depends on the donor atoms present. Fluorine forms very strong bonds, oxygen, weaker ones, and nitrogen, still weaker ones; when hydrogen coordinates with carbon, the bond is further reduced in value:

$$F > O > N > C^*$$

The term $C^*$ represents a carbon atom which is attached to an active (or coordinating) hydrogen and is also attached to the activating agent such as a nitrile or nitrate group, or more than one halogen atom. Hydrogen bonding is sometimes thought of as the special case of the orientation effect where the two dipoles approach each other much more closely than is normal because of the small size of the
active hydrogen which is taken to be a bare proton. More often, hydrogen bonding is simply the assumed mechanism for the formation of a new molecular aggregation which takes the form of a dimer (carboxylic acids), a linear chain (alcohols), or a three dimensional cluster (water). Chemical bonds, hydrogen bonds, and van der Waals effects differ from each other in terms of energy, specificity, and ease of reversibility.

D. EXCHANGE ENERGY

The tendency toward azeotropic formation depends primarily on two factors: (1) the magnitude of the exchange energy, and (2) the boiling point difference, \( \Delta \), between components. Azeotropy is favored by high \( |A_{12}| \) and low \( |\Delta| \). When \( A_{12} = 0 \) and \( \Delta = 0 \), a close boiling mixture exists. This case is similar to azeotrope (a constant boiling mixture) in the sense that it is difficult to separate. For azeotropy, \( A_{12} \neq 0 \) and \( |\Delta| \) cannot be \( \gg 0 \). The value of the exchange energy is controlled by differences in potential energies between like and unlike molecules:

\[
\bar{A}_{12} = (2 \varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22})
\]

(94)

For an ideal solution, \( \varepsilon_{11} = \varepsilon_{12} = \varepsilon_{22} \). Otherwise, it is possible that \( \varepsilon_{ij}, \varepsilon_{ij} > \varepsilon_{jj} \), or \( \varepsilon_{ii}, \varepsilon_{jj} > \varepsilon_{ij} \). The former condition results in a positive deviation from Raoult's law; the latter, a negative deviation. For nonideal solutions where only physical effects are significant, \( \varepsilon_{ii} > \varepsilon_{ij} > \varepsilon_{jj} \), and only minimum boiling azeotropes are possible. The formation of a maximum boiling azeotrope requires a specific chemical interaction between unlike molecules. Minimum
azeotropes are much more common. If $A_{12}$ is increased from zero to larger positive values, the solution passes through a succession of states: (1) ideal, (2) zeotropic (nonazeotropic), (3) homogeneous minimum azeotropic, (4) heterogeneous minimum azeotropic, and finally (5) immiscible. The limiting cases of ideality and immiscibility can be readily calculated; the intermediate ones must be modeled. If $A_{12}$ is decreased from zero, the pattern is ideal, zeotrope, maximum azeotrope, and finally chemical combination. Maximum azeotropes are never heterogeneous.

Prediction of the exchange energy is generally obtained from a form of the equation, $A_{12} = (\sqrt{c_{11}} - \sqrt{c_{22}})^2$. This expression is obviously limited by the appropriateness of the geometric mean assumption, $c_{12} = \sqrt{c_{11}c_{22}}$, and seems to be quantitatively useful only for nonpolar-nonpolar systems. According to van Laar's approach, $c_{ii} = a/b^2$; moreover, $a$ and $b$ are related, $a = 27b^2p_{c1}$, where $p_{c1}$ is critical pressure of component 1. In this case the exchange energy assumes a particularly simple form, $A_{12} = 27 (\sqrt{p_{c1}} - \sqrt{p_{c2}})^2$; that is, $p_{c1} = p_{c2}$ for ideal behavior. Unfortunately this expression is not very useful; and, van Laar later substituted the actual molal volumes for the $b$'s to improve the model. For the regular solution approach, $c_{ii} = \delta_i^2 = u_i/v_i$; hence, $A_{12} = (\delta_1 - \delta_2)^2$. It has already been noted that the regular solution model can be generalized if the volume concept is left open by using the effective volume $q_i$ in place of $v_i$. For example, $q = [p_i]^{2/3}$ according to Erdos.

1. Polar Effect

To account for the effect of polarity on the exchange energy, it
is convenient to return to the quasi-lattice model. If a common lattice describes the pure component and mixture environments, \( \sigma = \sigma_{11} = \sigma_{12} = \sigma_{22} \) by implication. Then, according to equations (89), (93), and (94):

\[
\bar{A}_{12} = \frac{1}{2\sigma^6} \left[ \frac{3}{4} I (\alpha_1 - \alpha_2)^2 + \frac{2}{3kT} (\mu_1^2 - \mu_2^2)^2 + 2 (\alpha_1 - \alpha_2) (\mu_1^2 - \mu_2^2) \right]
\]  

That is, \( \bar{A}_{12} \) can be constructed by summing dispersion, orientation, and induction contributions in the absence of chemical effects. Induction is usually negligible with respect to dispersion if not orientation and may be dropped from consideration:

\[
\bar{A}_{12} = \frac{1}{2\sigma^6} \left[ \frac{3}{4} I (\alpha_1 - \alpha_2)^2 + \frac{2}{3kT} (\mu_1^2 - \mu_2^2)^2 \right]
\]  

Then the exchange energy is composed of a nonpolar and polar term where each obeys the geometric mean for 1-2 interaction. The identification of polarity with orientation is appropriate only when the term has a significant value, that is, when \( \mu_1 \geq 1 \) debye. The pure component cohesive energy is the sum of nonpolar, polar and hydrogen bond values:

\[
u_1 = u_1 \text{ (nonpolar)} + u_1 \text{ (polar)} + u_1 \text{ (bond)}
\]  

then,

\[
c_{11} = \delta_1^2 = \lambda_1^2 + \gamma_1^2 + \beta_1^2
\]
where $\lambda_i^2 = u_i (\text{nonpolar}) / \nu_i$

$\tau_i^2 = u_i (\text{polar}) / \nu_i$

$\beta_i^2 = u_i (\text{bond}) / \nu_i$

If chemical effects are not significant, equation (96) provides a semitheoretical basis for modeling $A_{12}$ as follows:

$$A_{12} = \sqrt{(\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2}$$

(99)

For nonpolar-nonpolar systems, equation (99) degenerates into its most familiar form:

$$A_{12} = (\delta_1 - \delta_2)^2$$

(100)

Equation (99) was first proposed by van Arkel who included an induction term based also on the geometric mean. The nature of $\tau_i^2$ has been reviewed by Hildebrand and Scott, "Actually for most substances... the $\tau$'s are small compared with the $\lambda$'s and represent a small correction term. It should be recalled that $\tau$ is proportional to the square of the dipole moment, and $\tau^2$ to $\mu^4$, so the effect will increase rapidly with increasing dipole moment. In addition, buried dipoles (as in chloroform) produce smaller $\tau$'s than exposed ones (as in acetone)." The most important means of dividing $\delta_i^2$ into polar and nonpolar contributions is the homomorph concept which will be reviewed in the next section.

In addition to Langmuir (1925) and van Arkel (1936), another early investigator of the polar effect on solution nonideality was
Martin\textsuperscript{31,32} (1931). He considered polar-nonpolar systems where the components were similar in structure except for polarity as in the case of benzene-chlorobenzene. Martin used the ideal dilute solution convention, that is, Henry's law, in referencing the polar component. According to Henry's law, \( p_i = H_i x_i \), where \( H_i \) is constant. Let the activity coefficient \( \gamma_i^* \) represent the deviation from Henry's law:

\[
p_i = \gamma_i^* x_i H_i = \gamma_i x_i p_i^*
\]

(101)

Martin modeled the polar effect in terms of induction and obtained the following expression for the polar component:

\[
RT \ln \gamma_i^* = -\frac{\mu_i^2 N_o}{3 a_i^3} \left[ \frac{1}{D_j} - \frac{1}{D} \right]
\]

(102)

where

- \( a_i \) = molecular radius
- \( D_j \) = dielectric constant of the nonpolar component
- \( D \) = dielectric constant of the solution

Martin calculated \( a_i \) from experimental equilibrium data and obtained realistic results. The use of molecular concepts explicitly as in equation (102) is attractive and has been attempted elsewhere.\textsuperscript{33,34}

The major limitation of these approaches for real systems is the questionable validity of simple expressions such as London's dispersion law, Keesom's orientation effect, etc., coupled with the difficulty of modifying them in a practically useful way.

Since \( \delta_i^2 \) is a known pure component property, only one of the contributions, \( \lambda_i^2 \) or \( \gamma_i^2 \), needs to be estimated to define the
exchange energy in the absence of chemical effects. Martire and also Finch have attempted to model \( \tau_1^2 \). Martire assumed that:

\[
\tau_1^2 = -\frac{\varepsilon_{11} \text{ (orientation)}}{v_1} \quad | \quad r = \sigma
\]  

Equation (103) implies that \( \beta = 4 \). Martire replaced \( \varepsilon \) with Keesom's averaged expression, equation (84), and estimated that \( \sigma^6 = 1.54 v^2_s \) where the units of \( \sigma \) are centimeters and \( v_s \) is the molal volume of the solvent.

then, \[
(\tau_1 - \tau_2)^2 = \frac{3.25 \times 10^{-7}}{v_s^2 RT} \left[ \sqrt{\frac{\mu_1^4}{v_1}} - \sqrt{\frac{\mu_2^4}{v_2}} \right]^2
\]  

The use of equation (99) in conjunction with (104) leads to excessively large values for \( A_{12} \). Martire allowed \((\lambda_1 - \lambda_2)^2 = (\delta_1 - \delta_2)^2 \) although \( \lambda_i^2 \) can be readily calculated from \( \lambda_i^2 = (\delta_i^2 - \tau_i^2) \). Nevertheless, this does not account for the major error in \( A_{12} \). Martire assumed a new form of equation (99) which using slightly different symbols is:

\[
A_{12} = \left[ (\lambda_1 - \lambda_2)^2 + (\tau_1 - \tau_2)^2 - 2 \varphi_{12} \right]
\]  

where \( \varphi_{12} = \text{negative residue} \)

The term \( \varphi_{12} \) contains only those factors which lead to negative deviations from Raoult's law and which have not already been included. Possible factors are: (1) a significant molecular size difference, (2) a specific chemical effect between unlike molecules, and (3) a nondisappearing \( ij \) induction term especially when \( i \) is highly polar
and j is nonpolar. In dealing with infinite dilution coefficients for a series of nonpolar solutes in a polar solvent, Martire found that $\varphi_{12}$ was proportional to $\left(\frac{v_2}{v_1}\right) \left(\frac{\delta_1}{\delta_2}\right)$ where component 1 is polar.

Whereas Martire assumed Keesom's formulation of the orientation effect, Finch and Van Winkle developed $\tau_i^2$ from an unaveraged expression for $\varepsilon_{ii}$ (orientation) by assuming it to be proportional to $(\mu_i^2/r_{ii})^3$; that is, $f_{ii}$ was treated as a constant. If $r_{ii}$ is proportional to $v_1^2$:

$$\tau_i^2 = \left(\frac{\mu_i}{v_i}\right)^2$$

(106)

The term $K$ is an empirical constant which should be universal if polar-polar systems are to be modeled. For unassociated liquids, this seems to be true and $K = 598$. The authors studied polar-nonpolar systems defining the exchange energy via equation (99) in conjunction with (106). However, it was noticed that almost without exception the polar component had a smaller molar volume but a larger infinite dilution coefficient than the nonpolar component which represented a reversal in symmetry; that is, the ratio of the van Laar constants $A/B \neq v_1/v_2$. An empirical asymmetry parameter $K_A$ was correlated as a function of $(\delta_1 - \delta_2)^2$. The infinite dilution coefficient associated with the nonpolar component was then reduced in value through division by $K_A \geq 1$. Other details of this approach to vapor-liquid equilibrium prediction are included in the original article.
2. Homomorph Concept

The term homomorph (homo = like, morph = form) was first suggested by Brown in 1953, "it is proposed that molecules having the same or closely similar molecular dimensions be termed homomorphs". Bondi and Simkin used this concept to divide the heat of vaporization, \( \Delta h^V \), of hydrogen bonded substances into polar and nonpolar contributions. If the homomorph of a polar molecule is the equistructural nonpolar hydrocarbon evaluated at the same reduced temperature, \( T_r \):

\[
\Delta h^V = \Delta h^* + \delta \text{(BOND)}
\]  \hspace{1cm} (107)

where \( \Delta h^* \) = \( \Delta h^V \) of the homomorph at \( T_r \)

\( \delta \text{(BOND)} \) = hydrogen bond increment

Then, \( \Delta h^* \) is the apparent dispersion contribution, while \( \delta \text{(BOND)} \) includes orientation and hydrogen bond effects. The authors modeled \( \delta \text{(BOND)} \) as a function of bond type and temperature. The homomorph concept implicitly assumes that the dispersion energies of molecules such as ethanol and propane or their respective functional groups, hydroxyl and methyl, can be exchanged. Then according to London's dispersion law, the terms \( \left[ \frac{\alpha_i^2}{r_{ij}^6} \right] \) should be equal. Bondi and Simkin suggested a test of the homomorph concept using the molar refractivity, \( R_m \), as the measure of polarizability and assuming \( r_{ij}^6 \) to be proportional to \( v_i^2 \):

\[
\frac{R_{mi}}{v_i} \frac{v_i}{2} \frac{I_i}{I_j} = 1
\]  \hspace{1cm} (108)
The $ij$ components may be molecules or functional groups. The authors noted that, unless the importance of the functional group was exaggerated by the size of the molecule as in the case of methanol, the concept was probably sound. Anderson applied the test and obtained improved results when the molal volumes were assumed to be equal. He proposed that the homomorph be evaluated at the same volume as well as at the same reduced temperature of the polar molecule:

$$\lambda_i^2 = \delta_i^2 \text{(HOMOMORPH)} \mid \text{at } v_i, T_r$$  \hspace{1cm} (109)

However, only two variables can be independently specified from those of homomorph identity, volume, and temperature. Nevertheless, a homomorphic family can be indicated so that the homomorph of ethanol is "normal paraffin" rather than propane. Weimer and Prausnitz assumed Anderson's definition of a homomorph to quantify $\lambda_i^2$. For a given reduced temperature, the $\delta_i^2$ versus $v_i$ as a family of curves for fixed values of $T_r$ for paraffins (normal), cycloparaffins, and aromatics. The effect of branching was unfortunately neglected in applying the results, i.e. acetone should be modeled in terms of an iso rather than a normal paraffin plot. Since $\tau_i^2 = \delta_i^2 - \lambda_i^2$, the authors were able to calculate the exchange energy. They found that a negative residue, $\phi_{12}$, was required for meaningful prediction of $A_{12}$, and interpreted it as apparent induction between unlike molecules. In treating nonpolar compounds infinitely dilute in polar solvents, they were able to correlate $\phi_{12}$ as $\approx 0.4 \tau_p^2$ so that:

$$A_{12} = \left[ (\lambda_1 - \lambda_2)^2 + 0.2 \tau_p^2 \right]$$  \hspace{1cm} (110)
In a similar article, Helpinstill and Van Winkle\textsuperscript{41} accounted for the slight polarity of solute hydrocarbons such as olefins and aromatics, and obtained:

\[ A_{12} = \sqrt{(\lambda_1 - \lambda_2)^2 + 0.2(\tau_1 - \tau_2)^2} \]  

(111)

However, when \( \tau_1 \) is small, induction and orientation have roughly the same magnitude, hence the geometric mean assumption is suspect. Intermolecular concepts suggest, if anything, that \( \varphi_{12} \) is proportional to \( \lambda_{np} \) and that this correction should not be necessary for polar-polar systems. This form has in fact been used by Blanks and Prausnitz\textsuperscript{42}.

The requirement of a negative residual term in equation (105) if interpreted as induction violates theoretical anticipations. However, the traditional opinion on the induction contribution, at least with respect to the cohesive energy of polar molecules, has been challenged by Meyer and Wagner\textsuperscript{43}. Their interest is to define \( u \) (dispersion), \( u \) (induction), and \( u \) (orientation) for the ketone family. Dispersion is treated with what may be considered a new homomorphic model. That is, \( u \) (dispersion) = \( u \) (homomorph) when placed in a corresponding state format. A plot of \( u \) versus the carbon number, \( n \), was constructed where \( u \) was calculated at the temperature at which \( v_1 = v \) standard. This plot is shown in figure (1). For the homomorph (normal paraffin), the standard volume of a methylene group was assumed to be 19.08 cc/gmole, then \( v \) standard = 19.08 \( n \). If the volume of the carbonyl group = 11.07 cc/gmole, the corrected carbon number of the ketones \( n + \frac{1}{2} \) and the standard volume is readily calculated. The paraffins
Figure 1 Cohesive energy versus carbon number.
defined a straight line on the plot, while the ketones described a smooth curve. It would be anticipated that the curve would asymptotically approach the homomorphic line as orientation disappeared for larger ketones. The curve instead approaches a line parallel to that of the paraffins implying a nonvanishing induction term. As induction is least sensitive of the van der Waals effects to changes in molecular size, the authors assumed this value was the same for all ketones. If dispersion = homomorphic value and induction = some known constant, orientation can be calculated from the total energy. For methyl ethyl ketone at 40°C, the authors estimated 78% of the total energy to be dispersion, 14% induction, and 8% orientation.

The relative dispersion contribution calculated from known homomorphic models is always greater than that indicated by simple molecular laws. This reflects the fact that real molecules are polyatomic and nonspherical. If diethyl ketone is treated as in the Barker model, its composition can be visualized as 2 methyl, 2 methylene, and a single carbonyl unit; that is, 4 similar nonpolar units a, and one polar unit b. The possibility of aa, ab, and bb contacts exist, but only for bb is orientation relevant. Although the contact bb is preferred, the larger number of a units coupled with the fact that dispersion is relevant to all contacts means that the relative orientation effect is less than anticipated. Induction exists for both ab and bb contacts; hence, some explanation may be given to the induction obtained by Meyer and Wagner as well as to a negative residual term, $\varphi_{12}$. 

CHAPTER II REFERENCES


7. Ibid., p. 23.


30 Hildebrand and Scott, op. cit., p. 168.


CHAPTER III
STATE OF THE ART

A. AZEOTROPIC PREDICTION

I. Qualitative Method

In 1944 a method of predicting qualitatively when azeotropes may be expected was proposed by Ewell, Harrison, and Berg\(^1\) based on the idea that deviations from ideality to the extent of azeotropic formation depend primarily on hydrogen bond effects. This method will be described here using somewhat different language. If a hydrogen bond requires an active hydrogen and an electron donor atom (nitrogen, oxygen, or fluorine), organic families can be classified according to hydrogen bond potential depending on the existence of such groups. Furthermore, if it is realized that such groups as a double bond can also act as an electron donor, the classification can be generalized in terms of acid (proton donor) - base (electron donor) concepts for which the hydrogen bond is a special case. In the following classes, liquids which form three-dimensional networks of hydrogen bonds and those containing fluorine are excluded:

Class I - molecule contains both acidic and basic groups: alcohols, phenols, carboxylic acids, primary and secondary amines, nitro compounds with alpha hydrogen.

Class II - molecule contains basic group only: aldehydes, ketones, ethers, epoxides, esters, tertiary amines, pyridines, nitro compounds without alpha hydrogen, olefins, aromatics, aryl halides.

Class III - molecule contains neither group: paraffins, cycloparaffins, carbon tetrahalides, alkyl halides, \(\text{CS}_2\), etc.
Class IV - molecule contains acidic group only: certain polyhalogenated hydrocarbons such as the haloforms.

Based on class identity, the direction of departure from Raoult's law can be anticipated for a particular combination.

<table>
<thead>
<tr>
<th>System</th>
<th>Classes</th>
<th>Deviation</th>
<th>Chemical effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quasi-ideal</td>
<td>II-II</td>
<td>always +</td>
<td>~ none</td>
</tr>
<tr>
<td></td>
<td>III-III</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>IV-IV</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>II-III</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>III-IV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Negative</td>
<td>II-IV</td>
<td>always -</td>
<td>solvation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>or pseudoideal</td>
<td></td>
</tr>
<tr>
<td>Positive</td>
<td>I-III</td>
<td>always +</td>
<td>dissociation</td>
</tr>
<tr>
<td></td>
<td>I-IV</td>
<td></td>
<td>(slight solvation for I-IV)</td>
</tr>
<tr>
<td>Complex</td>
<td>I-I</td>
<td>usually +</td>
<td>dissociation and</td>
</tr>
<tr>
<td></td>
<td>I-II</td>
<td>some -</td>
<td>solvation</td>
</tr>
</tbody>
</table>

Members of the same organic family do not form azeotropes: like does not azeotrope with like. An exception to this rule exists when more than one class is represented within the same family as in the case of carbon tetrachloride - 12 dichloroethane. It should be noted that the rule is appropriate even for multi-component azeotropes. It is not surprising that the first quinternary azeotrope reported was composed of five different organic families: nitromethane, water, n propanol, tetrachloroethylene, n octane. In quasi-ideal systems, minimum azeotropes appear but only when the boiling points are similar, i.e. \(|\Delta|\) is small. They appear even for entirely nonpolar systems as in the case of benzene-cyclohexane. Significant chemical effects are not unknown in quasi-ideal systems. When a carbonyl group is placed in an aromatic environment, the basic role of the ring tends to convert the
oxygenated component from keto to enol and solvation exists so as to reduce the possibility of azeotropy in any form. In negative systems, solvation frequently leads to maximum azeotropes. However, if the class II component is aromatic, the tendency is a cancellation of physical and chemical effects so that a pseudoideal system exists as in 1,2-dichloroethane-toluene. Even if the magnitude of the negative deviation is significant as in chloroform-benzene, it does not generally produce maximum azeotropes. For positive systems, dissociation leads to minimum azeotropes which are frequently heterogeneous. In complex systems, both dissociation and solvation are significant and all possibilities exist: minimum azeotropes (ethanol-methylethyl ketone), maximum azetropes (phenol-n octanol), pseudoideal systems (pyridine-ethanol). The combinations of organic families in complex systems that result in maximum azetropes have been identified. The most important difference between the classification system used here with the original is that aromatics are considered to be basic rather than inert.

2. Quantitative Methods

Quantitative azeotropic prediction is difficult; however, for regular solutions the conditions of azeotropy can be simply expressed. The regular solution equation for each component according to equation (II-25) is:

\[ \ln \gamma_1 = \frac{v_1 A_{12}}{RT} \phi_2^2 \]  
\[ \ln \gamma_2 = \frac{v_2 A_{12}}{RT} \phi_1^2 \]
dividing,

\[
\frac{\ln \gamma_1}{\ln \gamma_2} = \frac{v_1 \phi_2^2}{v_2 \phi_1^2} = \frac{v_2 x_2^2}{v_1 x_1^2}
\]  \hspace{1cm} (3)

remembering that,

\[
y_i \pi = \gamma_i \chi_i \rho_i
\]  \hspace{1cm} (II-2)

at azeotropy,

\[
x_i = y_i
\]  \hspace{1cm} (4)

then,

\[
\gamma_i = \pi / \rho_i
\]  \hspace{1cm} (5)

combining equations (3) and (5),

\[
\frac{x_2}{x_1} = \frac{1 - x_1}{x_1} = \sqrt{\frac{v_1 \ln \pi / \rho_1}{v_2 \ln \pi / \rho_2}}
\]  \hspace{1cm} (6)

solving for \( x_1 \),

\[
x_1 \text{ azeo} = \frac{1}{1 + \sqrt{\frac{v_1 \ln \pi / \rho_1}{v_2 \ln \pi / \rho_2}}}
\]  \hspace{1cm} (7)

If \( v_1 = v_2 \) and \( \rho_1^* = \rho_2^* \), equation (7) assumes the form first derived by Kireev in 1941. The use of equation (7) requires that the azeotropic temperature be established. Letting \( \phi_2 = 1 - \phi_1 \), equations (1) and (2) can be combined in a manner that eliminates the composition.
dependency:

\[ 1 - \phi_1 = \sqrt{\frac{RT}{v_1 A_{12}}} \ln \gamma_1 = 1 - \sqrt{\frac{RT}{v_2 A_{12}}} \ln \gamma_2 \]  

(8)

combining equations (5) and (8),

\[ f(T) = 1 - \sqrt{\frac{RT}{v_1 A_{12}}} \ln \frac{\pi}{\pi_0^0} - \sqrt{\frac{RT}{v_2 A_{12}}} \ln \frac{\gamma}{\gamma_0^0} = 0 \]  

(9)

The function \( f(T) \) must be solved by trial and error to convergence at zero to obtain the azeotropic temperature, \( T_{azeo} \). Then the azeotropic composition can be immediately calculated from equation (7).

For regular solutions, the sufficient condition for azeotropy can also be developed.

subtracting equation (2) from (1),

\[ \ln \gamma_1/\gamma_2 = \frac{A_{12}^{12}}{RT} v_1 (1 - \phi_1)^2 - v_2 \phi_1^2 \]  

(10)

combining equations (5) and (10),

\[ \frac{RT}{A_{12}} \ln \frac{p_2^{p_2}}{p_1^{p_1}} = v_1 (1 - 2 \phi_1) + \phi_1^2 (v_1 - v_2) \]  

(11)

Since \( v_1 \) should be \( \approx v_2 \) for regular solution applications, the term \( \phi_1^2 (v_1 - v_2) \) may be neglected.

then,

\[ \phi_{1azeo} = \frac{1}{2} \left[ 1 + \frac{RT}{v_1 A_{12}} \ln \frac{p_1^{p_1}}{p_2^{p_2}} \right] \]  

(12)
For azeotropy, the following constraint exists:

\[ 0 < \phi_1 < 1 \]  \hspace{1cm} (13)

combining equations (12) and (13), and rearranging,

\[ -1 < \frac{RT}{v_1 A_{12}} \ln \left( \frac{P_1^*}{P_2^*} \right) < 1 \]  \hspace{1cm} (14)

then,

\[ \frac{v_1}{RT} |A_{12}| > \left| \ln \frac{P_1^*}{P_2^*} \right| \]  \hspace{1cm} (15)

remembering that \( A_{12}' = v_1 A_{12} \),

\[ \frac{|A_{12}'|}{R} > |\sim T \ln \frac{P_1^*}{P_2^*}| \]  \hspace{1cm} (16)

Equation (15) is the sufficient condition for azeotropy for a strictly regular solution. The role of the boiling point difference on azeotropic formation can now be shown using equation (16). The simplest integrated form of the Clapeyron equation is:

\[ \ln p^* = a - \frac{b}{T} \]  \hspace{1cm} (17)

If the constants, \( a \) and \( b \), are evaluated at the normal boiling point, equation (17) can be redefined:

\[ \ln p_1^* \text{ (in atm)} = \frac{\Delta h_{b_1}^{V}}{R T_{b_1}} \frac{T - T_{b_1}}{T} \]  \hspace{1cm} (18)
where \( T_{b_i} \) = normal boiling point of component \( i \)

\[ \Delta h_{b_i}^V = \Delta h^V \text{ at } T_{b_i} \]

For unassociated liquids, the ratio \( \Delta h_{b_i}^V / T_b \) has approximately a universal value referred to as Trouton's constant so that:

\[ \ln p_i^*(\text{in atm}) = 10.6 \frac{T-T_{b_i}}{T} \]

(19)

if \( \Delta = (T_{b1} - T_{b2}) \),

\[ \ln \frac{p_1^*}{p_2^*} = -\frac{10.6}{T} \Delta \]

(20)

combining equations (16) and (20),

\[ \frac{|A'_{12}|}{10.6R} > |\Delta| \]

(21)

Then, high \( |A'_{12}| \) and low \( |\Delta| \) are preferred for azeotropy. If \( \Delta = 0 \), any nonzero value of the exchange energy will lead to azeotropic formation.

The important equations (7) and (9) are also appropriate for most regular solution related models. Of these, the van Laar equations are most frequently used in practice in the form:

\[ \ln \gamma_1 = \frac{A}{B} \left[ \frac{B}{A} x_1 x_2 \right]^2 \]

(22)

\[ \ln \gamma_2 = \frac{B x_1^2}{x_1 + \frac{B}{A} x_2} \]

(23)
Expressions similar to equations (7) and (9) could be derived from (22,23). As $A = \frac{v_1 A_{12}}{RT}$ and $B = \frac{v_2 A_{12}}{RT}$, it is simpler to reform them directly:

\[
 x_1 \text{ azeo} = \left[ 1 + \frac{A \ln \frac{\pi/P_1}{\pi/P_2}}{B \ln \frac{\pi/P_1}{\pi/P_2}} \right]^{-1} \tag{24}
\]

\[
f(T) = 1 - \sqrt{\frac{\ln \frac{\pi/P_1}{\pi/P_2}}{A}} - \sqrt{\frac{\ln \frac{\pi/P_1}{\pi/P_2}}{B}} \tag{25}
\]

Quantitative approaches to azeotropic prediction date from Lecat's basic research of the early twentieth century. Lecat\textsuperscript{4,5} used a power series in the boiling point difference to correlate azeotropic data of a fixed component versus the members of an organic family or of one family against another:

\[
\delta = A_0 + A_1 |\Delta| + A_2 |\Delta|^2 + \ldots \tag{26}
\]

\[
 x_1 \text{ azeo} = B_0 + B_1 \Delta + B_2 \Delta^2 + \ldots \tag{27}
\]

where $\delta$ = azeotropic depression or elevation

$\overline{x_1}$ = weight fraction of component 1

$\Delta = T_{b1} - T_{b2}$

$A_0, \ldots, B_0, \ldots$ = constants

let $T_H$ = higher boiling point

$T_L$ = lower boiling point
For minimum azeotropes, \( \delta \) is the azeotropic depression represented by
\[
(T_L - T_{\text{azeo}}); \text{ for maximum azeotropes, } \delta \text{ is the elevation equal to }
(T_{\text{azeo}} - T_H).
\]
Johnson and Madonis\(^6\) used the equivalent of a first
order approximation of equation (26) for a number of family combina­
tions where at least one family was either hydrocarbons or halogenated
hydrocarbons. Their formula can be restated as:

\[
\delta = (C_1 - |\Delta|)/C_2 \tag{28}
\]

The parameters, \( C_1 \) and \( C_2 \), have been evaluated. The least sensitive
combination toward azeotropy was hydrocarbons versus hydrocarbons for
which \( C_1 = 10 \) and \( C_2 = 3\frac{1}{2} \). As expected the depression assumes its
maximum value when \( \Delta = 0 \), and monotonically decreases to zero as \(|\Delta|\)
increases. Figures (1), (2) plot \( x_1 \), \( \Delta \), \( \delta \) and \(|\Delta|\) respectively for
water-alcohol azeotropes. The former can be divided into regions of
partial and complete miscibility. Lecat's method is usually applied
graphically which unfortunately requires the separate plots for com­
position and temperature conditions. Graphical techniques have been
proposed by Rossini\(^7\) and Skolnik\(^8\) which use a single plot. These are
represented by figures (3) and (4) respectively; in practice, each is
susceptible to branching effects within an organic family. Whether
the approach of Lecat, Rossini, or Skolnik is used, a certain amount
of similar system data is required for prediction. According to
Skolnik's plot, the relationship between azeotropic composition and
temperature reduces to a straight line; if component 1 is fixed:

\[
\ln x_1 \text{ azeo} = a T_{\text{azeo}} + b \tag{29}
\]
Figure 1: Lecat Graph for azeotropic composition prediction.
Figure 2  Lecat Graph for azeotropic temperature prediction.
Figure 3 Rossini Graph for Azeotropic prediction.
Figure 4 Skolnik Graph for azeotropic prediction.
since $T_{\text{azeo}} = T_{\text{bl}}$ at $x_1 = 1$,

$$\ln x_1 \text{azeo} = a (T_{\text{azeo}} - T_{\text{bl}})$$  \hspace{1cm} (30)

Therefore, only one point is required to define the azeotropic line; however, the pure component curve cannot be as easily obtained. The methods of Lecat and Skolnik are similar in principle; if the azeotropic temperature is isolated as the dependent variable, it can be expressed as a power series in the azeotropic composition. Johnson and Madonis found that a particular function could be used to correlate azeotropic temperature data; however, no such form was discovered for the composition. The authors, following the lead of Meissner and Greenfield, used the equation:

$$x_1 \text{azeo} = a + b Y$$  \hspace{1cm} (31)

The term $Y$ is an unspecified variable that must be modeled for a particular combination of families. According to equation (27), $Y$ might be considered as proportional to $\Delta$ as a first approximation. If a regular solution is assumed, then combining equations (12) and (20):

$$\phi_{1 \text{azeo}} = \frac{1}{2} \left[ 1 - \frac{10.6 R}{A_{12}} \Delta \right]$$  \hspace{1cm} (32)

then,

$$x_1 \text{azeo} = a - b \Delta. \text{ (correction term)}$$  \hspace{1cm} (33)

The fact that the authors always use the variable $\Delta$ allows this interpretation of their models. Unfortunately the implicit correction
terms have no general form. Examples include unity, \( T_{b2}^2 \), \( T_{b2}^3 \), 
\( (T_{b1} + T_{b2}) \), \( T_{b2}'(T_{b1} + T_{b2})T_{b2}^2 \).

For a particular system the azeotropic point may be known at a single pressure, usually atmospheric, but rarely at other conditions of temperature and pressure. Most of the available data can be readily obtained from Horsley’s compilations \(^{10}\) (1952, 1962). Then, methods for predicting azeotropy at other system pressures from a single given point are of considerable interest. Such methods are usually based on the principle that an azeotrope like a pure component obeys the Clapeyron equation over the range of its existence. This suggests:

\[
\ln \pi = a - b/T_{\text{azeo}}
\]  

(34)

Orr and Coates \(^{11,12}\) have found this relationship to be valid. Licht and Denzler \(^{13}\) have evaluated the coefficients, \( a \) and \( b \), for 22 binary and 4 ternary azeotropes. Nutting and Horsley \(^{14}\) have used a Cox Chart to correlate azeotropic temperature and pressure data and also to estimate the points of transition from azeotrope to nonazeotrope, if any, from the assumed straight line relationship. It should be noted that at the transition point the latent heat of vaporization of the azeotrope will be equal to that of the corresponding pure component; hence, the intersection must be tangential. \(^{15}\) Then, curvature will exist in the regions of transition with respect to the azeotropic locus. Limited azeotropes are those which have transition points. They can be divided into three classes: azeotropes which vanish with increases in system pressure, vanish with decreases in
pressure, or both. An absolute azeotrope is one that exists at all system pressures. Equation (34) requires at least two experimental points to define the coefficients although only one may be available. Skolnik has proposed a graphical technique to generate the line from a single point. Two lines are constructed through the azeotropic point based on the pure component vapor pressure slopes; then, the azeotropic line must lie between. Skolnik then assumes that the mole fraction ratio of the components at one pressure fixes the contribution of each component to the boiling point at another pressure. Figure (5) describes the application of this approach.

Othmer and Ten Eyck have also studied the effect of pressure on azeotropy. They have derived an expression which relates azeotropic composition to pressure. The Clausius-Clapeyron equation for an azeotrope is:

\[ \frac{d (\ln \pi)}{d (1/T)} = - \frac{\Delta h^v_{\text{azeo}}}{R} \]  

(35)

for component \( i \),

\[ \frac{d (\ln p_i)}{d (1/T)} = - \frac{\Delta \tilde{h}_i^v}{R} \]  

(36)

where \( \Delta \tilde{h}_i^v \) = heat of vaporization of component \( i \) from solution dividing,

\[ \frac{d (\ln \pi)}{d (\ln p_i)} = \frac{\Delta h^v_{\text{azeo}}}{\Delta \tilde{h}_i^v} \]  

(37)

Equation (37) can be integrated if the latent heat ratio is
Figure 5 Skolnik Graph for Estimating the Effect of Pressure on Azeotropy.
assumed to be constant:

\[ \ln p_i = \frac{\Delta h_i^V}{\Delta h_{\text{azeo}}^V} \ln \pi + C \quad (38) \]

At azeotropy, \( p_i = \gamma_i \pi = x_i \pi \) for an ideal vapor, then:

\[ \ln x_i = \left[ \frac{\Delta h_i^V}{\Delta h_{\text{azeo}}^V} - 1 \right] \ln \pi + C \quad (39) \]

Thus, \( \ln x_i \) is a linear function of \( \ln \pi \): \( \ln x_i = m \ln \pi + C \). When only a single azeotropic point is known, the function can be defined in the following manner. The latent heats can be obtained at the azeotropic temperature for each of the pure components. The latent heat of the azeotrope, neglecting heats of solution, can be estimated as a weighted average depending on the composition of the azeotrope; then, the line is readily drawn through the given point with the calculated slope. The authors derived a number of other relationships from the Clausius-Clapeyron equation. It might be noted that a combination of equation (34) and (39) implies that \( \ln x_i \) is a linear function of reciprocal temperature. Such a form has been used by Hirose in correlating azeotropic data.

If homologous family data is available, Lecat's method may be applied. At any desired system pressure, the value of \( \Delta \) is known or can be estimated; hence, the azeotropic condition is immediately known from the \( \bar{x}_i - \Delta \) and \( \delta - |\Delta| \) plots.

The azeotropic point is defined by the three variables, pressure, temperature, and composition of which only two are independent. A
method for estimating the temperature effect on azeotropic composition was proposed by Carlson and Colburn.

restating equation (5),

\[ \gamma_i = \frac{\pi}{p_i} \approx \frac{\pi}{p_i^*} \text{ at azeotropy} \]

then,

\[ \frac{\gamma_1}{\gamma_2} = \frac{p_2^*}{p_1^*} \]

(40)

The ratio of the vapor pressures is a function of temperature which can usually be generated. If the ratio of the activity coefficients is assumed independent of temperature, it is a function of composition only. The authors used the van Laar equation to model \( \gamma_i \) (or \( \gamma_1/\gamma_2 \)).

Equations (22) and (23) can be rearranged as follows:

\[ A = \ln \gamma_1 \left( 1 + \frac{x_2 \ln \gamma_2}{x_1 \ln \gamma_1} \right)^2 \]

(41)

\[ B = \ln \gamma_2 \left( 1 + \frac{x_1 \ln \gamma_1}{x_2 \ln \gamma_2} \right)^2 \]

(42)

The van Laar constants can be evaluated from the given point using these expressions. If a plot is constructed with \( \gamma_1/\gamma_2 \) and \( p_2^*/p_1^* \) as a common ordinate as suggested by equation (40), the corresponding azeotropic composition and temperatures are immediately available as shown in Figure (6). Such a plot may indicate that the system is non-azeotropic. If the temperature difference between known and estimated azeotropes is significant, the temperature dependence of the van Laar constants should be considered. The exchange energy is
Figure 6 Carlson-Colburn Graph for Estimating the Effect of Temperature on Azeotropic Composition.
relatively temperature insensitive. Therefore, if $A = A'_{12}/RT$ and

$B = A'_{12}/\alpha RT$:

$$T_1 (A)_{T_1} \neq T_2 (A)_{T_2}$$

and

$$T_1 (B)_{T_1} \neq T_2 (B)_{T_2}$$

Then a series of curves for the function $\gamma_1/\gamma_2$ at values of temperature could be constructed on the Carlson-Colburn plot. Joffe\textsuperscript{20} has studied such temperature adjustments in detail.

B. VAPOR LIQUID EQUILIBRIUM PREDICTION

Azeotropic prediction is of course only a special case of vapor liquid equilibrium prediction. The regular solution approach is probably the greatest advance made thus far in equilibrium prediction from pure component properties only. For at least nonpolar systems, it gives practically useful results. If a regular or related solution model can be placed in the general form of equation (11-38), prediction requires that a volume concept be specified and an exchange energy calculated. For a given system pressure, the azeotropic temperature can then be obtained from equation (9), subsequently the composition from (7). The latter is often referred to as the Kireev equation.

1. Gilmont-Zudkevitch-Othmer Correlation

A general vapor liquid equilibrium prediction method has been proposed by Gilmont, Zudkevitch, and Othmer.\textsuperscript{21} It is based in part on a volume concept suggested by Erdos.\textsuperscript{22} His interest was to modify the regular solution model so that polar systems might be accurately
treated. For simplicity he studied only chemically similar binaries, that is, those containing the same functional group. Nevertheless, some systems did contain significant nonideality as water was considered to be the first member of the alcohol series. Erdos emphasized the peripheral nature of intermolecular forces between polyatomic molecules and assumed that the volume should be some measure of the surface of the molecule. In terms of macroscopic properties, this measure was taken to be \( [P_i]^{2/3} \) where \([P_i]\) = parachor of the \(i\)th component. Erdos' formulation is equivalent to equation (11-38) if the effective volume is defined as:

\[
q_i = k_i [P_i]^{2/3}
\]

(43)

also,

\[
A_{12} = \left[ \frac{u_1}{k_1 [P_1]^{2/3}} - \frac{u_2}{k_2 [P_2]^{2/3}} \right]^2
\]

(44)

where \(k_i\) = a constant associated with the alkyl group type contained by the \(i\)th polar molecule such as \(n\) alkyl, iso alkyl, etc.

If the components contain the same alkyl as well as functional groups, the force fields of the molecules are similar so that \(k_1 = k_2\). The Gilmont - Zudkevitch - Othmer method can now be stated. The formulations given below do not explicitly appear in the original article but can be generated in a straightforward manner. Also, two typographical errors were noted: (a) their equation (15) contained an extraneous \([2.303RT]\) term, and (b) their equation (18) should be
written as follows.

\[ \log \gamma_j = \frac{1}{2} (g' + g'') x_1^2 - \frac{2}{3} g'' x_1^3 \]

This represents a sign reversal on the right hand term. The exchange energy for their approach is simply equation (44) where the k's have been taken as unity:

\[ A_{12} = \left[ \sqrt[2/3]{\frac{u_1}{P_1^{2/3}}} - \sqrt[2/3]{\frac{u_2}{P_2^{2/3}}} \right]^2 \]  

(45)

However, the A and B parameters do contain a correction for the difference in molecular force fields:

\[ A = \frac{[P_1]^{2/3}}{F_{21}} \frac{A_{12}}{RT} \]  

(46)

\[ B = \frac{[P_2]^{2/3}}{F_{12}} \frac{A_{12}}{RT} \]  

(47)

where \( F_{ij} = ij \) field factor

The factors \( F_{ij} \) and \( F_{ji} \) represent the behavior of one species in the field of molecules of another species. The factors are available for many binary systems. Then, given sufficient pure component data, the activity coefficients can be readily calculated:

\[ \ln \gamma_1 = x_2^2 [A + 2 x_1 (B - A)] \]  

(48)

\[ \ln \gamma_2 = x_1^2 [B + 2 x_2 (A - B)] \]  

(49)
Equations (45) through (49) are the fundamental relationships of this method. The latter pair are similar to the Wohl equation of the third order which can be derived from equation (11-36):

\[ \ln \gamma_1 = Z_2^2 \left[ A + 2 Z_1 \left( B \frac{q_1}{q_2} - A \right) \right] \]  
\[ \ln \gamma_2 = Z_1^2 \left[ B + 2 Z_2 \left( A \frac{q_2}{q_1} - B \right) \right] \]

where,

\[ A = \frac{q_1}{RT} \left( 2a_{12} + 3a_{122} \right) \]  
\[ B = \frac{q_2}{RT} \left( 2a_{12} + 3a_{112} \right) \]

When \( q_1 = q_2 \), equations (50) and (51) become formally identical to equations (48) and (49); however, the theoretical interpretation of A and B differs. Equations of the form (48) and (49) are usually referred to as the Margules equations of the third order.

The correlation of field factors was based on a modified Ewell-Harrison-Berg classification system. The classes defined in the
previous section were divided into nine groups as follows:

<table>
<thead>
<tr>
<th>Class</th>
<th>group</th>
<th>members</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>carboxylic acids, phenols, aromatic alcohols</td>
</tr>
<tr>
<td>I</td>
<td>2</td>
<td>alcohols and water</td>
</tr>
<tr>
<td>II</td>
<td>3</td>
<td>ketones, nitriles without alpha hydrogen</td>
</tr>
<tr>
<td>II</td>
<td>4</td>
<td>esters</td>
</tr>
<tr>
<td>II</td>
<td>5</td>
<td>ethers</td>
</tr>
<tr>
<td>III</td>
<td>6</td>
<td>aromatic hydrocarbons, aryl halides</td>
</tr>
<tr>
<td>III</td>
<td>7</td>
<td>aliphatic hydrocarbons (except cyclohexane), silicoparaffins, CS₂, mercaptans, etc.</td>
</tr>
<tr>
<td>III</td>
<td>8</td>
<td>alkyl halides, carbon tetrahalides</td>
</tr>
<tr>
<td>IV</td>
<td>9</td>
<td>certain polyhalogenated hydrocarbons such as the haloforms</td>
</tr>
</tbody>
</table>

The field factors for most of the group combinations have been correlated. The matrix of values is given in table (1). All main diagonal elements are unity; that is, if the components belong to the same group, the molecular force fields are similar and \( F_{ij} = F_{ji} = 1 \). According to equation (45), the exchange energy must be positive; hence, the sign of the field factors controls the direction of deviation from Raoult’s law. The matrix is symmetrical with respect to sign, asymmetrical for magnitude. Table (2) considers the matrix in terms of sign. The regions of quasi-ideal, positive, negative, and complex systems are identified according to class. As expected, the first two contain only positive signs, the third only negative signs, while the last contains both. It should be noted that group 6 would be associated with class II according to section A - (1).
<table>
<thead>
<tr>
<th>Group for Component i</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.0</td>
<td>-1.0</td>
<td>-</td>
<td>-0.1</td>
<td>1.0</td>
<td>1.0</td>
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<td>0.4</td>
</tr>
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<td>1.0</td>
<td>2.5</td>
<td>0.4</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
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<td>1.3</td>
<td>1.0</td>
<td>-</td>
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<td>0.025</td>
<td>0.1</td>
<td>0.1</td>
<td>-0.035</td>
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<td>0.06</td>
<td>-0.035</td>
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<td>0.2</td>
<td>0.2</td>
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<td>0.4</td>
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### Table (2)

**Sign of Field Factors**

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**Complex**

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**Quasi-ideal**

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**Positive**

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<tbody>
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<td>+</td>
<td>+</td>
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<td>+</td>
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**Negative**

<table>
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<tbody>
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<tr>
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<tr>
<th>8</th>
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<tbody>
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<table>
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<tr>
<th>9</th>
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<tbody>
<tr>
<td>+</td>
</tr>
</tbody>
</table>
Erdos corrected the ideal effective volume, \( q_i = \left[ p_i \right]^{2/3} \), for differences in molecular force fields with the factor \( k_i \). He applied the reformed expression, equation (43), to all volume dependent terms of equation (II-38) which can be restated as:

\[
\ln \gamma_i = \frac{q_i}{RT} A_{12} \left( q_i, q_j \right) Z_j \left( q_i, q_j \right)
\]

The Gilmont-Zudkevitch-Othmer method neglects the analogous correction with regard to the exchange energy and composition terms by phrasing \( A_{12} \) in terms of the ideal effective volume and the composition in terms of mole fractions. This is not consistent with the usual approach; however, it would certainly facilitate \( F_{ij} \) evaluation.

2. Pierotti-Deal-Derr Method

As in azeotropy, there are homologous series approaches to vapor liquid equilibrium prediction. These methods use to advantage moreover require similar system data. They usually model the infinite dilution coefficients \( A = \ln \gamma_1^{\infty} \) and \( B = \ln \gamma_2^{\infty} \). Then, if the systems can be described with reasonable accuracy by a two constant expression such as the van Laar or Wilson equations, the activity coefficients can be calculated at any composition. Such a method has been proposed by Pierotti, Deal, and Derr. It considers the function \( \log \gamma_1^{\infty} \) for members of the solute family to be the sum of simple correlation terms, each of which is susceptible to semiempirical interpretation based on molecular interactions. If both the solute and solvent are monofunctional, the suggested relationship is:

\[
\log \gamma_1^{\infty} = a_{1j} + b_j \frac{n_i}{n_j} + c_i \frac{n_i}{n_1} + d \left( n_i - n_j \right)^2 + \frac{c_j}{n_j} + \left[ b_i \frac{n_i}{n_1} \right]
\]
let $R_i$ = alkyl radical of component $i$

$n_i$ = carbon number of $R_i$

$X_i$ = functional group of component $i$

The coefficients $[a_{ij}, b_j, c_j, d]$ depend on the functional group(s) indicated by the subscript. The terms $a_{ij}$ and $d (n_i - n_j)^2$ reflect the differences in $[X_1 - X_1, X_1 - X_2, X_2 - X_2]$ and $[R_1 - R_1, R_1 - R_2, R_2 - R_2]$ interactions respectively. If either $n_1$ or $n_2 = 0$, the latter term is not considered. For the limiting case where $n_1 = n_2 = 0$, log $\gamma_1^\infty$ is equal to $a_{ij}$. Since $d$ is independent of both $X_1$ and $X_2$, it should be a universal parameter. For a paraffin-paraffin mixture, log $\gamma_1^\infty = d (n_1 - n_j)^2$ so that $d$ can be directly calculated. In practice, $d$ may be treated as a constant $\approx -0.00055$. For like molecule interaction, the $X_1 - X_1$ combination is usually preferred; however, as $n_i$ increases this pairing is diluted. The term $c_j/n_j$ accounts for this effect. The $X_1 - X_1$ reduction is partly offset by the creation of $R_j - X_i$ pairs in the mixture environment; hence, a term $b_j n_j/n_i$ is postulated but only the one related to $X_solvent$ is required so that the right hand term of equation (55) is dropped:

$$\log \gamma_1^\infty = a_{ij} + b_j \frac{n_i}{n_j} + c_j \frac{1}{n_i} + d(n_i - n_j)^2 + \frac{c_j}{n_j}$$  \hspace{1cm} (56)$$

Equation (56) is the standard expression for the Pierotti-Deal-Derr method. Other forms are required in practice; however, these can usually be anticipated. An important special case of equation (56) occurs when the solvent is fixed; then, the terms $c_j/n_j$ and $b_j/n_j$ remain constant for all members of the solute family. If $K = a_{ij}$

$+ c_j/n_j$ and $b = b_j/n_j$;
The major problem is applying this method is the large number of coefficients that must be estimated coupled with the fact that each is a nonlinear function of temperature. If a value is assumed for \( d \), eight constants, four at each dilute condition, must be obtained from similar system data to predict \( A \) and \( B \) from equation (56).

3. Wehe-Coates Method

A homologous series approach that requires far less data has been proposed by Wehe and Coates.\(^{25}\) This method has also been studied by Tooke.\(^{26}\) It is based on an analogy between ideal and nonideal pure component vapor pressures and is best described in terms of an ideal vapor phase although not restricted to such a case. The authors considered isobaric systems where one component was fixed.

restating equation (II-2),

\[
\frac{y_i}{x_i} \approx \frac{\gamma_i^{\infty} p_i^*}{\pi} = \frac{P_i}{\pi}
\]  

where \( P_i \) = the nonideal vapor pressure of pure component \( i \) at infinite dilution,

\[
\left( \frac{y_i}{x_i} \right)_{x_i = 0} = \left( \frac{\partial y_i}{\partial x_i} \right)_{x_i = 0} = \left( \frac{P_i}{\pi} \right)
\]  

for an ideal solution,

\[
\left( \frac{\partial y_i}{\partial x_i} \right)_{x_i = 0} = \left( \frac{P_i}{\pi} \right)^*
\]  

\[
\left( \frac{\partial y_i}{\partial x_i} \right)_{x_i = 0} = \left( \frac{P_i}{\pi} \right)
\]
according to equation (17),

\[ \ln (p_i^*)_{x_i = 0} = a_i^* - b_i^*/T_{bj} \]  

(61)

by analogy,

\[ \ln (P_i)_{x_i = 0} = a_i - b_i/T_{bj} \]  

(62)

combining equations (58), (61) and (62),

\[ \ln \gamma_i = (a_i - a_i^*) - (b_i - b_i^*)/T_{bj} \]  

(63)

also, from equations (59) and (62),

\[ \frac{\partial \gamma_i}{\partial x_i} = \frac{1}{\gamma_i} \exp (a_i - b_i/T_{bj}) \]  

(64)

For the common solvent, the constants \( a_s^* \), \( b_s^* \), \( a_s \), \( b_s \) are fixed while \( T_{bj} \) varies according to the homologous series. Then, equation (64) indicates that \( \ln \left( \frac{\partial \gamma_i}{\partial x_i} \right)_{x_i = 0} \) is a linear function of the reciprocal boiling points. However, at the other dilute condition the temperature \( (T_{b1}) \) remains constant while the vapor pressure coefficients vary. The change in \( a_i^* \) and \( b_i^* \) for a homologous family is a function of the boiling points. For the special case of parallel vapor pressure lines the dependency can be phrased as follows:

for a common temperature,

\[ \ln p_i^* = c_i^* + d_i^*/T_{b1} \]  

(65)
by analogy,

$$\left( \frac{\partial y_i}{\partial x_1} \right)_{x_1 = 0} = \left( \frac{\partial y_s}{\partial x_s} \right)_{x_1 = 0} = \frac{1}{\pi} \exp \left( c_1 + d_1/T_{b1} \right) \quad (66)$$

According to equations (64) and (66), a plot of $\ln \left( \frac{\partial y_s}{\partial x_s} \right)$ (or $\ln \left( \frac{\partial y_i}{\partial x_i} \right)$) values at infinite dilution conditions versus the reciprocal boiling points of the homologous family would indicate a straight line for each dilute environment. Figure (7) is an example plot. Similar system data can potentially be used to define the lines which would then be available for $\gamma_i^\infty$ prediction for unknown cases by interpolation or extrapolation:

$$\gamma_i^\infty = \frac{\pi}{p_i^* (T_{b_i})} \left( \frac{\partial y_s}{\partial x_s} \right) \quad (67)$$

4. Tassios-Van Winkle Method

Tassios and Van Winkle have suggested a homologous series approach to prediction that is similar to the preceding treatment. Again one component is fixed, however they considered isothermal rather than isobaric systems. The fundamental assumption of their method is:

$$\left( \frac{\partial y_i}{\partial x_1} \right)_{x_1 = 0} = L \left( p_i^* \right)^c \quad (68)$$

for the common solvent,

$$\left( \frac{\partial y_s}{\partial x_s} \right)_{x_s = 0} = L' \left( p_i^* \right)^{c'} \quad (69)$$
Figure 7  Slope of X-Y Diagram at infinite dilution versus \( \frac{1}{T} \) for benzene-alcohol mixtures.
The terms $L, L', C, C'$ are constants which depend on the identity of the family and solvent as well as the system temperature but are independent of the members of the homologous series. Then, the values of $\gamma_i^\infty$ and $\gamma_s^\infty$ for family-solvent mixtures are the same provided that correction is made for the difference in vapor pressure between members.
CHAPTER III REFERENCES


CHAPTER IV

EXPERIMENTAL WORK

A. SYSTEMS

The vapor liquid equilibrium data for eight binary systems at atmospheric pressure has been collected. The purpose of this experimental work was to study the effect of polarity on the exchange energy while simultaneously generating new azeotropic points. The probability of azeotropic formation can be estimated by the techniques described in the preceding chapter. The polar effect can be isolated if polar-nonpolar systems with negligible chemical effects are examined. These cases include combinations of class II, III, IV polar compounds with paraffins, cycloparaffins, and to a lesser extent with aromatics, carbon tetrahalides, carbon disulfide, 1,4-dioxane, etc.

Of the polar compounds acceptable for these systems, only acetone is adequately represented in the literature. Because of the scarcity of halogenated hydrocarbon data, the following were taken as the polar component: 1,2-dichloroethane and dibromomethane (class IV), also ethyl iodide (class III). These were selected for operational convenience. Each was paired with heptane and 24 dimethyl pentane; ethyl iodide, also with carbon tetrachloride and benzene.

B. EXPERIMENTAL METHODS

1. Preparation of Reagents

All experimental materials were obtained from Matheson Coleman and Bell, Inc. The specifications of the polar compounds in terms of normal boiling point range in degrees centigrade were: 1,2-dichloroethane (83-84), dibromomethane (96-98), and ethyl iodide (70-72). Each was purified by distillation using a fifteen and/or thirty tray Oldershaw
column in the following manner. First, the column was charged and operated at total reflux for one hour. Then, the material was distilled at a fifteen to one reflux ratio. The middle fifty per cent by volume was collected. The process was repeated taking a slightly larger middle cut. It was noted that the boiling point of the final product over the range of collection was constant according to a 0.1°C division distillation thermometer. Four samples of each product were tested for purity by chromatographical analysis operating at different conditions and recording the response at low attenuation. Each sample was calculated to be > 99.8 mole % pure. The specification given for the nonpolar compounds was a purity of ≥ 99 mole %. Analysis revealed that heptane, benzene, and carbon tetrachloride were > 99.8 mole % pure; these materials were used without further purification. The nonpolar compound 24 dimethyl pentane was treated as outlined above. During thermocouple calibration with respect to the equilibrium still, the lack of fractionation for all materials implies high purity.

2. Equipment

The apparatus used in obtaining the present data was an equilibrium still designed by Jones, Schoenborn, and Colburn. This still is shown in figure (1). It was constructed of pyrex glass with a capacity of approximately seventy milliliters. Heat was supplied to the still by means of three coils of insulated nichrome wire. These coils were used to flash vaporize the returning condensate and to eliminate heat losses with respect to the liquid residue and overhead vapor line. Power input to the coils was controlled by variacs. It has been stated that the Jones-Schoenborn-Colburn still yields relatively precise data but its operation was somewhat difficult. The proper adjustment of the heating
colls is the major problem. The criterion for proper operation is that a drop of liquid remain at the bottom of the vaporization chamber.

The contents of the still were protected at all times from atmospheric moisture by means of a calcium chloride drying tube. A pressure of one atmosphere was maintained by a cartesian type manostat. Pressure variations were kept within ± 0.25 mm Hg. Atmospheric pressure was measured with a mercury barometer which could be read to the nearest 0.3 mm Hg. The difference between ambient and still pressure was measured by a differential oil manometer. The slight vacuum required was supplied by a water aspirator.

The temperature of the liquid residue was measured with a chromel-constantan thermocouple. A constant reference temperature was maintained by an insulated ice bath. A Leeds and Northrup potentiometer capable of detecting a voltage change of 0.005 millivolts, which corresponds to a temperature change of approximately 0.075°C, was used to measure thermocouple emf. Methanol, water, and the above stated experimental compounds were used to calibrate the thermocouple. The methanol, a product of Mallinckrodt, Inc., was specified to be ≥ 99.5 mole % pure, and was used without further purification. The water was twice distilled according to the procedure previously outlined. The thermocouple was calibrated under operational conditions. First, the equilibrium still was flushed with pure reagent, then operated in the usual manner. The final emf value was tabulated and the process repeated for each compound. The possibility of fractionation was investigated by chromatographical analysis. The normal boiling points taken as standards were obtained by averaging selected values of those compiled by Timmermans. The emf-boiling point data is given in table
(1). The variation of emf with temperature over the range of interest (60° - 100°C) can be described with a simple quadratic equation. The data and fitted curve are plotted in figure (2).

The residue and condensate samples were analyzed for composition with a Micro Tek GC 2500 R gas chromatograph utilizing a thermal conductivity detector with helium as the carrier gas. Helium was regulated to a pressure of 26 psig and a flow rate of approximately 50 cc/min. The liquid samples were injected with a Hamilton microliter syringe. Each sample was about one microliter. The column characteristics and operating conditions for each separation are given in table (3).

3. Procedure

The equilibrium still was prepared for operation by a thorough rinsing in one of the components of the binary system to be studied. The still was then charged and the vastras set. Heat inputs $H_1$, $H_2$, $H_3$ are labeled in figure (1). $H_3$ must be sufficient to prevent reflux in the overhead vapor line. $H_2$ begins the circulation by bringing the liquid to its boiling point. $H_1$ is adjusted so that only a single drop of liquid remains in the vaporization chamber. In general, $H_1 > H_2 > H_3$. The system pressure is regulated to one atmosphere. Required run time is approximately two hours. Equilibration is indicated by constancy of temperature, circulation rate, and liquid level in the respective chambers. The final temperature is recorded. Then, stopcock A in figure (1) is turned so as to separate condensate and residue chambers and equalize the pressure. Next, the heaters are shut down and samples taken. The residue sample must be cooled immediately to prevent evaporation. It was run through glass tubing with an ice jacket. The
<table>
<thead>
<tr>
<th>Compound</th>
<th>Thermal Response</th>
<th>Boiling Point (°C)</th>
<th>E.M.F. (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heptane</td>
<td>143</td>
<td>98.45</td>
<td>6.220</td>
</tr>
<tr>
<td>24 dimethyl pentane</td>
<td>130</td>
<td>80.50</td>
<td>5.015</td>
</tr>
<tr>
<td>benzene</td>
<td>99</td>
<td>80.10</td>
<td>4.990</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>108</td>
<td>76.75</td>
<td>4.770</td>
</tr>
<tr>
<td>12 dichloroethane</td>
<td>91</td>
<td>83.50</td>
<td>5.215</td>
</tr>
<tr>
<td>dibromomethane</td>
<td>80</td>
<td>96.95</td>
<td>6.120</td>
</tr>
<tr>
<td>ethyl iodide</td>
<td>92</td>
<td>72.30</td>
<td>4.475</td>
</tr>
<tr>
<td>methanol</td>
<td>-</td>
<td>64.65</td>
<td>3.985</td>
</tr>
<tr>
<td>water</td>
<td>-</td>
<td>100.00</td>
<td>6.325</td>
</tr>
</tbody>
</table>
Figure 1  Jones-Schoenborn-Colburn Still

Figure 2  Calibration Curve for Chromel-Constantan Thermocouple.
procedure was repeated so that the entire composition range of the binary system was covered.

A gas chromatograph was used to analyze the condensate and residue samples. This instrument required a warm-up period of one hour or more. The conditions of operation for each binary system are given in table (3). The compositions were calculated from the actual response areas using the thermal response method proposed by Rosie and Grob.\textsuperscript{4,5,6} The true response area is equal to the calculated area times the attenuation divided by the thermal response of the component. The true areas normalized yields the mole fraction. The thermal response may be regarded as a pure component property. The authors found it to be independent of such variables as temperature, concentration, carrier gas flow rate, and individual sensing unit. Of the compounds studied here, values have been published for benzene, heptane, 24 dimethyl pentane, and carbon tetrachloride.\textsuperscript{6} Benzene was used as the standard and assigned a value of 100. For convenience, heptane has been taken as the standard here with a thermal response of 143. The thermal response of the other materials have been obtained from heptane blends of known composition by weight. The data is given in table (2). Both literature and experimental values are listed in table (1).

The actual response areas were obtained by numerical integration where the peak width was taken as the dependent variable and the distance from the baseline as the independent variable. The usual recording paper divides the response peak into horizontal strips equally spaced. Adjusting the recorder speed, the peak width at each increment in height can be accurately measured with a ruler. If there are an even number
### Table (2)

**Calibration of Gas Chromatograph**

**Basis:** Thermal Response of Heptane = 143.

<table>
<thead>
<tr>
<th>Blend Component</th>
<th>Thermal Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>24 dimethyl pentane</td>
<td>130.2 130.4 129.9</td>
</tr>
<tr>
<td>benzene</td>
<td>99.7 99.1 59.2</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>107.7 107.6 107.9</td>
</tr>
<tr>
<td>12 dichloroethane</td>
<td>91.3 91.3 91.6</td>
</tr>
<tr>
<td></td>
<td>91.2 91.0</td>
</tr>
<tr>
<td>dibromomethane</td>
<td>79.9 80.2 80.2</td>
</tr>
<tr>
<td></td>
<td>80.1 80.5</td>
</tr>
<tr>
<td>ethyl iodide</td>
<td>91.4 91.9 92.3</td>
</tr>
<tr>
<td></td>
<td>92.0 91.9</td>
</tr>
</tbody>
</table>
### Table (3)

**Operating Conditions for the Gas Chromatograph**

**Column Type:** 1/4 inch O.D. by 6 ft. long stainless steel packed with Porapak Q.

<table>
<thead>
<tr>
<th>Separation</th>
<th>Column Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heptane - 12 dichloroethane</td>
<td>200</td>
</tr>
<tr>
<td>heptane - dibromomethane</td>
<td>200</td>
</tr>
<tr>
<td>heptane - ethyl iodide</td>
<td>200</td>
</tr>
<tr>
<td>24 dimethyl pentane - 12 dichloroethane</td>
<td>180</td>
</tr>
<tr>
<td>24 dimethyl pentane - dibromomethane</td>
<td>150</td>
</tr>
<tr>
<td>24 dimethyl pentane - ethyl iodide</td>
<td>180</td>
</tr>
<tr>
<td>benzene - ethyl iodide</td>
<td>170</td>
</tr>
<tr>
<td>carbon tetrachloride - ethyl iodide</td>
<td>155</td>
</tr>
</tbody>
</table>
of strips, the computer routine given in Table (4) applies Simpson's rule to calculate the relative area contained. For an odd number \( M \), the first \( M-1 \) strips are summed as before; the value of the final strip is then added according to the trapezoidal rule. It should be noted that the size of the increment is not included in the logic as it would cancel in the calculation of mole fraction. Table (4) summarizes the procedure for converting the chromatographic response to composition.

C. EXPERIMENTAL RESULTS

The vapor liquid equilibrium data for the eight binary systems studied here is given in Table (5). Figures (3) through (12) are \( y-x \) plots for each polar-nonpolar combination of the following components including experimental and/or literature data: 12 dichloroethane, dibromomethane, ethyl iodide, \( n \) heptane, 24 dimethyl pentane, benzene, and carbon tetrachloride. The data presented in Table (5) has been tested for thermodynamic consistency using Herington's method\(^7,8\) as outlined in Appendix B. The data appears to be consistent. A sample test plot of \( \ln \frac{y_1}{y_2} \) versus \( x_1 \) is given in Figure (13).

According to subroutine TEST, the function \( z = \ln \frac{y_1}{y_2} \) is fit to a polynomial.

\[
z = \ln \left( \frac{y_1 x_2 p_2}{y_2 x_1 p_1} \right) = a_0 + a_1 x_1 + \ldots + a_m x_1^m \tag{1}\]

The azeotropic composition can be obtained by fitting a similar function as suggested by Orr.\(^9\)

\[
\ln \left( \frac{y_1 x_2}{y_2 x_1} \right) = b_0 + b_1 x_1 + \ldots + b_m x_1^m \tag{2}\]
TABLE (4)

CONVERSION OF GC RESPONSE TO MOLE FRACTION

A = ATTENUATION
AREA = PEAK AREA
TR = THERMAL RESPONSE
M = NUMBER OF ORDINATES
NT = NUMBER OF EXP. POINTS
X = LIQUID PHASE MOLE FRACTION
Y = VAPOR PHASE MOLE FRACTION
Z = PEAK WIDTH

10 FORMAT(I2,3X,2F5.0,10A4)
11 FORMAT(I1,10A4//',X(I),Y(I))
12 FORMAT(I2,F10.0/8F10.0)
13 FORMAT(0*,2F10.4)

DIMENSION A(4),AREA(4),ANAM(10),TR(2),Z(50)
READ 10,NT,TR,ANAM
PRINT 11,ANAM
DO51=1,NT
DO4J=1,M
READ 12,M,A(J),Z(K),K=1,M
N=2*(((M-1)/2)+1
V1=V-1
V2=V-2
SUM1=0
SUM2=0
DO2K=2,V1,2
2 SUM1=SUM1+Z(K)
DO3K=3,V2,2
3 SUM2=SUM2+Z(K)
AREA(J)=(Z(V)+4.*SUM1+2.*SUM2+Z(N))/3.
IF(V*EQ.M) G0T04
AREA(J)=AREA(J)+(Z(N)+Z(M))/2.
4 AREA(J)=A(J)*AREA(J)
X=1./(1.+(AREA(1)*TR(1))/(AREA(1)*TR(2)))
Y=1./(1.+(AREA(4)*TR(1))/(AREA(3)*TR(2)))
PRINT 13,X,Y
STOP
END
### Table (5)

**Vapor Liquid Equilibrium Data**

**Basis:** 760 mm

#### 12 dichloroethane (1)-heptane (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1775</td>
<td>0.3791</td>
<td>88.10</td>
</tr>
<tr>
<td>0.2571</td>
<td>0.4740</td>
<td>85.50</td>
</tr>
<tr>
<td>0.2785</td>
<td>0.5029</td>
<td>84.25</td>
</tr>
<tr>
<td>0.4182</td>
<td>0.5999</td>
<td>82.10</td>
</tr>
<tr>
<td>0.4639</td>
<td>0.6172</td>
<td>81.45</td>
</tr>
<tr>
<td>0.5795</td>
<td>0.6805</td>
<td>80.45</td>
</tr>
<tr>
<td>0.6306</td>
<td>0.6901</td>
<td>80.20</td>
</tr>
<tr>
<td>0.6816</td>
<td>0.7200</td>
<td>80.15</td>
</tr>
<tr>
<td>0.7143</td>
<td>0.7308</td>
<td>80.15</td>
</tr>
<tr>
<td>0.7587</td>
<td>0.7537</td>
<td>80.10</td>
</tr>
<tr>
<td>0.8364</td>
<td>0.7987</td>
<td>80.20</td>
</tr>
<tr>
<td>0.8825</td>
<td>0.8242</td>
<td>80.55</td>
</tr>
<tr>
<td>0.9208</td>
<td>0.8668</td>
<td>81.10</td>
</tr>
</tbody>
</table>

#### 12 dichloroethane (1)-24 dimethyl pentane (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0904</td>
<td>0.1704</td>
<td>77.00</td>
</tr>
<tr>
<td>0.1392</td>
<td>0.2441</td>
<td>75.65</td>
</tr>
<tr>
<td>0.2112</td>
<td>0.3201</td>
<td>74.10</td>
</tr>
<tr>
<td>0.2874</td>
<td>0.3913</td>
<td>73.10</td>
</tr>
<tr>
<td>0.3561</td>
<td>0.4322</td>
<td>72.45</td>
</tr>
<tr>
<td>0.4354</td>
<td>0.4870</td>
<td>72.15</td>
</tr>
<tr>
<td>0.4765</td>
<td>0.5011</td>
<td>72.05</td>
</tr>
<tr>
<td>0.5069</td>
<td>0.5108</td>
<td>72.05</td>
</tr>
<tr>
<td>0.5731</td>
<td>0.5374</td>
<td>72.10</td>
</tr>
<tr>
<td>0.6550</td>
<td>0.5705</td>
<td>72.35</td>
</tr>
<tr>
<td>0.7827</td>
<td>0.6217</td>
<td>73.25</td>
</tr>
<tr>
<td>0.8156</td>
<td>0.6453</td>
<td>73.70</td>
</tr>
<tr>
<td>0.8903</td>
<td>0.7200</td>
<td>75.60</td>
</tr>
</tbody>
</table>

#### Dibromomethane (1)-Heptane (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0659</td>
<td>0.0962</td>
<td>79.35</td>
</tr>
<tr>
<td>0.1186</td>
<td>0.1638</td>
<td>78.60</td>
</tr>
<tr>
<td>0.1927</td>
<td>0.2303</td>
<td>77.85</td>
</tr>
<tr>
<td>0.2395</td>
<td>0.2763</td>
<td>77.70</td>
</tr>
<tr>
<td>0.2740</td>
<td>0.3005</td>
<td>77.50</td>
</tr>
<tr>
<td>0.3214</td>
<td>0.3287</td>
<td>77.45</td>
</tr>
<tr>
<td>0.3514</td>
<td>0.3565</td>
<td>77.45</td>
</tr>
<tr>
<td>0.4027</td>
<td>0.3819</td>
<td>77.50</td>
</tr>
<tr>
<td>0.4198</td>
<td>0.3933</td>
<td>77.55</td>
</tr>
<tr>
<td>0.4835</td>
<td>0.4178</td>
<td>77.75</td>
</tr>
<tr>
<td>0.6183</td>
<td>0.4688</td>
<td>78.50</td>
</tr>
<tr>
<td>0.6902</td>
<td>0.4909</td>
<td>78.85</td>
</tr>
<tr>
<td>0.7852</td>
<td>0.5228</td>
<td>80.00</td>
</tr>
</tbody>
</table>

#### Dibromomethane (1)-24 dimethyl pentane (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1104</td>
<td>0.1781</td>
<td>95.10</td>
</tr>
<tr>
<td>0.1265</td>
<td>0.2152</td>
<td>94.45</td>
</tr>
<tr>
<td>0.1872</td>
<td>0.2926</td>
<td>93.00</td>
</tr>
<tr>
<td>0.2901</td>
<td>0.3970</td>
<td>91.35</td>
</tr>
<tr>
<td>0.3386</td>
<td>0.4388</td>
<td>90.70</td>
</tr>
<tr>
<td>0.4592</td>
<td>0.5240</td>
<td>89.75</td>
</tr>
<tr>
<td>0.5114</td>
<td>0.5549</td>
<td>89.60</td>
</tr>
<tr>
<td>0.5437</td>
<td>0.5740</td>
<td>89.45</td>
</tr>
<tr>
<td>0.5831</td>
<td>0.5954</td>
<td>89.45</td>
</tr>
<tr>
<td>0.6579</td>
<td>0.6315</td>
<td>89.50</td>
</tr>
<tr>
<td>0.8103</td>
<td>0.7161</td>
<td>90.35</td>
</tr>
<tr>
<td>0.8657</td>
<td>0.7583</td>
<td>91.15</td>
</tr>
<tr>
<td>0.9296</td>
<td>0.8319</td>
<td>92.80</td>
</tr>
</tbody>
</table>
### Ethyl Iodide (1) - Heptane (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0544</td>
<td>0.1443</td>
<td>94.25</td>
</tr>
<tr>
<td>0.2717</td>
<td>0.5124</td>
<td>82.90</td>
</tr>
<tr>
<td>0.3696</td>
<td>0.6129</td>
<td>79.65</td>
</tr>
<tr>
<td>0.4257</td>
<td>0.6527</td>
<td>78.25</td>
</tr>
<tr>
<td>0.4825</td>
<td>0.6896</td>
<td>77.00</td>
</tr>
<tr>
<td>0.5272</td>
<td>0.7087</td>
<td>76.15</td>
</tr>
<tr>
<td>0.6520</td>
<td>0.7846</td>
<td>74.15</td>
</tr>
<tr>
<td>0.7054</td>
<td>0.8009</td>
<td>73.65</td>
</tr>
<tr>
<td>0.7267</td>
<td>0.8135</td>
<td>73.35</td>
</tr>
<tr>
<td>0.8035</td>
<td>0.8525</td>
<td>72.80</td>
</tr>
<tr>
<td>0.8531</td>
<td>0.8802</td>
<td>72.50</td>
</tr>
<tr>
<td>0.9048</td>
<td>0.9110</td>
<td>72.25</td>
</tr>
<tr>
<td>0.9257</td>
<td>0.9286</td>
<td>72.15</td>
</tr>
<tr>
<td>0.9699</td>
<td>0.9687</td>
<td>72.15</td>
</tr>
</tbody>
</table>

### Ethyl Iodide (1) - 24 Dimethyl Pentane (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1749</td>
<td>0.3213</td>
<td>73.65</td>
</tr>
<tr>
<td>0.2161</td>
<td>0.3650</td>
<td>72.60</td>
</tr>
<tr>
<td>0.3670</td>
<td>0.4892</td>
<td>69.80</td>
</tr>
<tr>
<td>0.4259</td>
<td>0.5417</td>
<td>68.90</td>
</tr>
<tr>
<td>0.4663</td>
<td>0.5625</td>
<td>68.55</td>
</tr>
<tr>
<td>0.5067</td>
<td>0.5879</td>
<td>68.25</td>
</tr>
<tr>
<td>0.5732</td>
<td>0.6207</td>
<td>67.85</td>
</tr>
<tr>
<td>0.6518</td>
<td>0.6674</td>
<td>67.70</td>
</tr>
<tr>
<td>0.7341</td>
<td>0.7198</td>
<td>67.70</td>
</tr>
<tr>
<td>0.8643</td>
<td>0.7953</td>
<td>68.45</td>
</tr>
<tr>
<td>0.9047</td>
<td>0.8345</td>
<td>69.10</td>
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</tbody>
</table>

### Ethyl Iodide (1) - Benzene (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1293</td>
<td>0.1943</td>
<td>77.35</td>
</tr>
<tr>
<td>0.2437</td>
<td>0.3294</td>
<td>75.55</td>
</tr>
<tr>
<td>0.2667</td>
<td>0.3477</td>
<td>75.20</td>
</tr>
<tr>
<td>0.3493</td>
<td>0.4201</td>
<td>74.30</td>
</tr>
<tr>
<td>0.4076</td>
<td>0.4778</td>
<td>73.80</td>
</tr>
<tr>
<td>0.4755</td>
<td>0.5367</td>
<td>73.05</td>
</tr>
<tr>
<td>0.6160</td>
<td>0.6506</td>
<td>72.40</td>
</tr>
<tr>
<td>0.6572</td>
<td>0.6854</td>
<td>72.30</td>
</tr>
<tr>
<td>0.7437</td>
<td>0.7504</td>
<td>71.95</td>
</tr>
<tr>
<td>0.7690</td>
<td>0.7752</td>
<td>71.95</td>
</tr>
<tr>
<td>0.8146</td>
<td>0.8160</td>
<td>71.90</td>
</tr>
<tr>
<td>0.9232</td>
<td>0.9167</td>
<td>72.05</td>
</tr>
</tbody>
</table>

### Ethyl Iodide (1) - Carbon Tetrachloride (2)

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Tp(°C)</th>
</tr>
</thead>
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<tr>
<td>0.0523</td>
<td>0.0799</td>
<td>75.75</td>
</tr>
<tr>
<td>0.0713</td>
<td>0.1064</td>
<td>75.45</td>
</tr>
<tr>
<td>0.1654</td>
<td>0.2230</td>
<td>73.90</td>
</tr>
<tr>
<td>0.2363</td>
<td>0.2992</td>
<td>73.15</td>
</tr>
<tr>
<td>0.2908</td>
<td>0.3543</td>
<td>72.60</td>
</tr>
<tr>
<td>0.3724</td>
<td>0.4265</td>
<td>71.85</td>
</tr>
<tr>
<td>0.4351</td>
<td>0.4797</td>
<td>71.50</td>
</tr>
<tr>
<td>0.4729</td>
<td>0.5115</td>
<td>71.30</td>
</tr>
<tr>
<td>0.5532</td>
<td>0.5746</td>
<td>71.00</td>
</tr>
<tr>
<td>0.6252</td>
<td>0.6338</td>
<td>70.95</td>
</tr>
<tr>
<td>0.6736</td>
<td>0.6705</td>
<td>70.95</td>
</tr>
<tr>
<td>0.7054</td>
<td>0.6957</td>
<td>70.95</td>
</tr>
<tr>
<td>0.8371</td>
<td>0.8172</td>
<td>71.15</td>
</tr>
<tr>
<td>0.9122</td>
<td>0.8878</td>
<td>71.60</td>
</tr>
</tbody>
</table>
Figure 3 X-Y Diagram for 12 dichloroethane - heptane.
Figure 6. X-Y diagram for L2 dichloroethane

Mole fraction of dichloroethane in vapor

Mole fraction of dichloroethane in liquid

1.0
0.5
0.0
0.0
Figure 5  X-Y Diagram for 12 dichloroethane - bensene.
Figure 6 X-Y Diagram for 12 dichloroethane - CCL4.
Figure 7 X-Y Diagram for dibromomethane - heptane.

Mole fraction of dibromomethane in liquid
Mole fraction of dibromomethane in vapor

Mole fraction of dibromomethane in liquid

2,4 Diethylpentane
Figure 9 X-Y Diagram for ethyl iodide - heptane.
Mole fraction of ethyl iodide in vapor

Figure 10: X-Y Diagram for ethyl iodide - 2,4-dimethyl pentane.
Mole fraction of ethyl iodide in liquid

**Figure 11** X-Y Diagram for ethyl iodide-benzene.
Figure 12 X-Y Diagram for ethyl iodide - carbon tetrachloride.
<table>
<thead>
<tr>
<th>System</th>
<th>( x_1 )</th>
<th>( t_p ) (°C)</th>
<th>( x_2 )</th>
<th>( t_p ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 dichloroethane (1) - heptane (2)</td>
<td>0.740</td>
<td>80.10</td>
<td>0.758</td>
<td>81.</td>
</tr>
<tr>
<td>12 dichloroethane (1) - 24 dimethyl pentane (2)</td>
<td>0.513</td>
<td>72.05 (35 vol%)</td>
<td>0.493</td>
<td>77.45 (35.8 vol%)</td>
</tr>
<tr>
<td>dibromomethane (1) - heptane (2)</td>
<td>0.722</td>
<td>89.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dibromomethane (1) - 24 dimethyl pentane (2)</td>
<td>0.493</td>
<td>77.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethyl iodide (1) - heptane (2)</td>
<td>0.965</td>
<td>72.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethyl iodide (1) - 24 dimethyl pentane (2)</td>
<td>0.764</td>
<td>67.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethyl iodide (1) - benzene (2)</td>
<td>0.902</td>
<td>71.90</td>
<td>0.80</td>
<td>74.5</td>
</tr>
<tr>
<td>ethyl iodide (1) - CCL4 (2)</td>
<td>0.662</td>
<td>70.95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
at azeotropy,

\[ b_0 + b_1 x_1 + \ldots + b_m x_1^m = 0 \]  \hspace{1cm} (3)

Equation (3) can be solved analytically or by direct search for the azeotropic composition. The points generated using this procedure along with literature values are presented in table (6). The azeotropic temperature given is the lowest experimental point. The variation of \( \ln \frac{y_1 x_2}{y_2 x_1} \) with \( x_1 \) is also shown on the test plot.

Lecat plots for the six hydrocarbon-halogenated hydrocarbon azeotropes observed are given in figures (14) and (15). Lecat used weight fraction as the measure of composition. However, this data required that mole fraction be used to construct a smooth curve.

The effect of polarity on the exchange energy is considered in the next chapter.
Figure 13 Thermodynamic Consistency Plot for ethyl iodide - 24 dimethyl pentane system.

\[ Z = \frac{y_1 x_2}{y_2 x_1} \]

\[ Z = \ln \frac{y_1}{y_2} \]
Figure 14 Lecat Graph for azeotropic composition of halogenated hydrocarbon (1) - paraffin (2) systems.
Figure 15 Lechat Graph for azeotropic temperatures of halogenated hydrocarbon (1) - paraffin (2) systems.
CHAPTER IV REFERENCES


CHAPTER V
PROPOSED METHOD

A. INTRODUCTION

Vapor liquid equilibrium prediction for nonpolar, quasi-ideal, and positive systems has been studied with special emphasis on developing a prediction method which requires pure component data only. As previously defined, quasi-ideal systems are those composed of the class combinations (II-II, III-III, IV-IV, II-III, III-IV), positive systems (I-III, I-IV). The organic families included here are: alcohols, ketones, esters, ethers, pyridines, hydrocarbons, and halogenated hydrocarbons. The bibliography and compilation provided by Hala et al. were particularly helpful in gathering the equilibrium data required for the general purposes intended here. Literature data was selected on the basis of completeness, availability of physical property data, and on thermodynamic consistency. The calculation of physical properties is outlined in appendix A. The computer subroutines applied in testing, correlating, and predicting equilibrium data are given in appendix B.

In general, two independent parameters are required to describe solution nonideality. The form that they may assume depends on the model which has been selected. The numerical values of the parameters were obtained here by the method of weighted least squares where the dependent variable is defined as \( z = \ln g_1/g_2 \). A derivation of the weighting factor has been given elsewhere. The factor applied in these calculations is stated in equation (B-2). The correlation coefficient squared will be taken as the measure of effectiveness in model development. It is stated in equation (B-5).
The regular solution model can be represented by equation (11-38) or (11-39). Solution nonideality is controlled by a symmetry factor and a magnitude condition. The former is given by $\alpha$, the effective volume ratio, while the latter is simply the exchange energy, $A_{12}$. In general, "effective volume" is given theoretical significance only in the case of associated liquids: that because of complex formation the effective volume is some multiple of the assumed monomer value. However, Langmuir has implied that it should be a function of molecular size and shape, also of polarity. This interpretation will be taken here. The pure component molal volume is only slightly sensitive to the effect of branching within an organic family. It reflects the size of the molecule. Then, if the effective volume is treated as some multiple of the pure component value, the multiplication factor should be modeled in terms of molecular shape and polarity. The effective volume is assumed to be a consistent quantity which can be generated from known physical properties, although its precise value is obscured by the fact that it always appears in terms of a ratio. Benzene will be used as the standard in effective volume correlation.

By definition, the effective volume of benzene is equal to its pure component molal volume evaluated at the system temperature.

The nature of the exchange energy was reviewed in chapter II. It depends on the differences in interaction energies between like and unlike molecules.

by definition,

$$A_{12} = (c_{11} + c_{22} - 2c_{12})$$ (II-21)

Unfortunately, the value of $c_{12}$ is unknown a priori. The pure component
cohesive energy is the sum of nonpolar, polar, and hydrogen bond contributions:

\[ u_i = u_i^{\text{(nonpolar)}} + u_i^{\text{(polar)}} + u_i^{\text{(bond)}} \]  

(II-97)

The contribution of the hydrogen bond is not treated explicitly here. Associated liquids will be modeled as simple polar compounds, that is, in terms of apparent polar and nonpolar energies. Let,

\[ u_i = u_i^n + u_i^p \]

The form of the exchange energy to be applied is:

\[ A_{12} = \left[ \left( \sqrt{u_1^n} - \sqrt{u_2^n} \right)^2 + \left( \sqrt{u_1^p} - \sqrt{u_2^p} \right)^2 + 2 \lambda_{12} \sqrt{u_1^n u_2^n} \right] \]  

(1)

The term \( \lambda_{12} \) is a measure of the deviation from the implied geometric mean assumption with respect to nonpolar-nonpolar interaction. It is small compared to unity and depends on the identity of the binary components; however, it may be considered as composition and temperature independent. Equation (1) is similar to equation (II-105). It implies that the negative residual term should assume the form:

\[ \varphi_{12} = -\lambda_{12} \lambda_1 \lambda_2 \]  

(2)

The meaning of \( \varphi_{12} \) is not to be regarded as apparent induction between unlike molecules. For systems which contain polarity, it is used to describe solvation, if any; otherwise, it is dropped from consideration.

It has become common practice to combine the regular solution
equation with the expression derived simultaneously by Flory\textsuperscript{6} and Huggins\textsuperscript{7} for the athermal solution in order to account for the effect of unequal volumes. Equation (11-38) is limited by the constraint: 
\[ \frac{1}{2} < \alpha < 2. \]
However, the use of effective volumes tends to draw the symmetry factor closer to unity than indicated by \( v_1/v_2 \). Nevertheless, a Flory-Huggins size correction is useful in that the exchange energy becomes somewhat more responsive to a general correlation. The combined expression takes the form:

\[
\ln \gamma_1 = \frac{A_{12}'}{RT} z_2^2 + \ln \frac{z_1}{x_1} + 1 - \frac{z_1}{x_1} \quad (3)
\]

and,

\[
\ln \gamma_2 = \frac{A_{12}'}{\alpha RT} z_1^2 + \ln \frac{z_2}{x_2} + 1 - \frac{z_2}{x_2} \quad (4)
\]

then,

\[
\ln \gamma_1/\gamma_2 = \frac{A_{12}'}{RT} \left[ z_1^2 \left( 1 - \frac{1}{\alpha} \right) - 2 z_1 + 1 \right]
+ \ln \alpha - \frac{(\alpha - 1)}{x_1 (\alpha - 1) + 1} \quad (5)
\]

The models proposed in this chapter are based on equation (5).

B. NONPOLAR SYSTEMS

Some simple correlations can be offered for nonpolar systems. A correlation for those quasi-ideal systems which contain polarity will be stated in the next section. This will require that both the volume concept and the geometric mean deviation be adjusted for overall consistency. For nonpolar systems, it is sufficient to consider only one of these variables. Simultaneous adjustment merely generates a larger
number of parameters which do not significantly increase the overall correlation coefficient. The locus of minimum points of the least squares objective function with respect to the variables $\alpha$ and $l_{12}$ for the system methyl cyclopentane-benzene is traced in figure (1). The best fit value for $\alpha$ when $l_{12} = 0$, also the value of $l_{12}$ when $\alpha = v_1/v_2$ are shown. If the geometric mean is assumed, two nontrivial roots will always appear. The one nearest unity is usually preferred. However, if one is known, the other can be located:

$$\text{Root } 2 = \left[2 \sqrt{\frac{u_1}{u_2}} - \sqrt{\text{Root } 1}\right]^2$$

A series of assumptions were made in the preceding section to serve as a preliminary basis for effective volume correlation. The effective volume is treated as some multiple of the pure component volume. A problem involved in modeling paraffins lies in the fact that the pure component volumes are closely related to hydrogen number. This means that an adjustment is automatically made on cycloparaffins that is not made on branched paraffins which are similar in effect. To obtain a physical property that can be used to model the multiplication factor for all paraffins is difficult. Fortunately, a parameter has been recently defined by Selleck and Chong which can be applied. It will be referred to as the branching parameter, $bp_i$:

$$bp_i = \frac{\text{number of methyl carbons of paraffin } i}{\text{carbon number of paraffin } i}$$

This term varies from 0.0 for cyclopentane and cyclohexane to 0.8 for neopentane.
Figure 1 Locus of minimum points for the weighted least squares objective function.
Combinations of paraffins, aromatics, carbon tetrachloride, and dioxane have been considered here. A basis of 806 experimental points was initially taken. Then 124 points, marginal with respect to thermodynamic consistency, were added and the multiplication factors re-evaluated.

\[ \text{Basis: } l_{12} = 0 \]

\[ q_{\text{benzene}} = v_{\text{benzene}} \]

\[ q_{\text{paraffin}} = \left( C_1 + C_2 b_{p1} + C_2 b_{p1}^2 \right) v_1 \]

\[ q_1 = MF_1 v_1 \]

\[ r^2 = 0.9539 \quad \text{806 points} \]

\[ r^2 = 0.9467 \quad \text{930 points} \]

<table>
<thead>
<tr>
<th></th>
<th>806 points</th>
<th>930 points</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1 )</td>
<td>1.212</td>
<td>1.213</td>
</tr>
<tr>
<td>( C_2 )</td>
<td>-0.807</td>
<td>-0.810</td>
</tr>
<tr>
<td>( C_3 )</td>
<td>0.534</td>
<td>0.525</td>
</tr>
<tr>
<td>MF dioxane</td>
<td>0.967</td>
<td>0.965</td>
</tr>
<tr>
<td>MF toluene</td>
<td>1.065</td>
<td>1.059</td>
</tr>
<tr>
<td>MF ethyl benzene</td>
<td>1.073</td>
<td>1.069</td>
</tr>
<tr>
<td>MF CCL4</td>
<td>1.091</td>
<td>1.090</td>
</tr>
</tbody>
</table>

Table (1) in appendix D contains the supporting data for this correlation. It compares the correlation coefficients for each binary system when the symmetry factor is allowed to be the best fit value, \( q_1/q_2 \), and \( v_1/v_2 \) in turn. It is recommended that the multiplication factors for other aromatics be obtained by extrapolating the values for toluene and ethyl benzene according to carbon number.

The branching parameter was defined in order to model \( l_{12} \) where
One component was fixed and the other component was varied through the paraffin family. That is, $l_{12}$ was taken as a simple function of the branching parameter and no binary formula was attempted. For these purposes a simple relation was found to be reasonably effective from a number attempted. The above analysis was then repeated considering geometric mean deviation only.

**Basis:**

\[ l_{12} = l_1 + l_2 \]

\[ \alpha = \frac{v_1}{v_2} \]

\[ l_{\text{paraffin}} = C_1 + C_2 b_{p1} + C_3 b_{p1}^2 \]

\[
\begin{array}{lll}
& r^2 = 0.9475 & r^2 = 0.9389 \\
& 806 \text{ points} & 930 \text{ points} \\
C_1 & 0.0088 & 0.0097 \\
C_2 & -0.0574 & -0.0556 \\
C_3 & 0.0292 & 0.0268 \\
l_{\text{dioxane}} & 0.0151 & 0.0124 \\
l_{\text{aromatic}} & 0.0046 & 0.0033 \\
l_{\text{CCL4}} & -0.0008 & -0.0006 \\
\end{array}
\]

Table (2) in appendix D contains the supporting data for this correlation. Best fit values of $l_{12}$ are compared with the predicted values on a basis of correlation coefficient for each binary system. Either method presented here is an effective means of predicting solution nonideality. The theoretical basis of $l_{12}$ might be established from London's dispersion law, equation (II-87). It is interesting that the aromatics can be modeled with a single value.
C. QUASI-IDEAL SYSTEMS

The form that the exchange energy should take for systems which contain polarity is well known. The fundamental problem in accounting for this effect is dividing the pure component cohesive energy into polar and nonpolar contributions. It is proposed here that the following homomorphic model be applied to this purpose:

\[
\begin{align*}
   u_{r_i}^{\text{nonpolar}} &= u_{r_i}^{\text{homomorph}} \\
   \text{where} \quad u_{r_i} &= \frac{u_i}{kT_c} \\

A generalized correlation has been developed for model application. It is based on 486 points generated from the hydrocarbons listed in appendix A. It has the form:

\[
\begin{align*}
   u_{r_i}^{\text{homomorph}} &= C_1 + C_2 T_r + C_3/T_r \\
   &+ \frac{\omega_{H_1}}{T_r} \left[ (C_4 + C_5/T_r)T_r + \omega_{H_1} (C_6 + C_7/T_r^2) \right]
\end{align*}
\]

\[
\begin{align*}
   r^2 &= 0.9991 \\
   C_1 &= 11.02024 & C_5 &= -0.95254 \\
   C_2 &= -7.15616 & C_6 &= 2.04901 \\
   C_3 &= -1.38854 & C_7 &= 0.88732 \\
   C_4 &= 4.55655
\end{align*}
\]
Constraints:

\[ 0.5 \leq T_r \leq 0.8 \]

\[ 0.100 \leq \omega_H \leq 0.550 \]

The term \( \omega_H \) is the acentric factor of the homomorph associated with the polar component. For hand calculations the following expression is convenient:

\[
\begin{align*}
\delta_i (\text{homomorph}) &= 4.193088 + 3.08865 \frac{\omega_H}{T_r^2} \\
\text{r}^2 &= 0.9765
\end{align*}
\]  \hspace{1cm} (9)

The development of the homomorph concept was traced in chapter II. The models described there were tested in the preliminary phase of this investigation. Weimer and Prausnitz\(^{10}\) published plots of \( \delta_i^2 \) (homomorph) versus \( v_i \) as a family of curves for fixed values of \( T_r \). These were found to be of little use for the purposes intended here. An effort was made to reduce the plots to a series of simple equations. It was observed that cycloparaffins and aromatics do not actually form smooth curves because of branching and/or polar effects. Expressions were obtained for normal paraffins and iso paraffins. These are given in table (1).

Of the polar compounds appropriate to quasi-ideal systems, acetone is best represented in the literature. If \( \alpha \) and \( u(\text{polar}) \) are selected as the independent variables and allowed to seek their best fit values for polar-nonpolar mixtures, then the percentage of the total cohesive energy which is associated with polarity falls in the range 11.5 to 15.0% which may be compared to predicted values.
Table (1)

A Homomorphic Model

Basis: $\lambda_i^2 = \delta_i^2(\text{Homomorph})$ at $v_i$, $T_r$

$$\delta_i^2(\text{Homomorph}) = C_1 + C_2 v_i + C_3 v_i^2 + C_4 v_i^3 + C_5 T_r$$

$$+ C_6 T_r^2 + C_7 T_r^3 + C_8 v_i T_r + C_9 v_i^2 T_r$$

$$+ C_{10} v_i T_r^2$$

<table>
<thead>
<tr>
<th>Normal Paraffin</th>
<th>Iso Paraffin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>1.656069 E 02</td>
</tr>
<tr>
<td>$C_2$</td>
<td>-1.251350 E-01</td>
</tr>
<tr>
<td>$C_3$</td>
<td>1.229129 E-03</td>
</tr>
<tr>
<td>$C_4$</td>
<td>-2.514437 E-06</td>
</tr>
<tr>
<td>$C_5$</td>
<td>-3.059341 E 02</td>
</tr>
<tr>
<td>$C_6$</td>
<td>3.619207 E 02</td>
</tr>
<tr>
<td>$C_7$</td>
<td>-2.037743 E 02</td>
</tr>
<tr>
<td>$C_8$</td>
<td>-3.969312 E-01</td>
</tr>
<tr>
<td>$C_9$</td>
<td>-4.137364 E-05</td>
</tr>
<tr>
<td>$C_{10}$</td>
<td>3.382912 E-01</td>
</tr>
</tbody>
</table>

Constraints: $50 < v_i < 180$  $70 < v_i < 180$

$0.50 < T_r < 0.80$  $0.50 < T_r < 0.80$
<table>
<thead>
<tr>
<th>Source</th>
<th>Temperature (°C)</th>
<th>$u^P/u^T \times 100$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weimer - Prausnitz</td>
<td>45</td>
<td>39.0</td>
</tr>
<tr>
<td>Helpinstill - Van Winkle</td>
<td>45</td>
<td>38.0</td>
</tr>
<tr>
<td>Meyer - Wagner</td>
<td>51</td>
<td>31.2</td>
</tr>
<tr>
<td>DeAcetis</td>
<td>-</td>
<td>17.0</td>
</tr>
<tr>
<td>Equation (7)</td>
<td>40</td>
<td>11.5</td>
</tr>
</tbody>
</table>

The first two values are based on the same model. If they were obtained from an iso rather than a normal paraffin plot, as indicated by the fact that isobutane is the homomorph of acetone, the values would ordinarily be increased. Because the volume of acetone falls out of the range of iso paraffins, the ratio can not be obtained in this way. Weimer and Prausnitz assumed a negative residual term as shown in equation (II-110) to reduce the value of the exchange energy to the proper level. Nevertheless, it is very difficult to generate consistent results using this approach. A major advantage of the proposed model is that it does not require a negative residual term. The methods of Meyer and Wagner, also of DeAcetis do not lend themselves to general application.

The accuracy of the proposed model depends on the importance of the functional group with respect to the molecule. In general, the first member of an organic family may require some adjustment. It has been observed that, if the critical compressibility factor is $z_c < 0.250$, the nonpolar contribution is overcalculated somewhat. For $z_c > 0.280$, the nonpolar contribution is undercalculated. A standard means of adjusting the homomorphic prediction could be developed using $z_c$. However, for best results the homomorphic acentric factor should
be adjusted. The following changes have been made:

<table>
<thead>
<tr>
<th>compound</th>
<th>true value</th>
<th>adjusted value</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>0.185</td>
<td>0.165</td>
</tr>
<tr>
<td>pyridine</td>
<td>0.212</td>
<td>0.190</td>
</tr>
<tr>
<td>chloroform</td>
<td>0.185</td>
<td>0.200</td>
</tr>
<tr>
<td>dibromomethane</td>
<td>0.152</td>
<td>0.207</td>
</tr>
</tbody>
</table>

For quasi-ideal systems which contain polarity but not significant chemical effects, the geometric mean deviation factor will be taken as zero. The way in which the homomorphic model was applied allows this statement to be made. The total number of parameters that must be considered in a general correlation is decreased. For simple polar systems, the problem reduces to effective volume correlation. Here, the change in the multiplication factor, which again is to be applied to the pure component volume, may depend on polarity as well as molecular shape. It has been observed that $M_F$ is directly proportional to the following measure of polarity: the ratio of $u(\text{polar})$ to the total cohesive energy. This property will be referred to as the degree of polarity, $d_{p_1}$. It has proved useful in dealing with the effective volumes of polar families.

The term quasi-ideal implies that there are no significant chemical effects present. However, the following exceptions have been observed: combinations of ketones or esters with aromatics or carbon tetrachloride. The exchange energy is greatly reduced in value but remains positive. Nevertheless, the modeling of these cases is similar to that of negative systems. The appropriateness of applying a physically oriented model here can only be justified on the basis that
equilibrium prediction within the limits of engineering accuracy results. Certain negative systems will be correlated simultaneously with quasi-ideal. The following terms are available for describing chemical effects in an empirical manner: \( \lambda_1 \lambda_2 \), \( \lambda_1 \tau_j \) and \( \tau_1 \tau_2 \). The term \( \tau_1 \tau_2 \) has proven ineffective for this purpose. The best one is \( \lambda_1 \lambda_2 \); that is, chemical effects will be modeled in terms of the geometric mean derivation factor which has been made available for this function. The term \( \lambda_1 \lambda_2 \) will assume a constant value depending on the chemical effect implied by the binary combination. For this study three parameters were required.

A correlation has been established for quasi-ideal systems based on the concepts outlined thus far. The coefficients are listed in table (2). The supporting data is compiled in table (3) of appendix D. The latter compares the correlation coefficients for each binary system when the parameters are first predicted and then allowed to seek their best fit values.

D. POSITIVE SYSTEMS

It is proposed that positive systems can be treated as simple polar mixtures if the homomorphic acentric factors are properly adjusted. An arbitrary division of the pure component cohesive energy into apparent polar and nonpolar contributions accounts for the effect of dissociation in a manner similar to applying a geometric mean deviation factor. It was anticipated that building a consistent model of the exchange energy for these systems might require that a composition dependency be included. Dissociation should be a function of the amount of diluent present. Alcohol-inert mixtures were studied
Table (2)
Quasi-Ideal System Correlation

Basis: \( q_{\text{benzene}} = v_{\text{benzene}} \)

\[ q_{\text{paraffin}} = (1.212 - 0.807bp_i + 0.534bp_i^2) v_i \]

\[ q_i = MF_i \cdot v_i \]

\[ r^2 = 0.9851 \]
867 points

<table>
<thead>
<tr>
<th>Component(s)</th>
<th>MF (_i^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ketone</td>
<td>1.661 + 0.453 dp(_i)</td>
</tr>
<tr>
<td>ester</td>
<td>1.339 + 2.485 dp(_i)</td>
</tr>
<tr>
<td>ether</td>
<td>1.14</td>
</tr>
<tr>
<td>polar chloro - and bromo-</td>
<td>1.148 + 1.496 dp(_i)</td>
</tr>
<tr>
<td>hydrocarbons</td>
<td></td>
</tr>
<tr>
<td>ethyl iodide</td>
<td>1.050</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0.909</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>1.490</td>
</tr>
<tr>
<td>pyridine</td>
<td>1.406</td>
</tr>
<tr>
<td>ketone - aromatic</td>
<td>-0.0797</td>
</tr>
<tr>
<td>miscellaneous:</td>
<td>-0.0558</td>
</tr>
<tr>
<td>ketone - CCL4</td>
<td></td>
</tr>
<tr>
<td>ester - CCL4</td>
<td></td>
</tr>
<tr>
<td>ester - aromatic</td>
<td></td>
</tr>
<tr>
<td>negative system</td>
<td>-0.0664</td>
</tr>
</tbody>
</table>
point by point to observe the effect of composition on the apparent value of $u$(nonpolar). It was found that the exchange energy could be considered as composition independent. For some cases, this will lead to error in the dilute regions; however, a general model of this effect is difficult to obtain. Again, the appropriateness of using a physically oriented approach is suspect. However, some useful results have been obtained.

The combination of alcohols with paraffins or carbon tetrachloride was considered here. The effective volume parameters previously developed for these nonpolar compounds were retained. An objective was to define consistent homomorphic acentric factors and effective volumes for alcohols. Experimental data was selected for analysis only in the range: $0.05 < x < 0.95$. A slight solvation effect between alcohols and carbon tetrachloride was observed; however, it need not be evaluated to obtain accurate results. The following parameters were correlated:

**Basis:**

<table>
<thead>
<tr>
<th>Basis</th>
<th>$\mathbf{l}_{12}$</th>
<th>$q_{\text{CCL4}}$</th>
<th>$q_{\text{paraffin}}$</th>
<th>$q_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>1.091 $v_{\text{CCL4}}$</td>
<td>$(1.212 - 0.807 b_{p_{i}} + 0.534 b_{p_{i}}^2)v_{i}$</td>
<td>$MF_{i}v_{i}$</td>
</tr>
</tbody>
</table>
Alcohol & MF & $\omega$ & n propanol & 2.34 & 0.514 \\
& &  & iso propanol & 2.15 & 0.546 \\
& &  & n butanol & 2.09 & 0.543 \\

The supporting data is compiled in table (4), appendix D. The comparison given there is based on all experimental points. The marked change in MF from ethanol to n propanol can be explained in terms of degree of polarity. Figure (2) shows the relationship between MF and $d_p$ where the latter has been calculated at the same reduced temperature. It indicates that the effective volume of alcohols can be modeled as a function of $d_p$. Using the same experimental basis and data as before:

$$ q_{\text{alcohol}} = (0.0579 + 22.00 d_p - 21.01 d_p^2) v_f $$

and $r^2 = 0.9834$

Although this approach is a simple extension of concepts appropriate to quasi-ideal systems, it has been shown as very effective in describing solution nonideality for these cases.

E. ALTERNATE METHODS

Other approaches to vapor liquid equilibrium prediction were studied in this investigation. The Gilmont - Zudkevitch - Othmer method was described in detail in chapter III. It proved to be completely unsatisfactory. The same observation has been made elsewhere.
Figure 2 Volume correction according to polar extent for the alcohol family.
The problem appears to be related to the form of the exchange energy that was selected. According to equation (III-45),

$$A_{12}' = \left( \sqrt{\alpha u_1} - \sqrt{\alpha u_2} \right)^2$$  \hspace{1cm} (10)

where $\alpha = \left( \frac{[P_1]}{[P_2]} \right)^{2/3}$

The above expression should predict values that are too high for positive or negative systems, too low for simple polar systems. Apparently, the field factors are unable to adjust for this tendency in a regular manner.

The Barker model\textsuperscript{16,17} has been studied with respect to quasi-ideal, negative and positive systems. For vapor liquid equilibrium prediction, it requires that the following be specified: (a) the coordination number, (b) the external contacts of each molecule, and (c) the exchange energies. Questions of coordination and external contacts were considered in chapter II. The logic of subroutine BARKER indicates most of the assumptions that have been taken in applying this model. A single physical-effects exchange energy was allowed. For each distinct chemical effect, an additional one was added. The relationship between the Barker and regular solution models has previously been emphasized. In the absence of significant chemical effects, the major difference is volume concept. In this case equations (II-80) and (II-81) imply that:

$$A_{12}(\text{Barker}) \equiv \frac{A_{12}'}{2} \left[ \frac{1}{Q_1} + \frac{1}{\alpha Q_2} \right]$$  \hspace{1cm} (11)

The term $A_{12}(\text{Barker})$ is simply the exchange energy associated with
the Barker model; \( Q_i \) was previously defined as the number of external contact points of type \( i \). Equation (11) should be regarded as the relationship between the physical effects energies of these approaches. For quasi-ideal systems, the best fit value for the Barker model can be closely estimated from this expression. In general, the Barker model can fit equilibrium data no better than the general approach proposed here. Often, it is less effective due to the fact that the concept of site was developed from the pure component rather than the effective volume. Even if this were corrected, the simpler general model would be preferred to the highly implicit Barker expression. However, because it does give chemical effects formal representation, it is interesting to compare these values with the ones generated by the proposed approach. It indicates that the concepts presented here are appropriate at least in a quantitative manner.

The Wehe-Coates method was discussed in chapter II. It is restricted only in the sense that it is homologous series approach. It can be applied regardless of the chemical effects which may be present. It was decided that the method could be used to best advantage if both isothermal and isobaric data in the neighborhood of the desired system pressure could be applied. The symmetry factor and the exchange energy are relatively insensitive to change in temperature. Therefore, it is recommended that they be selected as the independent variables and fit to the equilibrium data according to the weighted least squares method which has been followed here. Let \( T_{B1} \) represent the boiling point at component \( i \) at the desired pressure, \( T_{BS} \) for the solvent, then the ordinates for each dilute condition with respect to the Wehe-Coates
The adjusted vapor pressures must be evaluated at the appropriate pressure, temperature and composition. The Wehe-Coates method has been found to be an effective means of predicting vapor liquid equilibrium. Figures (3) through (8) illustrate the plots for a variety of systems.
Reciprocal Boiling Point of Paraffin

Figure 3 Wehe-Coates Plot for dioxane-paraffin mixtures.
Figure 4. Wehe-Coates Plot for acetone-aromatic mixtures.
Figure 5: Wehe-Coates Plot for 12 dichloroethane-alcohol mixtures.
Reciprocal Bolling Point of Alcohol

Figure 6: Wehe-Coates Plot for ethyl acetate-alcohol mixtures.
Figure 7 Wehe-Coates Plot for pyridine-paraffin mixtures.
Reciprocal Boiling Point of Paraffin

Figure 8 Wehe-Coates Plot for acetone-paraffin mixtures.
CHAPTER V REFERENCES


CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

As a result of this work, it is possible to predict solution non-ideality for many binary systems from pure component properties only. It has been shown that the effect of polarity on the exchange energy can be treated in a general manner so that a regular solution related model can be applied to polar systems with practically useful results. In general, a Flory-Huggins size correction is necessary to stabilize the apparent contributions to the exchange energy so that they can be modeled. The major difficulty involved in the proposed method is that the homomorphic acentric factor must be adjusted for associated liquids. However, it is a consistent property for both associated and unassociated compounds and may be established from reliable vapor liquid equilibrium data. The homomorphic concept provides a convenient basis for dealing with quasi-ideal and positive systems.

The effective volume was also found to be a consistent property. It can be treated as a continuous function within an organic family. However, it appears that the family concept can be applied in a less restricted manner. For example, it may be possible to correlate the effective volumes of pyridine, aryl halides, and aromatics with a single expression due to similarity of form.

A point that has not been justified with respect to the proposed method was the geometric mean assumption taken for polar-polar interaction. As its basis was semitheoretical, it should be examined as the appropriate data becomes available.

The approach taken here was based on a division of binary mixtures
into quasi-ideal, negative, positive, and complex systems. Further investigation should proceed on these lines. Negative systems were considered only on a preliminary basis. An understanding of negative systems may be a prerequisite to modeling complex systems.

Whereas extension of this approach to complex systems will be difficult, the homologous series method developed by Wehe and Coates can be used no matter what chemical effects are present. It appears that the Wehe-Coates method is the preferred one in complex system prediction at the current state of the art.
SELECTED BIBLIOGRAPHY


APPENDIX A

CALCULATION OF PHYSICAL PROPERTIES

Solubility Parameter

A pure component property fundamental to regular and related solutions is the solubility parameter $\delta$. As indicated in chapter II, the theoretical basis of these solution models is suspect. Consequently, the solubility parameter need not be rigorously calculated, but it should be treated in a reasonably accurate and consistent manner. This property is simply related to the energy of complete vaporization and the saturated liquid volume.

by definition,

$$\delta = \frac{U}{V}$$

Let $u^o$ be the molal energy of the ideal gas, while $u_G^*$ and $u_L^*$ are the saturated state molal energies of the gas and liquid respectively.

then,

$$u = u^o - u_L^*$$

or,

$$u = \Delta u^v + (u^o - u_G^*)$$

remembering that $h = u + zRT$,

$$u = \Delta h^v - RT \Delta V^v + (u^o - u_G^*)$$

The heat of vaporization is usually calculated from saturated vapor pressure data according to the Clapeyron equation:

$$\frac{dp^*}{dT} = \frac{\Delta h^v}{T\Delta V^v}$$
equivalently,

$$\frac{d \ln p^*}{dT} = \frac{\Delta h^v}{RT^2} \frac{\Delta z^v}{v}$$

(6)

combining equations (4) and (6),

$$u = RT \Delta z^v \left[ T \frac{d \ln p^*}{dT} - 1 \right] + (u^o - u_G^*)$$

(7)

dividing by v,

$$\delta^2 = \left[ \frac{z^*RT}{v} - p^* \right] \left[ T \frac{d \ln p^*}{dT} - 1 \right] + \frac{(u^o - u_G^*)}{v}$$

(8)

It will be convenient to consider equation (8) as the sum of three terms:

$$\text{term 1} = \frac{z^*RT}{v} \left[ T \frac{d \ln p^*}{dT} - 1 \right]$$

(9)

$$\text{term 2} = -p^* \left[ T \frac{d \ln p^*}{dT} - 1 \right]$$

(10)

$$\text{term 3} = \frac{(u^o - u_G^*)}{v}$$

(11)

In order to compare these contributions to the true value of $\delta^2$ for a given temperature, the following properties must be calculated:

$v$, $p^*$, $z^*$, and $(u^o - u_G^*)$. The saturated liquid volume is considered in the next section. The Antoine equation will be used to describe vapor pressure data in this report:

$$\log p^* = a - \frac{b}{t+c}$$

(12)

where $a, b, c =$ Antoine constants

$t =$ temperature ($^\circ$C)
The Antoine constants are listed in table (3). The compressibility factor of the saturated gas can be estimated from the virial equation of state:

\[ z = \frac{\pi v_G}{RT} = 1 + \frac{B}{v_G} + \frac{C}{v_G^2} + \ldots \] (14)

where \( v_G \) = molal volume of the gas

- \( B \) = second virial coefficient
- \( C \) = third virial coefficient

For low to moderate pressure systems, only \( B \) needs to be considered. Then,

\[ z^* = 1 + \frac{Bp^*}{z^* RT} \] (15)

Solving for \( z^* \),

\[ z^* = \frac{1}{2} \left[ 1 + \sqrt{1 + \frac{4Bp^*}{RT}} \right] \] (16)

An excellent correlation for the second virial coefficient of pure, nonpolar gases has been given by Pitzer and Curl.\(^1\) It has the form:

\[ B = \frac{RT_c}{p_c} \left[ f^I(T_r) + \omega f^{II}(T_r) \right] \] (17)

The functions \( f^I(T_r) \) and \( f^{II}(T_r) \) are stated in subroutine VIRIAL. Again \( \omega \) is the acentric factor.
An expression for \( u^0 - u_G^* \) can be derived from the thermodynamic functions given by Hirschfelder, Buehler, McGee, and Sutton. The resulting relation is:

\[
(u^0 - u_G^*) = \frac{P_c V_c^2}{v_G^*} \left[ k_o + \frac{2k_1}{T_r} - \frac{k_2}{T_r} \frac{v_c^*}{v_G^*} \right] 
\]

where \( k_o = 4.71 \)

\[ k_1 = \beta - k_o \]

\[ k_2 = \frac{(1 - k_o - \alpha + 2 \beta)}{2} \]

\[ \alpha = \text{Riedel factor} \]

\[ \beta = f(z_c) \]

also,

\[ z_c = \frac{B(3B-1)}{(B+1)^3} \]  \hspace{1cm} (19)

and,

\[ v_G^* = \frac{z RT}{p} \]  \hspace{1cm} (20)

The relationships developed thus far are best applied to non-polar compounds whose properties have been well established. For these cases, the contributions to \( \delta^2 \) can be properly evaluated. Much of the required pure component data is listed in table (4), the remainder was obtained elsewhere. Table (1) compares the terms defined by equations (9,10,11) for the range of interest: 0.5 \( \leq T_r \leq 0.8 \). Terms 2 and 3 are very much smaller than term 1 moreover are opposite in sign so that their net effect is a negligibly small positive value. If \( \delta^2 \) is modeled as simply term 1, the maximum error will occur at
Table 1

Contributions to the Solubility Parameter

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tr</th>
<th>Term 1</th>
<th>Term 2</th>
<th>Term 3</th>
<th>$\delta_i^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethane</td>
<td>0.50</td>
<td>67.78</td>
<td>-0.033</td>
<td>0.057</td>
<td>67.81</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>58.06</td>
<td>-0.204</td>
<td>0.318</td>
<td>58.17</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
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<td>-0.681</td>
<td>1.008</td>
<td>48.44</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>37.29</td>
<td>-1.603</td>
<td>2.333</td>
<td>38.02</td>
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<td>butane</td>
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<td>-0.015</td>
<td>0.025</td>
<td>64.09</td>
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<tr>
<td></td>
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<td>0.183</td>
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<td>44.74</td>
</tr>
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<td>hexane</td>
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<td>61.92</td>
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<td>0.463</td>
<td>42.41</td>
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<td>0.80</td>
<td>32.43</td>
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<td>1.302</td>
<td>32.78</td>
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<td>octane</td>
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<tr>
<td></td>
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<td>-0.045</td>
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<td>49.74</td>
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<td></td>
<td>0.70</td>
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<td>-0.239</td>
<td>0.323</td>
<td>40.54</td>
</tr>
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<td></td>
<td>0.80</td>
<td>30.93</td>
<td>-0.760</td>
<td>1.003</td>
<td>31.17</td>
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<tr>
<td>isobutane</td>
<td>0.50</td>
<td>59.89</td>
<td>-0.016</td>
<td>0.025</td>
<td>59.90</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>50.36</td>
<td>-0.122</td>
<td>0.177</td>
<td>50.42</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>41.27</td>
<td>-0.462</td>
<td>0.639</td>
<td>41.45</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>31.72</td>
<td>-1.171</td>
<td>1.606</td>
<td>32.16</td>
</tr>
<tr>
<td>isopentane</td>
<td>0.50</td>
<td>59.92</td>
<td>-0.011</td>
<td>0.020</td>
<td>59.93</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>50.26</td>
<td>-0.100</td>
<td>0.154</td>
<td>50.31</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>41.21</td>
<td>-0.405</td>
<td>0.590</td>
<td>41.40</td>
</tr>
<tr>
<td></td>
<td>0.80</td>
<td>31.75</td>
<td>-1.077</td>
<td>1.537</td>
<td>32.21</td>
</tr>
<tr>
<td>benzene</td>
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<td>88.78</td>
<td>-0.018</td>
<td>0.029</td>
<td>88.79</td>
</tr>
<tr>
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<td>0.60</td>
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<td>-0.152</td>
<td>0.228</td>
<td>73.81</td>
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<td>0.70</td>
<td>59.92</td>
<td>-0.608</td>
<td>0.867</td>
<td>60.18</td>
</tr>
<tr>
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<td>0.80</td>
<td>45.72</td>
<td>-1.593</td>
<td>2.239</td>
<td>46.36</td>
</tr>
</tbody>
</table>
the upper boundary, $T_r = 0.8$, and should be $< 1.5\%$. Therefore, equation (8) can be reduced to a more convenient form:

$$
\delta^2 = \frac{u}{v} = \frac{z^*RT}{v} \left[ T \frac{d \ln p^*}{dT} - 1 \right]
$$

Equation (21) has been selected to represent the solubility parameter in this investigation. The major problem will be to accurately predict $z^*$ for polar and/or uncommon substances. An approach that is frequently used is to assume $z^* = 1$; however, this will lead to serious error when $T_r > 0.60$. The Pitzer - Curl correlation has been extended to polar systems by O'Connell and Prausnitz. Their method will be described shortly.

It should be mentioned that a generalized correlation for the solubility parameter as well as the saturated liquid volume is available, appropriate for nonpolar or slightly polar compounds.

Liquid Density

Three methods of liquid density calculation are given in subroutine PROPS. The first two are preferred because they are based on experimental data. The third is a generalized approach to prediction where a single density measurement has been selected as a reference. The variation of density with temperature is frequently described with a polynomial:

$$
\rho = a_0 + a_1t + a_2t^2 + \ldots
$$

where $\rho$ = saturated liquid density

$a_0$, $a_1$, $\ldots$ = constants
Usually the quadratic form is applied. If appropriate data is available, the constants can be readily obtained by multiple linear regression. Table (5) lists these coefficients for the relevant cases. Francis has taken a less conventional approach. He proposed that the following expression would allow saturated density data to be modeled at all temperatures less than \( \sim 20^\circ C \) of critical:

\[
\rho = a_0 + a_1 t - \frac{a_2}{a_3 - t}
\]  

(23)

Francis gathered and correlated data for 130 diverse pure liquids. The mean error was \( \equiv 0.1\% \). Most compounds studied here are treated according to these constants.

Even for uncommon substances, at least one measurement, usually at \( 20^\circ \) or \( 25^\circ C \), can be located. Then a generalized approach can be applied with reasonable accuracy using this value as a reference condition according to the identity:

\[
\frac{\rho_1}{\rho_{r1}} = \frac{\rho_2}{\rho_{r2}}
\]  

(24)

Lydersen, Greenkorn, and Hougen developed a generalized correlation for liquid density using the critical compressibility factor as the third parameter. They presented the results in a series of tables. The saturated state values have been placed in a more convenient form by Wicks:

\[
\rho_r = 1.20 + (5.563 - 11.03 z_c)(1-T_r) 0.800 z_c + 0.310
\]  

(25)

constraints:

\[
0.25 \leq z_c \leq 0.29
\]

\[
T_r \leq 0.99
\]
The use of equation (25) in conjunction with (24) has been tested. Table (2) describes the error, where the values generated by the Francis method are assumed to be correct. The reference densities required in this study are listed in table (6).

Whatever method is used, the molal volume is immediately known. If \( MW \) represents the molecular weight:

\[
v = \frac{MW}{\rho}\quad (26)
\]

**Adjusted Vapor Pressure**

In 1952 the term adjusted vapor pressure was suggested by Redlich, Kister and Turnquist\(^{11}\), and given the form:

\[
p_i^* = p_i^* \frac{\phi_i^*}{\phi_i} \exp \left[ v_i \frac{(\pi - p_i^*)}{RT} \right] \quad (27)
\]

where \( \phi_i \) = vapor phase fugacity coefficient of component \( i \)

then, for a real system,

\[
y_i^* = y_i x_i p_i^* \quad (28)
\]

The exponential term is often referred to as the Poynting correction. Equation (27) may be regarded as thermodynamically rigorous except that the Poynting correction has been simplified in the usual manner. The fugacity coefficient can be stated exactly:\(^{12}\)

\[
\ln \phi_i = \frac{1}{RT} \int_{V_G}^{\infty} \left[ \frac{\partial \pi}{\partial n_i} - \frac{RT}{V_G} \right] dV_G - \ln z \quad (29)
\]

A useful expression can be derived from this relation if a pressure explicit equation of state such as equation (14) is applied:
### Table (2)

**Test of Wicks Equation**

**Basis:** Reference Density Selected at 25°C

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tr</th>
<th>true density (g/ml)</th>
<th>estimated density (g/ml)</th>
<th>error</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>0.50</td>
<td>0.8330</td>
<td>0.8321</td>
<td>-0.101</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.7758</td>
<td>0.7764</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.7143</td>
<td>0.7131</td>
<td>-0.163</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>0.50</td>
<td>0.9383</td>
<td>0.9376</td>
<td>-0.081</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.8746</td>
<td>0.8749</td>
<td>0.041</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.8064</td>
<td>0.8040</td>
<td>-0.296</td>
</tr>
<tr>
<td>ethyl ether</td>
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<td>0.7800</td>
<td>0.7827</td>
<td>0.345</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.7291</td>
<td>0.7305</td>
<td>0.189</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.6740</td>
<td>0.6714</td>
<td>-0.391</td>
</tr>
<tr>
<td>benzene</td>
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<td>0.8919</td>
<td>0.8910</td>
<td>-0.100</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.8319</td>
<td>0.8320</td>
<td>0.004</td>
</tr>
<tr>
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<td>0.7680</td>
<td>0.7655</td>
<td>0.325</td>
</tr>
<tr>
<td>chlorobenzene</td>
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<td>1.0820</td>
<td>1.0819</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>1.0120</td>
<td>1.0099</td>
<td>-0.206</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.9358</td>
<td>0.9286</td>
<td>-0.765</td>
</tr>
<tr>
<td>hexane</td>
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<td>0.6937</td>
<td>0.6948</td>
<td>0.160</td>
</tr>
<tr>
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<td>0.60</td>
<td>0.6483</td>
<td>0.6485</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.5993</td>
<td>0.5963</td>
<td>-0.504</td>
</tr>
<tr>
<td>cyclohexane</td>
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<td>0.7945</td>
<td>0.7936</td>
<td>-0.109</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>0.7410</td>
<td>0.7410</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>0.6840</td>
<td>0.6816</td>
<td>-0.345</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>0.50</td>
<td>1.6230</td>
<td>1.6216</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>1.5149</td>
<td>1.5141</td>
<td>0.049</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>1.3991</td>
<td>1.3929</td>
<td>-0.445</td>
</tr>
<tr>
<td>chloroform</td>
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<td>1.5355</td>
<td>1.5343</td>
<td>-0.079</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
<td>1.4329</td>
<td>1.4342</td>
<td>0.087</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>1.3232</td>
<td>1.3218</td>
<td>-0.101</td>
</tr>
</tbody>
</table>
Table (3)

Antoine Constants

<table>
<thead>
<tr>
<th>Compound</th>
<th>Range(°C)</th>
<th>a</th>
<th>b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>5 to 95</td>
<td>7.16746</td>
<td>1236.19</td>
<td>232.26</td>
</tr>
<tr>
<td>butyl acetate</td>
<td>60 to 127</td>
<td>7.06707</td>
<td>1396.06</td>
<td>207.28</td>
</tr>
<tr>
<td>carbon disulfide</td>
<td>0 to 80</td>
<td>6.94484</td>
<td>1170.28</td>
<td>241.73</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>5 to 120</td>
<td>6.78897</td>
<td>1159.30</td>
<td>219.86</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>60 to 180</td>
<td>6.97825</td>
<td>1430.30</td>
<td>217.37</td>
</tr>
<tr>
<td>chloroform</td>
<td>0 to 100</td>
<td>7.08386</td>
<td>1238.02</td>
<td>233.39</td>
</tr>
<tr>
<td>dioxane</td>
<td>20 to 125</td>
<td>7.34721</td>
<td>1500.76</td>
<td>234.75</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>20 to 130</td>
<td>6.99515</td>
<td>1187.81</td>
<td>211.53</td>
</tr>
<tr>
<td>isopropyl ether</td>
<td>20 to 70</td>
<td>6.76963</td>
<td>1105.09</td>
<td>215.71</td>
</tr>
<tr>
<td>methyl acetate</td>
<td>5 to 100</td>
<td>7.07597</td>
<td>1165.67</td>
<td>220.76</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>0 to 100</td>
<td>7.09490</td>
<td>1279.93</td>
<td>224.14</td>
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<tr>
<td>methyl isobutyl ketone</td>
<td>20 to 143</td>
<td>6.66821</td>
<td>1175.11</td>
<td>193.68</td>
</tr>
<tr>
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<td>45 to 102</td>
<td>6.96683</td>
<td>1254.83</td>
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<tr>
<td>pyridine</td>
<td>45 to 117</td>
<td>6.89438</td>
<td>1286.39</td>
<td>205.06</td>
</tr>
</tbody>
</table>

Antoine constants for those compounds not listed above were taken from the well known compilations of the American Petroleum Institute, and the Manufacturing Chemists Association.
Table (4)

Tabulation of Pure Component Constants

<table>
<thead>
<tr>
<th>Compound</th>
<th>ID</th>
<th>Tc(°K)</th>
<th>pc(atm)</th>
<th>vc(cc/gmole)</th>
<th>w_c</th>
<th>w_h</th>
<th>μ</th>
<th>η</th>
<th>[F]</th>
</tr>
</thead>
<tbody>
<tr>
<td>methanol</td>
<td>2</td>
<td>513.2</td>
<td>78.5</td>
<td>118.0</td>
<td>0.555</td>
<td>0.105</td>
<td>1.66</td>
<td>1.21</td>
<td>88.5</td>
</tr>
<tr>
<td>ethanol</td>
<td>2</td>
<td>516.0</td>
<td>63.0</td>
<td>167.0</td>
<td>0.636</td>
<td>0.152</td>
<td>1.69</td>
<td>1.10</td>
<td>127.</td>
</tr>
<tr>
<td>propanol</td>
<td>2</td>
<td>536.7</td>
<td>51.0</td>
<td>218.0</td>
<td>0.621</td>
<td>0.201</td>
<td>1.68</td>
<td>0.57</td>
<td>165.</td>
</tr>
<tr>
<td>isopropanol</td>
<td>2</td>
<td>508.2</td>
<td>47.0</td>
<td>220.0</td>
<td>0.667</td>
<td>0.185</td>
<td>1.66</td>
<td>0.80</td>
<td>164.</td>
</tr>
<tr>
<td>butanol</td>
<td>2</td>
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<td>43.6</td>
<td>275.0</td>
<td>0.589</td>
<td>0.252</td>
<td>1.65</td>
<td>0.45</td>
<td>204.</td>
</tr>
<tr>
<td>acetaldehyde</td>
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<td>461.0</td>
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<td>168.0</td>
<td>0.306</td>
<td>0.152</td>
<td>2.70</td>
<td>0.0</td>
<td>125.</td>
</tr>
<tr>
<td>acetone</td>
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<td>213.0</td>
<td>0.304</td>
<td>0.185</td>
<td>2.88</td>
<td>0.0</td>
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</tr>
<tr>
<td>methyl ethyl ketone</td>
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<td>0.217</td>
<td>2.87</td>
<td>0.15</td>
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</tr>
<tr>
<td>methyl isobutyl ketone</td>
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<td>36.1</td>
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<td>0.305</td>
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<td>0.50</td>
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</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>Compound</td>
<td>ID</td>
<td>Tc(°K)</td>
<td>pc(atm)</td>
<td>vc(cc/gmole)</td>
<td>w_c</td>
<td>w_h</td>
<td>μ</td>
<td>η</td>
<td>P</td>
</tr>
<tr>
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<td>--------------</td>
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</tr>
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<td>0.254</td>
<td>0.212</td>
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<td>0.20</td>
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<td>60.0</td>
<td>1.8426</td>
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<td>isopropanol</td>
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<td>0.6581</td>
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<td>0.7204</td>
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<td>methyl ethyl ketone</td>
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<td>methyl isobutyl ketone</td>
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<td>0.7249</td>
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<td>propyl bromide</td>
<td>30.0</td>
<td>1.33675</td>
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<td>propyl chloride</td>
<td>30.0</td>
<td>0.87994</td>
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<td>pyridine</td>
<td>90.0</td>
<td>0.9111</td>
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<tr>
<td>2,2,2 trimethyl butane</td>
<td>25.0</td>
<td>0.68588</td>
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</table>
for a moderate pressure,

\[ \frac{\pi}{RT} = \frac{1}{V_G} + \frac{B}{2V_G} \]  

(30)

or,

\[ \frac{\pi}{RT} = \frac{n_1 + n_1}{V_G} + \frac{n_1^2 B_{11} + 2n_1 n_i B_{1i} + n_1^2 B_{11}}{V_G^2} \]  

(31)

then,

\[ \frac{\delta \pi}{\delta n_i} = RT \left[ \frac{1}{V_G} + \frac{2 \Sigma n_i B_{1i}}{V_G^2} \right] \]  

(32)

combining equations (29) and (32),

\[ \ln \phi_i = \int \frac{2 \Sigma n_i B_{1i}}{V_G^2} \, dV_G - \ln z \]  

(33)

integrating,

\[ \ln \phi_i = \frac{2 \Sigma n_i B_{1i}}{V_G} - \ln z \]  

(34)

or,

\[ \ln \phi_i = \frac{2 \Sigma y_i B_{1i}}{V_G} - \ln (1 + B/V_G) \]  

(35)

also,

\[ \ln \phi_i^* = \frac{2 B_{1i}}{V_G^*} - \ln (1 + B_{1i}/V_G^*) \]  

(36)

According to equations (27, 35, 36), adjusted vapor pressure calculation reduces to the problem of estimating the second virial coefficients.
O'Connell and Prausnitz have developed a method which treats polar as well as nonpolar gases; it has the form:

\[
\frac{P_{ci}}{RT_{ci}} = f^I(T_r) + \omega_{H_1} f^{II}(T_r) + f^{III}(\mu_{ri}, T_r) + \eta_i f^{IV}(T_r) \tag{37}
\]

where \( \omega_{H_1} \) = acentric factor of the homomorph of \( i \)

\( \mu_{ri} \) = reduced dipole moment of \( i \)

\( \eta_i \) = association constant of \( i \)

by definition,

\[
\mu_{ri} = \frac{10^5 \mu^2_{i} P_{ci}}{T_{ci}^2} \tag{38}
\]

The first two functions are identical to the Pitzer-Curl correlation except that the homomorphic rather than the pure component acentric factor is selected. The third considers the additional effect of polarity, while the last function reflects the tendency of a component to associate with itself to form dimers. Equation (37) can also be used to estimate \( B_{12} \) if suitable mixing rules are established for the various properties. The functions are stated in subroutine VIRIAL.
APPENDIX A REFERENCES


Appendix B contains the subroutines necessary for the theoretical part of this investigation. These routines can be used to test vapor liquid equilibrium data for thermodynamic consistency, to develop and/or apply solution models, to predict the azeotropic condition from known properties only, etc. A sample main program is attached to indicate some of these uses. The subroutines are listed in the same order as the following descriptions.

Subroutine INPUT

INPUT should always be called first. It reads the required pure component properties then seeks vapor pressure, liquid density, and vapor liquid equilibrium data in turn. The Antoine equation is used to represent vapor pressure. If Antoine constants are not available, experimental data must be supplied. In this case, the constants are initialized using Thomson's rule and an estimate of the heat of vaporization at the normal boiling point, then best fit values are obtained via subroutine PATERN. Generalized correlations exist for vapor pressure; however, the importance of this property in the calculations presented here preclude their use. If liquid density data is given, POLY is called to generate the \((n+1)\) coefficients of \(nm\) degree polynomial. In testing and modeling equilibrium data additional properties will be required. It is convenient to call PROPS at this point to obtain these values.

Subroutine PATERN

PATERN is a general multivariable search routine. Its
form is an alternating series of exploratory and pattern moves. The
former involves perturbation about each independent variable in turn.
This establishes the pattern or direction of improvement with respect
to the objective function for each variable. Then, the pattern move,
an acceleration step, is executed based on the assumption that what­
ever constituted a successful set of moves in the past is likely again
to prove successful. If no better value of the objective function
can be found by either move type, the size of each exploratory step
is reduced by a factor of ten and the process repeated. This sub­
routine was adapted from one given by Moore et al.\textsuperscript{5} PATERN requires:
(a) a starting point, (b) initial step sizes, (c) number of step re­
ductions, and (d) a companion subroutine to evaluate the objective
function. Constraints are treated through a logical variable.

Subroutine GOLDEN

This routine is the golden section search plan described by Wilde.\textsuperscript{6}
It is a one dimensional, sequential search appropriate for a strictly
unimodal objective function. It has been programmed here for mini­
mization where the initial interval of uncertainty is defined and the
maximum acceptable length of the final interval is designated. GOLDEN
also required a separate routine for objective function evaluation.

Subroutine QFUNC

In general, the above stated search plans will be used to minimize
a weighted least squares objective function. QFUNC calculates its
value.

\[
Q = \sum_{i=1}^{N} \left[ w_i (z_i - \hat{A}_i)^2 \right] \quad (1)
\]
where $N =$ total number of data points

$w_i =$ weighting factor for $i$ th point

$z_i =$ observed value of dependent variable

$\hat{z}_i =$ estimated value of dependent variable

The form that the weighting factor should assume for correlation of vapor liquid equilibrium data has been studied. If $z = \ln \frac{\gamma_1}{\gamma_2}$, a simple but reasonable expression is:

$$w = \frac{32}{\left( \frac{1}{x_1^2 x_2^2} + \frac{1}{y_1^2 y_2^2} \right)} \quad (2)$$

QFUNC is simply a collection of objective functions. The appropriate one is located by the index NQ which is stored in common.

Subroutine POLY

While direct search is convenient for nonlinear regression, it is unnecessary for linear expressions such as a polynomial:

$$z = a_0 + a_1 x + a_2 x^2 + \ldots + a_m x^m \quad (3)$$

applying the weighted least squares method,

$$a_0 \Sigma w_i + a_1 \Sigma w_i x_1 + \ldots + a_m \Sigma w_i x_1^m = \Sigma w_i y_1$$

$$a_0 \Sigma w_i x_1 + a_1 \Sigma w_i x_1^2 + \ldots + a_m \Sigma w_i x_1^{m+1} = \Sigma w_i x_1 y_1$$

$$\vdots$$

$$a_0 \Sigma w_i x_1^m + a_1 \Sigma w_i x_1^{m+1} + \ldots + a_m \Sigma w_i x_1^{m+m} = \Sigma w_i x_1^m y_1 \quad (4)$$

POLY defines the augmented matrix of equation (4), then calls GUASS to obtain the solution vector of the coefficients $a_0, a_1, \ldots, a_m$. The
degree of the polynomial must be specified.

Subroutine GUASS

Frequently a set of simultaneous linear algebraic equations must be solved. Here, Gaussian elimination using the largest pivot element is applied. The logic was developed elsewhere.\(^9\)

Subroutine FIT

This routine calculates the multiple correlation coefficient:

\[
r^2 = 1 - \frac{\sum w_i (z_i - \bar{y}_i)^2}{\sum w_i z_i^2 - (\sum w_i z_i)^2} \quad (5)
\]

Subroutine VIRIAL

This subroutine calculates the second virial coefficients for the binary mixture. It has been taken almost directly from Prausnitz et al.\(^{10}\) It represents an extension of the Pitzer-Curl correlation to polar systems as proposed by O'Connell and Prausnitz.

Subroutine PROPS

PROPS calculates such properties as the solubility parameter, liquid density, and adjusted vapor pressure. These are treated as outlined in Appendix A. Consequently, this subroutine requires VIRIAL. An ENTRY statement allows only those properties which depend on vapor phase composition or system pressure to be recalculated at a fixed temperature. PROPS includes a generalized correlation for the saturated vapor phase fugacity coefficient.\(^{11}\)

It has the form:

\[
\ln \phi_i^* = f^I(T_p) + w_i f^{II}(T_p) \quad (6)
\]
Subroutine TEST

In this routine, vapor liquid equilibrium data is tested for thermodynamic consistency by Harington's method.\textsuperscript{12,13} His approach is the familiar area test generalized to include isobaric systems. Here, the data is fit to a nm degree polynomial where nm must be specified. The appropriate areas can then be calculated and the test applied. This method appears to be satisfactory with the exception of near ideal systems.

Subroutine BARKER

This subroutine initiates the search for the exchange energies associated with the Barker model described in chapter II. It is divided into sections according to the interactions that must be considered: quasi-ideal, negative, and positive systems. In the first, the single physical-effect energy is obtained via subroutine GOLDEN. Where a significant chemical effect is anticipated, a corresponding energy is added and subroutine PATERN is required. In either case, equation (II-74) must be solved for all experimental points for each set of values. Subroutine NEWTON has been programmed for this special purpose. The final values are printed.

Subroutine NEWTON

This routine employs the Newton-Raphson method\textsuperscript{14} to solve equation (II-74) which is now restated:

\[
\sum_{i} x_{i} \sum_{j} x_{j} \eta_{ij} = \frac{Q_{4} x_{k}}{2}
\]

let,

\[
f_{i} = x_{i} \left[ x_{i} + \sum_{j} x_{j} \eta_{ij} \right] - \frac{Q_{4} x_{k}}{2} = 0
\]
linearizing,

\[
\sum_i \left[ \frac{\Delta f_i}{\Delta x_j} = \Delta x_j \right]
\] (9)

NEWTON defines the augmented matrix of equation (9), then calls GUASS to obtain the solution vector of \( \Delta x_j \). The process is repeated until all \( \Delta x_j \) are zero.

**Subroutine AZEO**

This subroutine predicts the azeotropic condition for isobaric systems from pure component properties only. The isothermal case would be easier to treat. For regular and related solutions, equation (III-9) yields the azeotropic temperature by trial and error. GOLDEN is applied for this purpose. Then, the Kireev equation or its equivalent calculates the azeotropic composition directly. The Gilmont-Zudkevitch-Othmer correlation \(^{15}\) can also predict azeotropy. Here, the variables temperature and composition are searched simultaneously using PATERN. The field factors are stated in subroutine QFUNC. Another approach that lends itself to computer application is the one proposed by Johnson and Madonis. \(^{16}\) All calculations are direct for their method.
SAMPLE MAIN PROGRAM

LOGICAL LV
REAL MU,MW,P(4),STEP(4)
COMMON LV(5),I,J,NQ,C(7,2),CL,MW(2),PCR(2),R,TBK(2),dC(2),RATIO
COMMON /A/ANAM(8),AREF(9),TPEXP,W1EXP
COMMON /B/N,Z(50),E(50),W(50),X(50),Y(50),PI(50),TPK(50),TP(50)
COMMON /C/T(2,2),PC(2,2),WC(2),WH(2),MU(2),ETA(2)
COMMON /D/VPCORR(50,2),VOL(50,2),U(50,2),SOLP(50,2)
COMMON /E/TPREF(2),DNREF(2)
COMMON /F/QP(6),ID(2),M(6,6),S(2)/G/T(4),TBH,TBL

READ DATA AND TEST FOR THERMODYNAMIC CONSISTENCY

CALL INPUT
IF (.NOT. LV(2)) GOTO1C
CALL TEST(2)

FIND PARAMETERS OF EQUATION (V-5)

A=T(1)
B=-(T(1)+T(2)+T(3)+T(4))
P(1)=A/B
I=N/2
P(2)=A*TPK(I)
IF (ABS(A)*GT.0.070 AND ABS(B)*GT.0.070) GOTO1
P(1)=VOL(I,1)/VCL(I,2)
P(2)=VOL(I,1)*(SOLP(I,1)-SOLP(I,2))**2
1 DO2 J=1,2
2 STEP(J)=I*P(J)
NQ=3
CALL PATERN(3,2,P,STEP)
CALL FIT

C
C WEHE-COATES PLOT
C
DO5K=1,2
I=N+K
X(I)=FLOAT(K-1)
Y(I)=X(I)
PI(I)=760.
TPK(I)=TBK(3-K)
DO5J=1,2
CALL PROPS(TPK(I))
A12=P(2)
GAM1=A12/(R*TBK(2)) + ALG(P(I)) + 1. - P(1)
GAM2=A12/(P(1)*R*TBK(1)) + ALG(1.0/P(1)) + 1. - 1. - P(1)
Y1=GAM1 + ALG(VPCORR(N+1,1)/760.)
Y2=GAM2 + ALG(VPCORR(N+2,2)/760.)
RTP1=1.0/TBK(2)
RTP2=1.0/TBK(1)
PRINT 11,Y1,Y2,RTP1,RTP2

C
CALL BARKER
CALL AZED
STOP
END

SUBROUTINE INPUT
LOGICAL LV
REAL LB,MU,MW,P(4),STEP(4),VC(2)
COMMON LV(5),I,J,NQ,C(7,2),CL,MW(2),PCR(2),R,TPK(2),AC(2)
COMMON /A/ANAM(8),AREF(9),TPEXP,WT1EXP
**COMMON**

- COMMON /B/N*(50), X(50), Y(50), PI(50), TP*(50), TP*(50)
- COMMON /C/T(12, 2), PC(2, 2), ZC(2, 2), WH(2, 2), MU(2), ETA(2)
- COMMON /D/VPCORR(50, 2), VOL(50, 2), UI(50, 2), SOLP(50, 2)
- COMMON /E/T*REF(2), DN*REF(2)
- COMMON /F/QP(46), IO(42)

**FORMAT**

- 50 FORMAT(3F7.0, 8F5.0, 12)
- 51 FORMAT(3F9.0, 5F7.0, 2F4.0)
- 52 FORMAT(2L1, 12, F8.0, 17A4)
- 53 FORMAT(4L1, 2F5.0, F1C.0)
- 54 FORMAT(12/(8F1C.0))
- 55 FORMAT('O', 'ANTOINE CONSTANTS'///' COMPONENT ', 11///' I   P(I)
- 56 FORMAT('O', '12, E17.6)
- 57 FORMAT('O', 'I   X(I)', 'Y(I) - OBS', 'Y(I) - CALC', 'DIFERENCE')
- 58 FORMAT('O', 'I2, F10.2, 2F15.5, E2C.6)
- 59 FORMAT(L1)
- 60 FORMAT(12/L1, 8F1C.0)
- 61 FORMAT('O', 'DENSITY CONSTANTS'///' COMPONENT ', 11///' I   P(I)
- 62 FORMAT(L1, 2F9.0)
- 63 FORMAT('I', 'SYSTEM = ', 8A4, 'REFERENCE = ', 9A4)
- 64 FORMAT('O', 'NO = ', 15, 5X, 'VALUE = ', F10.2)

**READS INPUT AND OBTAINS UNKNOWN PARAMETERS**

- R = 1.9872
- CL = 2.3025851

**READ PHYSICAL PROPERTIES DATA**
DO1: J=1,2
READ 50, M(J), TBK(J), TC(J, J), PC(J, J), VC(J), WC(J), WH(J), MU(J), ETA(J)
1, PCR(J), OP(J), ID(J)
READ 51, (C(K, J), K=1, 7), DNREF(J), TPREF(J)
C
C READ VAPOG PRESSURE DATA
C
IF(C(1, J), NE, C) GT05
READ 54, N, (X(I), Z(I), I=1, N)
DO1 I=1, N
W(I)=1,
1 Z(I)=ALOG10(Z(I))
TBC=TBK(J)-273.16
P(I)=239.-.19*TBC
LB=TBK(J)*5.*ALOG10(PC(J, J))-.217/(.93-TBK(J)/TC(J, J))
RIEDEL
P(2)=LB/(R*CL)*(TBC+P(3))/TBK(J)**2
TOMSON
P(1)=2. 8808136+P(2)/(TBC+P(3))
DO2 I=1, 3
2 STEP(I)=.1*P(I)
NQ=1
CALL PATERN(4, 3, P, STEP)
PRINT 55, J
DO3 I=1, 3
C(I, J)=P(I)
3 PRINT 56, I, P(I)
PRINT 57
DO4 I=1, N
DIFF=Z(I)-FZ(I)
4 PRINT 58, I, X(I), Z(I), EZ(I), DIFF
CALL FIT
C
C READ LIQUID DENSITY DATA
5 READ 59, LV(4)
   IF(.NOT. LV(4)) GO TO 10
   READ 60, N, NM, (X(I), Z(I)), I=1, N
   DO 61 I=1, N
6   W(I)=1.
   CALL POLY(NM, P)
   PRINT 61, J
   NP=NM+1
   DO 71 I=1, NP
      C(I+3, J)=P(I)
   PRINT 56, J, P(I)
   DO 81 I=1, NP
      EZ(I)=P(I)*X(I)*(P(2)+X(I)*(P(3)+X(I)*P(4))
      DIFF=Z(I)-EZ(I)
   PRINT 58, I, X(I), Z(I), EZ(I), DIFF
   CALL FIT

C READ VAPOR LIQUID EQUILIBRIUM DATA
C
10  ZC(J)=(PC(J, J)*VC(J))/((82.06*TC(J, J))
   TC(1, 2)=SQRT(TC(1, 1)*TC(2, 2))
   PC(1, 2)=4.*TC(1, 2)*PC(1, 1)*VC(1)/TC(1, 1)+PC(2, 2)*VC(2)/TC(2, 2))/
   VC(1)**(1./3.)*VC(2)**(1./3.)*3
   READ 52, LV(2), LV(3), N, VALUE, ANAM, AREF
   READ 62, LV(5), TPEXP, WT1EXP
   IF(.NOT. LV(2)) RETURN
   READ 53, (X(I), Y(I), TP(I)), I=1, N
   PRINT 63, ANAM, AREF
   PRINT 64, N, VALUE
   IF(LV(3)) GO TO 12
   DO11 I=1, N
   PI(I)=TP(I)
TP(I) = VALUE
11 TPK(I) = TP(I) + 273.15
GOTO 14
12 DO 13 I = 1,N
   PI(I) = VALUE
13 TPK(I) = TP(I) + 273.16
14 DO 15 J = 1,2
   I = 1
   CALL PROPS(TPK(I))
   DO 15 I = 2,N
   SOLP(I,J) = SOLP(I-1,J)
   U(I,J) = U(I-1,J)
   VOL(I,J) = VOL(I-1,J)
   IF(TPK(I) .EQ. TPK(I-1)) CALL PROP1
15 IF(TPK(I) .NE. TPK(I-1)) CALL PROPS(TPK(I))
16 DO 16 I = 1,N
   W(I) = 32.0 / ((1.0/(X(I)*(1.0-X(I))))**2 + (1.0/(Y(I)*(1.0-Y(I))))**2)
   Z(I) = ALOG((VPCORR(I,2)*(1.0)/(X(I)-1.0)/(VPCORR(I,1)*(1.0/Y(I)-1.0)))
RETURN
END

SUBROUTINE PATTERNINPASS(NP,P,STEP)
LOGICAL LV
COMMON LV(1)
DIMENSION PINPI,STEP(NP),B1(10),B2(1C),S(10),T(10)
100 FORMAT('C',5X,'PARAMETERS')
1:1 FORMAT(' ',5X,'PARAMETERS')
C**********************************************************************
C
C PATTERN SEARCH
C
C**********************************************************************
INITIALIZATION

1  IC=2
   DO2I=1, NP
   B1(I)=P(I)
   B2(I)=P(I)
   T(I)=P(I)
   S(I)=STEP(I)
   CALL QFUNC(P, Q1)

EXPLORATORY MOVES

2  DO19NRD=1, NPASS
   IFAIL=0
   DO8I=1, NP
   IC=0
   P(I)=T(I)+S(I)
   IC=IC+1
   CALL QFUNC(P, Q2)
   IF(LV(1)) GOT05
   IF(Q1-Q2)5,5,7
   IF(IC.EQ.2) GOT06
   S(I)=-S(I)
   GOT04
   IFAIL=IFAIL+1
   P(I)=T(I)
   GOT08
   T(I)=P(I)
   Q1=Q2
   CONTINUE

CHANGE IN OBJECTIVE FUNCTION
C
IF(IFAIL.LT.NP) GOTO12
IF(ICK.EQ.2) GOTO18
IF(ICK.EQ.1) GOTO12
CALL QFUNC(T,Q2)
IF(Q1-Q2) 9,11,11
9  ICK=1
DO10 I=1,NP
B1(I)=B2(I)
P(I)=B2(I)
10  T(I)=B2(I)
GOTO3
11  Q1=Q2
12  IB1=0
DO13 I=1,NP
B2(I)=T(I)
IF(ABS(B1(I)-B2(I)).LT.1.0E-20) IB1=IB1+1
13  CONTINUE
IF(IB1.EQ.NP) GOTO18
C
C PATTERN MOVE
C
ICK=0
SJ=1.
DO15 II=1,11
DO14 I=1,NP
14  P(I)=T(I)
CALL QFUNC(T,Q3)
IF(.NOT.LV(I)) GOTO16
SJ=SJ-.1
IF(II.EQ.11) ICK=1
15  CONTINUE
SUBROUTINE GOLDEN(P, X10, X20, EPSI)
DIMENSION X(?), QF(2)
C******************************************************************************
C * GOLDE*) SECTION SEARCH *
C                                      *
C******************************************************************************
C SET INITIAL BASE POINT
C
16 DO 17 I = 1, NP
17 B1(I) = B2(I)
GOTO 3
C STEP REDUCTION
C
18 DO 19 I = 1, NP
19 T(I) = B2(I)
19 S(I) = S(I)/10.
C FINAL VALUES
C
20 DO 20 I = 1, NP
20 P(I) = T(I)
RETURN
C ENTRY OUTPUT
PRINT 100
PRINT 101, (I, P(I), I = 1, NP)
RETURN
END
K=0
X1=X10
X2=X20

2 IF(K.LT.0) GOTO3
X(1)=X1+.382*(X2-X1)
CALL QFUNC(X(1),QF(1))

3 IF(K.GT.0) GOTO4
X(2)=X1+.618*(X2-X1)
CALL QFUNC(X(2),QF(2))

4 IF(QF(1).GT.QF(2)) GOTO5
IF(QF(1).LT.QF(2)) GOTO6
K=0
X1=X(1)
X2=X(2)
GOTO7

5 K=-1
X1=X(1)
X(1)=X(2)
QF(1)=QF(2)
GOTO7

6 K=1
X2=X(2)
X(2)=X(1)
QF(2)=QF(1)

7 IF(X2-X1.GT.EPSI) GOTO2
P=(X(1)+X(2))/2.
RETURN
END

SUBROUTINE QFUNC(P,Q)
LOGICAL LV
REAL MU,MW,L12

COMMON LV(5), I, J, NQ, C(7, 2), CL, MW(2), PCR(2), R, TBK(2), MC(2), RATIO
COMMON N, Z(50), EZ(50), M(50), X(50), Y(50), PI(50), TP(50), TP(50)
COMMON C, PC(2, 2), ZC(2), *H(2), MU(2), BP(2)
COMMON VPCORR(50, 2), VOL(50, 2), J(50, 2), SOLP(50, 2)
COMMON F/QP(61, 1D(2), M(6, 61), S(2)/G/T(4), TBH, TBL
DIMENSION ETA(6), F(9, 9), P(4), XC(6), XI(6), DISP(2), TAU(2),
LV(2), DP(2)
DATA F/1., 1., -1., -1., -1., 1., 1., 5., 4,
2 1., 1., 2., 1., 2., 5., 4., 5., 5., 6,
3 -1., 1.3, 1., 1., 5., 025., 1., 1., -0.35,
4 -1., 1., 1., 1., 5., 015., 08., 06., -0.35,
5 -1., 1., 3., 5., 5., 1., 2., 2., 2., -1.,
6 1., 5., 02., 01., 2., 1., 5., 5., -0.3,
7 1., 6., 08., 06., 2., 5., 1., 5., 5.
8 0.5., 05., 1., 2., 5., 1., 1.,
9 0.4., 4., -0.25., -0.25., 1., -0.25., 5., 1., 1.

C**************************************************************
C DEFINES FUNCTION TO BE MINIMIZED
C**************************************************************

Q = 0
LV(1) = .FALSE.,
GOTO(15, 10, 20, 30, 50), NQ

C ANTOINE EQUATION
C
1 DO2I = 1, N
EZ(I) = P(1) - P(2)/(X(I) + P(3))
2 Q = Q + (Z(I) - EZ(I))**2
RETURN

C XCEPT SEARCH
C 5  Q=ABS(T(1)+P(1)*(T(2)+P(1)*(T(3)+P(1)*T(4))))
RETURN
C  EQUATION (V-5)
C 10  RATIO=P(1)
     A12=P(2)
     IF(RATIO.LE.0.0) GO TO 9
     DO11 I=1,N
     A=A12/(R*TPK(I))
     SUM=X(I)*(RATIO-1.0)+1.0
     Z1=X(I)*RATIO/SUM
     EZ(I)=A*(Z1*(Z1*(1.0-1.0/RATIO)-2.0)+1.0)+ALOG(RATIO)+(1.0-RATIO)/SUM
11  Q=Q+W(I)*(Z1-EZ(I))**2
RETURN
C  KIREEV EQUATION
C 20  TPK(I)=P(1)
     DO22 J=1,2
22  CALL PROPS(TPK(I))
     DO25 J=1,2
     DISP(J)=U(I,J)
     TAU(J)=0.0
     DP(J)=0.0
     IF(MU(J).LT.1.0) GO TO 23
     WHCOR=WH(J)
     IF(ID(J).EQ.2) WHCOR=0.299
     IF(ID(J).EQ.2.AND. WC(J).GT.0.560) WHCOR=0.543
     IF(ID(J).EQ.2.AND. WC(J).GT.0.615) WHCOR=0.514
     IF(ID(J).EQ.2.AND. WC(J).GT.0.630) WHCOR=0.419
     IF(ID(J).EQ.2.AND. WC(J).GT.0.650) WHCOR=0.546
GOTO 24
IF(ID(J).EQ.3 .AND. WC(J).LT.0.35) WHCOR=0.165
IF(ID(J).EQ.6 .AND. MU(J).GT.2.00) WHCOR=0.190
IF(ID(J).EQ.9 .AND. MU(J).LT.1.10) WHCOR=0.230
TR=TPK(I)/TC(J,I)
UR=11.020236-7.15616*TR-1.38854/TR+WHCOR*((4.55655-J)*95254/TR)/TR+
WHCOR*{(2.0491-C+88732/TR**2))/TR
DISP(J)=R*TC(J,J)*UR
TAU(J)=U(I,J1-DISP(J)
DP(J)=1.-DISP(J)/U(I,J)

23
VL(J)=VOL(I,J)
IF(ID(J).EQ.6 .AND. WC(J).GT.0.220) VL(J)=1.065*VOL(I,J)
IF(ID(J).EQ.6 .AND. WC(J).GT.0.260) VL(J)=1.073*VOL(I,J)
BP(J)=ETA(I)
IF(ID(J).EQ.7) VL(J)=(1.212+BP(J)*(-.837+BP(J)*934))*VOL(I,J)
IF(MU(1).LT.1.0 .AND. MU(2).LT.1.0) GOTO24
IF(ID(3-J).EQ.2) GOTO24
IF(ID(J).EQ.2) VL(J)=(1.0579+DP(J)*(22.30-DP(J)*21.01))*VOL(I,J)
IF(ID(J).EQ.3) VL(J)=(1.661+.453*DP(J))*VOL(I,J)
IF(ID(J).EQ.4) VL(J)=(1.339+2.485*DP(J))*VOL(I,J)
IF(ID(J).EQ.5) VL(J)=1.137*VOL(I,J)
IF(ID(J).EQ.6 .AND. MU(J).GT.1.0) VL(J)=(1.148+1.50*DP(J))*VOL(I,J)
IF(ID(J).EQ.6 .AND. MU(J).GT.2.0) VL(J)=1.406*VOL(I,J)
IF(ID(J).EQ.7 .AND. WC(J).LT.0.120) VL(J)=1.49*VOL(I,J)
IF(ID(J).EQ.8) VL(J)=(1.148+1.50*DP(J))*VOL(I,J)
IF(ID(J).EQ.8 .AND. MU(J).LT.1.0) VL(J)=0.9085*VOL(I,J)
IF(ID(J).EQ.9) VL(J)=(1.148+1.50*DP(J))*VOL(I,J)
GOTO25

24
IF(ID(J).EQ.5) VL(J)=0.967*VOL(I,J)
IF(ID(J).EQ.8) VL(J)=1.091*VOL(I,J)

25 CONTINUE
RATIO=VL(1)/VL(2)
K=1
IF(ID(11).LT.ID(12)) K=2
L=3-K
L12=I.C.
IF(MU(K),GT.1.C) GOTO26
IF(ID(L),LE.2) GOTO27
IF(ID(L),EQ.3.AND.ID(K),EQ.6) L12=-.0797
IF(ID(L),LE.4.AND.ID(K),EQ.8) L12=-.3558
IF(ID(L),EQ.4.AND.ID(K),EQ.6) L12=-.0558
IF(ID(L),LE.6.AND.ID(K),EQ.9) L12=-.0664
CONTINUE
U12=(1.-L12)*SQRT(RATIO*DISP(1)*DISP(2))
IF(TAU(1),GT.0.AND.TAU(2),GT.0.) U12=U12+SQRT(RATIO*TAU(1)*TAU(2))
A12=(U(1,1)+RATIO*U(1,2)-2.*U12)
A=A12/(R*TPK(1))
B=A/RATIO
Q=ABS(1.-SQRT(ALOG(P1(I)/VPCORR(I,1)))/A)-SQRT(ALOG(P1(I)/VPCORR(I, 121)/B))
RETURN

BARKER MODEL

IF(P(I),LT.C.0) GOTO93
NR=0
DO32 J=1,2
NO=NR+1
NR=NR+M(J,J)
DO31 K=NO,NR
XC1(K)=QP(K)/FLOAT(2*M(J,J))
XI(K)=1.
TEMP=TPK(1)
IF(LV(3)) TEMP=C(2,J)/(C(1,J)-ALOG10(P1(I)))-C(3,J)+.73.16
DO31 L=1,N:
IF(K,LE,L) GOTO31
JJ=M(K,L)
ETAI(L) = EXP(-P(J)/R*TEMP)
ETAL(K) = ETA(K,L)
31 CONTINUE
IF(NO.LT.NR) CALL NEWTON(NO, NR, XCI, XI, ETA)
32 IF(NO.EQ.NR) XCI(NC) = SQRT(QP(NO)/2.)
   DO 37 I = 1, N
   DO 35 K = 1, NR
   XI(K) = X(I)
   IF(K.GE.NO) XI(K) = 1. - X(I)
   XCI(K) = XI(K) * XCI(K)
   DO 35 L = 1, NR
35 IF(K.NE.L) ETA(K,L) = ETA(K,L) ** (TEMP/TPK(I))
   TEMP = TPK(I)
   CALL NEWTON(1, NR, XC, XI, ETA)
   SUM1 = 0
   SUM2 = 0
   DO 36 K = 1, NR
      ADD = QP(K) * ALOG(XC(K)) / (XI(K) * XCI(K))
   IF(K.LT.NO) SUM1 = SUM1 + ADD
   IF(K.GE.NO) SUM2 = SUM2 + ADD
36 EZ(I) = SUM1 - SUM2 + S(I) * ALOG(X(I)) * (1. - S(2)/S(1)) + S(2)/S(1) - S(2) * ALOG
1*(X(I) * S(1)/S(2) - 1.) + 1.
37 Q = Q + W(1) * (Z(I) - EZ(I)) ** 2
RETURN
C
C GILMONT-ZUDKEVITCH-OTHMER CORRELATION
C
50 IF(P(1).GE.(TBL-.04). AND. P(1).LE.(TBH+.04)) GOTO90
   IF(P(2).LE.0.2. OR. P(2).GE.50) GOTO90
   TPTEST = P(1)
   X(I) = P(2)
   Y(I) = X(I)
   F12 = F(I)(D2, ID(1))
ETA(K,L) = EXP(-P(JJ)/(R*TEMP))
ETA(L,K) = ETA(K,L)

31 CONTINUE
IF(NO.LT.NR) CALL NEWTON(NO,NR,XC1,XI,ETA)

32 IF(NO.EQ.NR) XC1(NO) = SQRT(QP(NO)/2.)

33 DO35K = 1, NR
X1(K) = XI(K)
IF(K.GE.NO) XI(K) = 1. - XI(K)
XC(K) = XI(K) * XC1(K)

35 IF(K.NE.L) ETA(K,L) = ETA(K,L)**(TEMP/TPK(I))
TEMP = TPK(I)
CALL NEWTON(1, NR, XC, XI, ETA)
SUM1 = 0
SUM2 = 0

36 DO36K = 1, NR
ADD = QP(K) * ALOG(XC(K)/(XI(K) * XC1(K)))
IF(K.LT.NO) SUM1 = SUM1 + ADD

36 IF(K.GE.NO) SUM2 = SUM2 + ADD
EZ(I) = SUM1 - SUM2 + S(1) * ALOG(X(I) * (1. - S(2)/S(1)) + S(2)/S(1)) - S(2) * ALOG
1(X(I)) * (S(1)/S(2) - 1.) * 1.

37 Q = Q*W(I)*(Z(I) - EZ(I))**2
RETURN

C GILMONT-ZUDEKEVITCH-OTHMER CORRELATION
C
50 IF(P(1).GE.(TBL-.04) .AND. P(1).LE.(TBL+.04)) GO TO 90
IF(P(2).LE.0.02 .OR. P(2).GE.0.98) GO TO 90
TPTEST = P(1)
X(I) = P(2)
Y(I) = X(I)
F12 = F(ID(2), ID(1))
F21=F(ID(1),ID(2))
P1=PCR(1)**(2/3)
P2=PCR(2)**(2/3)
DO51J=1,2
51 CALL PROPS(TPTEST)
   A12=(SQRT(U(1,1)/P1)-SQRT(U(1,2)/P2))**2
   A=(P1*A12)/(F21*R*TPTEST)
   B=(P2*A12)/(F12*R*TPTEST)
   EZ(I)=A+X(I)*((-4*A+2*B)+3*X(I)*(A-B))
   Q=ABS(ALOG(VPCORR(I,2)/VPCORR(I,1))-EZ(I))
RETURN
C 90 LV(I)=.TRUE.
RETURN
END

SUBROUTINE POLY(NM,A1)
COMMON /B/N,Z(5C),EZ(5C),W(5C),X(5C)
DIMENSION A(6),B(6,7)
C**********************************************************************
C
C WEIGHTED LEAST SQUARES METHOD FOR POLYNOMIAL
C
C**********************************************************************
C
NR=NM+1
NC=NM+2
DO1I=1,6
DO1J=1,7
A(I)=.0
1 B(I,J)=.0
DO3I=1,N
   F=W(I)
SUBROUTINE GUASS(NO,NR,A,B)
DIMENSION A(6),B(6,7)

C******************************************************************************
C
C GAUSSIAN ELIMINATION USING LARGEST PIVOT ELEMENT
C
C******************************************************************************

NC=NR+1
NM=NR-1

C SEARCH FOR LARGEST PIVOT ELEMENT

DO7K=NO,NM
JJ=K
BIG=ABS(B(K,K))
KP1=K+1

B(1,1)=B(1,1)+F
B(1,NC)=B(1,NC)+F*Z(I)
DO2J=2,NR
F=F*X(I)
B(J,1)=B(J,1)+F
DO3J=2,NC
F=F*X(I)
B(NR,J)=B(NR,J)+F
DO4J=2,NR
DO4K=1,NM
B(K,J)=B(K+1,J-1)
CALL GUASS(1,NR,A,B)
RETURN
END
DO21=KP1,NR
AB=ABS(B(I,K))
IF(BIG-AB)=1,2,2
1 BIG=AB
JJ=I
2 CONTINUE
C
C ROW INTERCHANGE
C
IF(JJ-K)3,5,3
3 DO4J=K,NC
TEMP=B(JJ,J)
B(JJ,J)=B(K,J)
4 B(K,J)=TEMP
C
C ELEMENTS OF NEW MATRIX
C
5 DO6I=KPI,NR
QUOT=B(I,K)/B(K,K)
DO6J=KPI,NC
6 B(I,J)=B(I,J)-QUOT*B(K,J)
DO7I=KPI,NR
7 B(I,K)=0
C
C BACK SUBSTITUTION PROCESS
C
A(NR)=B(NR,NC)/B(NR,NR)
DO9NN=NC,NM
SUM=0
I=NM-NN+NO
IP1=I+1
DO8J=IP1,NR
8 SUM=SUM+B(I,J)*A(J)
A(I) = (B(I, NC) - SUM) / B(I, I)
RETURN
END

SUBROUTINE FIT
COMMON /B/N, Z(50), EZ(50), W(50)
DIMENSION SUM(4)

1C FORMAT ('G', 5X, 'SUM OF SQUARES OF [OBS - ZCALC] = ', E15.6, /, 'GOODNESS OF FIT = ', F15.6)

C***************************************************************
C
C CALCULATES GOODNESS OF FIT
C
C***************************************************************

DO 11 I = 1, N
  SUM(I) = 0
  DO 2 I = 1, N
    SUM(1) = SUM(1) + W(I) * (Z(I) - EZ(I))**2
    SUM(2) = SUM(2) + W(I) * Z(I)**2
    SUM(3) = SUM(3) + W(I) * Z(I)
  2 SUM(4) = SUM(4) + W(I)
  R2 = 1.0 - SUM(1) / (SUM(2) - SUM(3)**2 / SUM(4))
PRINT 10, SUM(1), R2
RETURN
END

SUBROUTINE VIRIAL(B, TEMP)
REAL B(2, 2), MU
COMMON /C/TC(2, 2), PC(2, 2), ZC(2), WH(2), MU(2), ETA(2)

C***************************************************************
C
C***************************************************************
C CALCULATES SECOND VIRIAL COEFFICIENTS *
C ************************************************************
DO3I=1,2
DO3J=1,2
IF(I.GT.J)GOTO3
TR=TEMP/TC(I,J)
C CALCULATE NONPOLAR VALUE FROM PITZER-CURL CORRELATION
W=.5*(WH(I)+WH(J))
VIR=.1445-(.330+ (.3485+ .0121/TR)/TR)/TR+W*(.373+(.46-1.50+.097*
1.0873/TR**51/TR)/TR)/TR/I
C
C ADD POLAR CONTRIBUTION
RD=10.E04*MU(I)*MU(J)*PC(I,J)/(TC(I,J)**2)
IF(RD.LE.4)GOTO2
RDL=ALOG(RD)
VIR=VIR-5.237229*RDL*(5.665807+RDL*(-2.133816+RDL*2525373))1+
1(5.769770+RDL*(-6.181427+RDL*(2.283270-RDL*2649074111)/TR
C
C ADD MOLECULAR ASSOCIATION CONTRIBUTION
IF(ETA(I)+ETA(J))2,2,1
1 VIR=VIR-5*(ETA(I)+ETA(J))*EXP(6.6*(.7-TR))
2 B(I,J)=(VIR*82.057*TC(I,J))/PC(I,J)
3 CONTINUE
RETURN
END

SUBROUTINE PROPS(TEMP)
REAL MB(2,2)
CMN /E/TPREF(2),DONREP(2)
COMMON /D/PQD(R(50,2),YVL(50,2),SOLP(50,2))
COMMON /C /IC(Z),(Z)
COMMON /B/N,Z(250),E(250),X(250),Y(250),P(150),P(150)

LOGICAL LV

CALL VIRTUAL(0,TEMP)

*****
*  CALCULATES PHYSICAL PROPERTIES
*  *****

IF (C(2),NE.C(2)) GO TO 10

IF (L(2)) GO TO 10

CALCULATION HAS BEEN IMPROPORLY TRANSLATED!

REAL MB(2,2)
CMN /E/TPREF(2),DONREP(2)
COMMON /D/PQD(R(50,2),YVL(50,2),SOLP(50,2))
COMMON /C /IC(Z),(Z)
COMMON /B/N,Z(250),E(250),X(250),Y(250),P(150),P(150)

LOGICAL LV

CALL VIRTUAL(0,TEMP)
SPHI = 1. / (1. + A(J, J) / VG) * EXP(2. * B(J, J) / VG)
GOTO 5

4

SPHI = EXP(-3.5C21358 + (1.57335C15 / TR - 3.765741 / TR + 5.6585595) / TR
1 + W(J, J)) * (-3.7694018 + ((((((((((1.2089114 / TR - 0.15172164) / TR - 0.065803
2516) / TR + 0.24364816) / TR + 0.14936906) / TR + 0.18927357) / TR - 0.12147346) / TR
3 - 1.66573C1 / TP - 1.6622831 / TR + 1.2666184) / TR + 3.1661371) / TR + 4.3538729)
4 / TR)
ENTRY PROPI

5

PITEST = 380. * TEMP * (Y(II) * PC(1, 1) + (1 - Y(II)) * PC(2, 2)) / (Y(II) * TC(1, 1) +
1 - Y(II) * TC(2, 2))
IF (PI(II) . GE. PITEST) PRINT 10
BMIX = Y(II) ** 2 * B(1, 1) + 2 * Y(II) * (1 - Y(II)) * B(1, 2) + (1 - Y(II)) ** 2 * B(2, 2)
ZMIX = 5 * (1 + SQRT(1 + (4 * BMIX * PI(II)) / (62370. * TEMP)) / PI(II))
VMIX = (ZMIX * 62370. * TEMP) / PI(II)
PHI = 1. / (1 + BMIX / VMIX) * EXP(2. * Y(II) * B(1, J) + (1 - Y(II)) * B(J, 2)) / VMIX
POYN = EXP(VOL(II, J) / (62370. * TEMP) * (PI(II) - VPRESS))
VPCORR(I, J) = VPRESS * (POYN * SPHI / PHI)
RETURN
END

SUBROUTINE TEST(NM)
LOGICAL LV
REAL J, TBK(2)
COMMON LV(5), I, JJ, NQ, C(7, 2), CL
COMMON /8/N, Z(50), EZ(50), W(50), X(50), Y(50), PI(50), TP<(50) / G / P(4)
10 FORMAT(*0.5, 'TEST INFORMATION' / 6X, *A= ', F7.3, 5X, *B= ', F7.3)
11 FORMAT(*0.5, 'XCEPT AREA1 AREA2 D J
1 TEST' / 1X, 3F10.4, 3F10.2)
C**************************************************************C
C
DATA IS TESTED FOR THERMODYNAMIC CONSISTENCY BY HERINGTONS METHOD
C******************************************************************************
C
C DATA FIT TO NM DEGREE POLYNOMIAL
C
1 NQ=2
CALL POLY(NM,P)
A=P(1)
B=-(P(1)+P(2)+P(3)+P(4))
IF(A*B.LT.0.) RETURN
CALL GOLDEN(XCEPT,.0,1.,.0001)

C CONSISTENCY TEST

AREA1=XCEPT*(P(1)+XCEPT*(P(2)/2. + XCEPT*(P(3)/3. + XCEPT*(P(4)/4.)))
AREA2=P(1)+P(2)/2. + P(3)/3. + P(4)/4. - AREA1
D=100.*ABS(AREA1+AREA2)/(ABS(AREA1)+ABS(AREA2))
J=0
IF(.NOT.LV(3))GOTO4
DD2K=1,2

2 TBK(K)=C(2,K)/(C(1,K)-ALOG10(PI(11))-C(3,K)+273.16
TPH=AMAX1(TBK(1),TBK(2))
TPL=AMIN1(TBK(1),TBK(2))
DO3I=1,N
TPH=AMAX1(TPH,TPK(I))
TPL=AMIN1(TPL,TPK(I))
J=150.*(TPH/TPL-1.)

4 TEST=D-J-10.

C PRINT RESULTS

PRINT 10,A,B
PRINT 11,XCEPT,AREA1,AREA2,D,J,TEST
D05I=1,N
5 FZ(I) = P(1) + X(I) * (P(2) + X(I)) * (P(3) + X(I)) * P(4)
CALL FIT
RETURN
END

SUBROUTINE BARKER
COMMON LV(5), I, J, NQ/F/QP(6), ID(2), M(6, 6), R(2)
DIMENSION P(4), STEP(4)
100 FORMAT('O', 'BARKER MODEL - QUASI IDEAL SYSTEMS')
101 FORMAT('O', 'BARKER MODEL - NEGATIVE SYSTEMS')
102 FORMAT('O', 'BARKER MODEL - POSITIVE SYSTEMS')
103 FORMAT('O', 5X, 'PARAMETER=', 'E11.4')

C*********************************************************
C
C BARKER MODEL
C
C*********************************************************
K=1
NQ=5
IF(ID(1).LT.ID(2)) K=2
L=3-K
P(1)=50.
P(2)=-100.
DO1 J=1, 2
STEP(J)=10.
1 R(J)=QP(J)/2.
DO2 I=1, 6
DO2J=1, 6
2 M(I, J)=1
IF(ID(L).LE.2) GOTO3C
IF(ID(L).GE.7) GOTO1C
IF(ID(K).EQ.9) GOTO20
C QUASI IDEAL SYSTEMS

C

1C PRINT 100
IF (ID(L) .LE. 4 .AND. ID(K) .EQ. 6) GOTO 22
CALL GOLDEN(P(1), C, 3), .111
PRINT 103, P(1)
CALL FIT
RETURN

C NEGATIVE SYSTEMS

C

2C DO 21 J = 2, 3
P(J) = -1000.
21 STEP(J) = 100
PRINT 101
22 DO 25 J = 1, 2
23 M(J, J) = 2
IF (ID(L) .EQ. 4) GOTO 25
M(4, 2) = 2
QP(3) = QP(2)
QP(2) = 1.
QP(4) = 1.
IF (ID(L) .EQ. 3) QP(2*L) = 2.
IF (ID(L) .EQ. 6) QP(2*L) = 3.
DO 24 J = 1, 3, 2
24 QP(J) = QP(J) - QP(J + 1)
NP = 2
GOTO 50
25 M(L, L) = 3
QP(2*L - 1) = QP(L) - 3.
QP(3*K - 2) = QP(K) - 1.
QP(2*L) = 2.
SUBROUTINE NEWTON(N,O,NX,A,XI,ETA)
COMMON /F/QP(6)
DIMENSION A(6),B(6,7),DA(6),ETA(6,6),XI(6)
C:******************************

CI O  o  o
O (2*L+1)=1.
O P(3*K-1)=1.
M(K+,3,2)=2
M(5,K+1)=3
NP=3
GOTO 50

C POSITIVE SYSTEMS
C
30 IF(ID(K),LE.,5) RETURN
PRINT 102
M(L,L)=3
M(L+2,L+1)=2
QP(3*K-2)=QP(K)
QP(L)=QP(L-2).
QP(L+1)=1.
QP(L+2)=1.
31 NP=2
P(2)=-3000.
STEP(2)=100.
GOTO 50C
C
50 CALL PATERN(4,NP,P,STEP)
CALL OUTPUT
CALL FIT
RETURN
END
SOLUTION OF EQUATION (II-74) *
BY NEWTON-RAPHSO METHOD *

******************************************************************************
1 DO31 = NO, NR
   SUM = 0
   DO2J = NO, NR
   IF(I .EQ. J) GOTO2
   B(I, J) = ETA(I, J) * A(I)
   SUM = SUM + ETA(I, J) * A(J)
2 CONTINUE
   B(I, I) = 2. * A(I) + SUM
   B(I, NR+1) = (QP(I) * XI(I)) / 2. - A(I) * (A(I) + SUM)
   CALL GAUSS(NO, NR, DA, B)
   DO4I = NO, NR
3 A(I) = A(I) + DA(I)
   DO5I = NO, NR
   IF(ABS(DA(I)) .GT. 0.00001) GOTO1
4 CONTINUE
   RETURN
END

SUBROUTINE AZEO
LOGICAL LV
REAL MW
COMMON LV(5), I, J, NO, C(7, 2), CL, MW(2), PCR(2), R, TBK(2), DC(2), RATIO
COMMON /A/ ANAM(8), AREF(9), TPEXP, WT1EXP
COMMON /B/N, Z(5G), EZ(5G), W(5G), X(5G), Y(5G), PI(5G), TP(5G)
COMMON /D/VPCORR(5G, 2), VOL(5G, 2), U(5G, 2), SOLP(5G, 2)
COMMON /F/QP(6), ID(2), M(6, 6), S(2), G/T(4), TBH, TBL
DIMENSION CJM(7, 3), P(4), STEP(4)
12*3. /
50 FORMAT(  'O', 'AZEOTROPIC PREDICTION',4X,'XAZEO  TPAZEO  TBL
1  TBH')
51 FORMAT(  'O', 'EXPERIMENTAL VALUES',4X,F10.4,F10.1,2F10.1)
52 FORMAT(  'O', 'KIREEV EQUATION',5X,F10.4,F10.1)
53 FORMAT(  'O', 'GZO CORRELATION',5X,F10.4,F10.1)
54 FORMAT(  'O', 'JM CORRELATION',15X,F10.1)
C***********************
C
C AZEOTROPIC PREDICTION
C
C***********************
I=N+1
PI(I)=760.
DO1 J=1,2
1  TBK(J)=C(2,J)/(C(1,J)-ALOG10(P1(I)))+C(3,J)+273.16
  TBL=AMIN1(TBK(1),TBK(2))
  TBM=AMAX1(TBK(1),TBK(2))
  IF(.NOT.LV(5)) GOTO2
  TPEXP=TPEXP+273.16
  X1EXP=1./1.+(MW(1)/MW(2))*(1./WT1EXP-1.)
  XAZEO=X1EXP:
  PRINT 51,X1EXP,TPEXP,TBL,TBH
C
C KIREEV EQUATION
C
2  Y(I)=5
  K=1
  IF(I(D(I)).LT.I(D(2))) K=2
  L=3-K
  X1=TBH+.01
  X2=TBH+1C.
TP0 = TBH + 5.
IF (ID(L).LE.6. AND. ID(K).EQ.9) GO TO 3
X1 = TBL - 40.
X2 = TBL - 1.
TP0 = TBL - 5.
NQ = 4
CALL GOLDEN (TPAZEO, X1, X2, 01)
IF (TPAZEO.GE.(TBL -.05).AND. TPAZEO.LE.(TBH + .05)) GO TO 6
XAZEO = 1./((1.*SQRT(RATIO*ALOG(P(1)/VPCORR(1, 1)))/ALOG(P(1)/VPCORR(1, 1)) + T.)

II + II)
X(I) = XAZEO
IF (ABS(Y(I) - XAZEO).LT.0.0001) GO TO 5
Y(I) = XAZEO
GOTO 4
PRINT 52, XAZEO, TPAZEO

C GILMONT-ZUKKEVITCH-OHTMER CORRELATION
C
NQ = 6
P(1) = TP0
P(2) = 5
STEP(1) = .05
STEP(2) = .05
CALL PATTERN(3, 2, P, STEP)
IF (P(1).GE.(TBL -.05).AND. P(1).LE.(TBH + .05)) GO TO 20
IF (P(2).LE.0.91 OR. P(2).GE.0.99) GO TO 20
PRINT 53, P(2), P(1)

C JOHNSON-MADONIS CORRELATION
C
20 IF (ID(K).LE.5) GO TO 30
IF (ID(K).GE.8) GO TO 25
IF (ID(L).EQ.4 OR. ID(L).EQ.5) GO TO 30
C2=3.5
C1=CMJ(ID(L),1)
GOT027
25 IF(ID(L).EQ.1.OR.ID(L).GE.8) GOT030
C1=CMJ(ID(L),2)
C2=CMJ(ID(L),3)
27 TPAZEO=TBL-(C1-ABS(TBK(1)-TBK(2)))/C2
IF(TPAZEO.GE.TBL) RETURN
PRINT 54,TPAZEO
30 RETURN
END
APPENDIX B REFERENCES


11. Ibid., p. 143.


APPENDIX C

NOMENCLATURE

\( A, a \) Helmholtz free energy
\( A, B \) van Laar constants
\( \overline{A}_{12}, A_{12}, A'_12 \) exchange energy (cal/pair, cal/cc, cal/g mole)
\( a, b \) van der Waals constants
\( B_{ij} \) second virial coefficient
\( b_{pi} \) branching parameter
\( c_{ij} \) cohesive energy density
\( D_i \) dielectric constant
\( d_{pi} \) degree of polarity
\( F_{ij} \) \( ij \) field factor
\( G, g \) Gibbs free energy
\( H, h \) enthalpy
\( I_i \) ionization energy
\( K \) equilibrium constant
\( k \) Boltzmann constant
\( l_{12} \) geometric mean deviation factor
\( MF_i \) multiplication factor
\( MW \) molecular weight
\( N_i \) number of molecules
\( N_{ij} \) number of nearest neighbor \( ij \) molecular pairs
\( N_o \) Avogadro's number
\( n_{i} \) number of moles
\( n \) carbon number
\( P_i \) nonideal pure component vapor pressure
\[ [P_i] \] parachor
\[ p_i \] partial pressure
\[ p_i^* \] pure component vapor pressure
\[ p_i^\circ \] adjusted vapor pressure
\[ Q_i \] number of external contacts
\[ q_i \] effective volume
\[ R \] gas constant
\[ R_m \] molar refractivity
\[ r \] correlation coefficient
\[ r_i \] number of sites occupied
\[ r_{ij} \] intermolecular distance
\[ S, S \] entropy
\[ T \] absolute temperature (°K)
\[ t \] temperature (°C)
\[ U, u \] energy
\[ V, v \] volume
\[ w_i \] weighting factor
\[ X_{ii} \] = \( \sqrt{N_{ii}/N} \)
\[ x_i \] liquid phase mole fraction
\[ \bar{x}_i \] liquid phase weight fraction
\[ y_i \] vapor phase mole fraction
\[ Z_i \] effective volumetric fraction
\[ z \] coordination number
\[ z \] compressibility factor
\[ z = \ln \frac{\gamma_1}{\gamma_2} \]
<table>
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<tr>
<th>Greek Symbols</th>
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<td>$\Delta$</td>
<td>boiling point difference</td>
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<tr>
<td>$\delta$</td>
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<td>$\delta_i$</td>
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<tr>
<td>$\xi_{ij}$</td>
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<tr>
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<td>$= \exp\left(-\frac{A_{ij}}{2kT}\right)$</td>
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<td>$\pi$</td>
<td>total pressure</td>
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<tr>
<td>$\rho_i$</td>
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<td>$\sigma_{ij}$</td>
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<td>$\phi_i$</td>
<td>vapor phase fugacity coefficient</td>
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<td>$\gamma_{12}$</td>
<td>negative residue</td>
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<td>$\omega_i$</td>
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APPENDIX D

DATA COMPILATIONS

Appendix D contains the supporting data for the models offered in chapter V. The correlating expression taken throughout was equation (V-5). The tables list for each entry the identity of the binary mixture, a reference number, the number of experimental points along with the best fit and predicted parameter(s) and corresponding values $r^2$. The nomenclature common to these tables is given below:

- $A_{12}$: best fit value of $A_{12}^{'}$
- $A_{12}(EST)$: estimated value of $A_{12}^{'}$
- $L_{12}$: best fit value of $L_{12}$
- $L_{12}(EST)$: estimated value of $L_{12}$
- $N$: number of experimental points
- $QRAT10$: average effective volume ratio
- $RATIO$: best fit symmetry factor
- $R2$: correlation coefficient squared
- $REF$: reference number
- $VRAT10$: average value of $v_1/v_2$
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The year the data was originally published is also listed. Vapor liquid equilibrium data that appeared in the literature before June, 1965, has been collected and placed in a general bibliography by Hala et al. The source entry INDEX NO refers to this numbered bibliography:


Again the year of publication is given. The entry JCHED means the *Journal of Chemical and Engineering Data*. Where it is used the volume number, year, and page number are stated in that order. The term author refers to experimental data.
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VITA

The author was born August 14, 1943 in Houston, Texas. He attended the public schools of Austin, Texas and graduated from McCallum High School in 1961. He enrolled at the University of Texas in September 1961 and subsequently received a Bachelor of Arts Degree in History in June 1965. He remained at the University of Texas and earned a Bachelor of Science Degree in Chemical Engineering in January 1967.

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EXAMINATION AND THESIS REPORT

Candidate:  Harry Douglas Pruett III

Major Field:  Chemical Engineering

Title of Thesis:  Prediction of Binary Azeotropes

Approved:

[Signatures]

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

May 15, 1971