ABSTRACT

VAPOR-LIQUID PHASE EQUILIBRIA OF NONIDEAL FLUIDS WITH A G^E-EoS MODEL

by
Socrates Ioannidis

This study dealt with the prediction and correlation of vapor-liquid equilibria behavior of nonideal fluids. The thermodynamic formalism of the G^E-EoS models, which combines the two traditional methods $\gamma-\phi$ and $\phi-\phi$ used so far for low and high pressure phase equilibria correlations respectively, has been combined with the $1FG^E$ model, based on one-fluid theory, to produce a more consistent approach to the phase equilibrium problem.

In the first part of our study we examine the predictive abilities of our model for vapor-liquid equilibria of highly nonideal fluids. The results establish the fact that the Huron-Vidal mixing rule with a one parameter version of the $1FG^E$ model, is able to successfully utilize available experimental information at low pressures for phase equilibria predictions of multicomponent mixtures over an extended range of pressures and temperatures.

In the second part of the study we perform an analysis of the correlative abilities of the $1FG^E$ model, as applied to hydrogen-hydrocarbon mixtures. The results of this part suggest that the unique local composition character of the $1FG^E$ model, along with its one size and one temperature-dependent energy parameter, make it able to adequately describe vapor-liquid equilibria behavior of multicomponent mixtures for this highly asymmetric class of mixtures. Moreover, it is shown that the model parameters for binary

hydrogen-hydrocarbon mixtures can be correlated to the acentric factor of the hydrocarbon.

The important class of the refrigerant mixtures was modeled in the third part of this study. The 1FG^E model was introduced into the Wong-Sandler mixing rule, based on the infinite pressure state thermodynamic formalism. The results for these systems showed that a limited amount of experimental data, either at low or high pressures can be utilized to provide a parameter which is practically independent of the temperature set used. As shown from the results, this single parameter can be used to extend vapor-liquid equilibria predictions over a range of conditions for this difficult class of systems. More importantly, we set a heuristic rule able to screen multiparameter and one parameter models. A coordination temperature-parameter planet can be used as a predictive tool from a limited amount of information.

Our model comes in lieu of the G^E models based on two-fluid theory, which are inconsistent with the one fluid character of an EoS. The 1FG^E-EoS framework proposed in this work meets current needs in the area of Applied Thermodynamics, which require that the model's parameters can be obtained from a limited information of experimental data and can give for accurate phase equilibria predictions of nonideal mixtures from low to high pressures.

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by
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This dissertation is dedicated to
my parents

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NOMENCLATURE

Notation

A	molar Helmholtz energy, bars cm^3 mol^{-1} parameter in the van Laar model (equation 2-55) parameter in the NRTL expression (equation 6-1, 7-4) parameter defined in equation A-2-13
$\underline{A}$	total Helmholtz energy, bars cm^3
a	energy parameter in an equation of state (EoS), bars cm^6 mol^{-2}
B	second virial coefficient, cm^3 mol^{-1}
b	size parameter in an equation of state (EoS), cm^3 mol^{-1}
C	EoS constant dependent on the EoS used energy parameter in equation 4-27
D	variable of the Wong-Sandler mixing rule (equation 2-51)
F	density dependent interpolation function
f	fugacity, bars
G	molar Gibbs energy, bars cm^{-3} mol^{-1} NRTL parameter (equation 2-57) UNIFAC parameter (App. A-4)
$\underline{G}$	total Gibbs energy, bars cm^{-3}
H	molar enthalpy, bars cm^3 mol^{-1}
I	total number of pair interactions in the mixture
k	binary interaction parameter Boltzmann's constant, erg molecule^{-1} K^{-1}
l	binary interaction parameter
N	number of data points number of molecules number of pair interactions
n	number of moles
P	experimental pressure, bars
p	binary parameter (equation 4-28)

Q	variable in the Wong-Sandler mixing rule (equation 2-50) area group parameter for the UNIFAC model (App. A-4)
q	dimensionless fugacity parameter in the MHV1 model Bondi's area parameter
R	universal gas constant, bars cm^3 mol^{-1} K^{-1} volume group parameter for the UNIFAC model (App. A-4)
r	mixture parameter in equation 4-3 Bondi's volume parameter
S	molar entropy, bars cm^3 mol^{-1} K^{-1}
s	energy parameter in the UNIFAC model (App. A-4)
T	thermodynamic temperature, K
U	molar internal energy, bars cm^3 mol^{-1}
u	dimensionless volume parameter in the MHV1 model
$\underline{v}$	total volume, cm^3
v	molar volume, cm^3 mol^{-1}
$\underline{X}$	denominator of the atteractive term of the Peng-Robinson EoS (in total volume)
x	overall mole fraction local composition fraction
y	vapor phase mole fraction
Z	compressibility factor
z	characteristic number for pair interactions

NOMENCLATURE

Greek Symbols

α	temperature dependent function of the EoS energy parameter dimensionless energy parameter in the MHV1 model nonrandomness parameter in the NRTL expression (equation 2-57) binary parameter in equation 7-1
β	parameter in the equation 5-3
γ	activity coefficient
Δ	difference
δ	parameter in the equation 5-2 Kronecker's delta
ε	pair interaction energy
ϑ	area fraction
κ	parameters in the Peng-Robinson EoS and its modifications PRSV, PRSV2.
λ	binary energy parameter of the 1FG^E model, bars cm^3 mol^{-1}
μ	chemical potential, bars cm^3
τ	energy parameter in the NRTL expression, bars cm^3 mol^{-1} energy group parameter for the UNIFAC model (App. A-4)
φ	volume fraction
ϕ	fugacity coefficient
ω	acentric factor

NOMENCLATURE

Superscripts

1,2	pseudopure fluid 1 or 2
ath	athermal solution
E	excess energy
EoS	equation of state
l	liquid phase
o	reference state
p	pure component
s	saturated phase
t	total property
v	vapor phase
^	component's molar property in a mixture
*	solution model
∞	infinite dilution state

NOMENCLATURE

Subscripts

c	critical property
i,j,k	component i, or j, or k indicates group for UNIFAC (App. A-4)
m	mixture property indicates group for UNIFAC (App. A-4)
o	zero pressure state
r	residual property reduced property
x	pseudopure fluid property
∞	infinite pressure state

CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 Introduction

Vapor-liquid equilibria of highly nonideal fluids are of great interest to the chemical process industry. For example in the oil industry hydrogenation reactions have to be performed under extreme operating conditions. There we need a tool to describe the solubility of hydrogen at equilibrium, in mixtures of various degrees of polarities. Additionally in the refrigeration industry there is a need for accurate predictive models in order to be able to analyze refrigeration cycles, something that will facilitate the replacement procedures of the ozone destroying molecules. Moreover, the solution of model problems will help us extend our understanding towards more complicated phase equilibria phenomena, as for the cases involving macromolecules in the blood stream or alloys in the area of solid state physics.

Semiempirical equations of state (EoS) have been successfully used for modeling the volumetric properties of pure fluids. Mixing rules for the EoS parameters are used for examining the phase behavior of mixtures. While the mixing rules traditionally used are based on molecular considerations, recently the mixture parameters are derived from a solution [excess Gibbs energy, (G^E)] model, through the so-called G^E-EoS mixing rules, [Huron and Vidal, (1979)].

The G^E-EoS models have been introduced into the area of Applied Thermodynamics to meet the current need for predictive tools. In the past the term "predictive" has been claimed for phase behavior analysis of multicomponent mixtures with the use of binary parameters obtained from correlation of binary systems over a range of temperatures, or a temperature near to the temperature of the multicomponent mixture. Michelsen (1990), used the term "predictive" for phase equilibria predictions of binaries as well as multicomponent mixtures over a range of conditions, from knowledge of only a few experimental binary data given at a certain temperature.

A large amount of low pressure experimental data exists in data banks, as for example the Dechema Data Series, [Ghmeling and Onken, (1977)]. Moreover, for only a few of these low pressure systems does there exist accurate experimental data over a range of conditions, up to very high pressures, as for example several water-alcohol mixtures. These systems, called in this work hereafter "test systems", have been mainly used in the recent years [Wong et al, (1992), Huang and Sandler, (1993)], to test the ability of the G^E-EoS models to extend vapor-liquid equilibria predictions over a range of conditions for binary and multicomponent systems, based on a limited amount of available experimental information given at low pressures.

In another use of a G^E-EoS model as a predictive tool for vapor-liquid equilibria of nonideal systems, the available experimental information can be obtained at any temperature, and then used for calculations at other higher or lower temperatures. In this form we expect the model's fugacity coefficient to assume its correct composition and pressure dependence no matter the temperature used to reveal physical information about the system considered. A general framework for G^E-EoS model development used for a predictive tool is given in Figure 1-1.

An EoS is combined with a G^E model and the model's parameters are obtained from correlation of few experimental data at a certain condition. Then phase equilibria predictions follow over an extended range of conditions. The G^E model can in principle draw information from statistical mechanics as well as molecular thermodynamics tailored to the specific class of systems modeled. Various thermodynamic formalisms can be employed for the G^E-EoS coupling.

The G^E models that have been incorporated into the G^E-EoS models so far are mainly based on the local composition approach and the two-fluid theory. These models, as for example the Wilson equation [Wilson, (1964)], the Non-Random-Two-Liquid

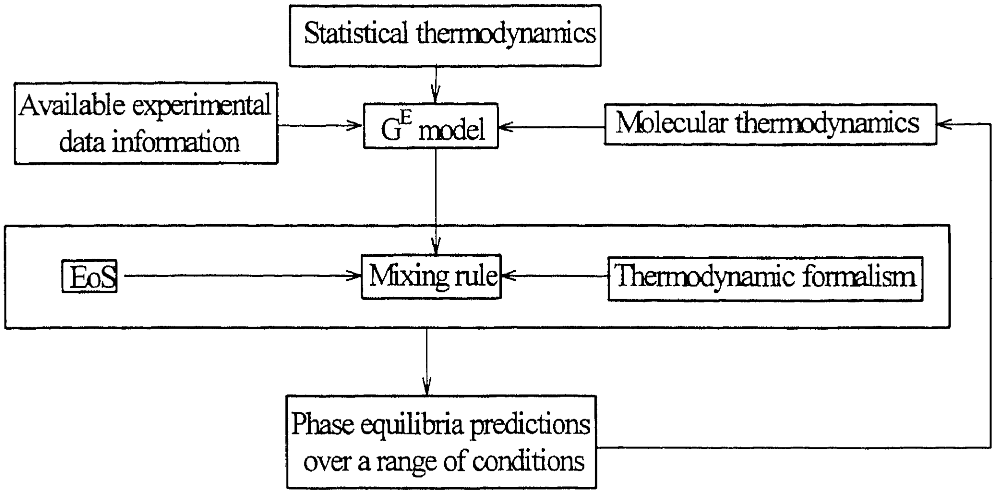

Figure 1-1 Framework for mixing rule development (G^E-EoS models)

Theory (NRTL) [Renon amd Prausnitz, (1968)], and the UNIQUAC equation [Abrams and Prausnitz, (1975)] have been traditionally used in the $\gamma-\phi$ approach to phase equilibria modeling, good only for low pressures.

The local composition concept was introduced into the area of solution models by Wilson (1964). The idea is that the local ordering of molecules at equilibrium conditions, does not follow the overall mixture composition. The local composition fractions satisfy rigorous mole balances. This concept has been incorporated in all successful solution models used nowadays.

Two-fluid theory assumes two hypothetical fluids in the binary mixture, with each one having its own properties and local ordering. This theory is in contrast to the one-fluid van der Waals theory where the binary mixture is treated as a pseudopure fluid. For the one-fluid theory the Gibbs energy of the mixture is, [Scott, (1956)]:

$$G_m(T,P,x) = G_x(T,P,x) + RT\sum_i x_i \ln x_i \qquad (1\text{-}1)$$

where subscript x denotes the pseudopure fluid. In the case of the two-fluid theory model each component in the mixture is treated as a pseudopure fluid. The Gibbs energy of the mixture is, [Scott, (1956)]:

$$G_m(T,P,x) = \sum_i x_i G_x(T,P,x_i) + RT\sum_i x_i \ln x_i \qquad (1\text{-}2)$$

The term $RT\sum_i x_i \ln x_i$ denotes the ideal Gibbs energy of mixing. The G^E for the two-fluid theory solution models as for example for the NRTL is:

$$G^E = x_1 G^{(1)} + x_2 G^{(2)} \qquad (1\text{-}3)$$

where $G^{(i)}$ is the Gibbs energy of the pseudopure fluid.

The G^E is defined as:

$$G^E = G_m(T,P,x) - RT\sum_i x_i \ln x_i \qquad (1\text{-}4)$$

1.2 Objectives

The G^E-EoS methodology is discussed in more details in chapter two. It is based on equation 2-25 and so far only solution models based on the two-fluid theory have been used. On the other hand the assumption underlying the G^E derived from an EoS is the one-fluid van der Waals approach (e.g. equation 2-26 for the RK-EoS). In general, two fluid theory has received less attention with respect to the formulation of the EoS composition dependence of parameters, [Malanowski and Anderko, (1992)].

This observation is used to set the main objective of this work. A solution model has to be developed that is consistent with the one-fluid character of the EoS ($1FG^E$ model). The G^E model will be incorporated in G^E-EoS thermodynamic formalisms for vapor-liquid equilibria prediction behavior of highly nonideal systems over an extended range of conditions, so that its utility can be rigorously validated. For this reason, three different cases will be studied.

Another objective of this work is the development of a general density dependent mixing rule in order to resolve the issue of using different models for both the liquid and vapor phases, so that the correct low- and high- pressure limits (set from the second virial coefficient and the solution model) can be satisfied. Density dependent mixing rules have been the focus of a great deal of research in the recent years, [Panagiotopoulos (1986), Dimitrelis and Prausnitz (1991)]. The utility of the density dependent formalism for high pressure phase equilibria in the sense of a predictive tool as required in the area of Applied Thermodynamics will be examined.

An additional objective of this work is to test the ideal solution assumption of equation 2-28, so that available low pressure experimental information can be utilized for the Huron-Vidal model through the use of equations 2-52 to 2-54 and 4-11. Successful application of our idea will yield another thermodynamic formalism for the G^E-EoS models by which they can be used as predictive tools. Although Huron and Vidal (1979) have paved the way for the new generation of the G^E-EoS models, so far their model has not been used as a predictive tool.

I. Case Study One

In chapter five we will examine the model's ability to incorporate available experimental data at low pressures for phase equilibria predictions over an extended range of conditions. "Test systems" will be used to meet this objective. For comparison, the performance of the alternative reformulated Wong-Sandler model [Orbey and Sandler, (1995b)] will be analyzed as well.

II. Case Study Two

The correlative abilities of our model will be examined from the simultaneous reduction of ternary as well as binary systems. "Difficult" model systems for this purpose can be taken from the highly asymmetric class of the hydrogen containing systems. Moreover, the model's ability to assign physical meaning to its parameters will be examined. As Malanowski and Anderko (1992) pointed out, it is difficult to assign physical meaning to the NRTL parameters due to a poor theoretical background. This point is expected from other two fluid theory models as well. The results of the study of case two are presented in chapter six.

III. Case Study Three

In chapter seven we search for a G^E-EoS model able to predict P-x diagrams over a range of conditions with limited amount of experimental information taken at any condition. This is a particular challenge for a G^E-EoS model, since we expect the parameters taken from an overall fit to be within the range defined from the parameters obtained from correlation of the individual sets of temperatures of the system. For this objective, highly nonideal systems are examined taken from the class of refrigerant mixtures.

CHAPTER 2

THEORY

2.1 Fundamentals

Classical Thermodynamics provides the conditions for equilibrium between a vapor (v) and a liquid (l) phase. The thermal, mechanical and chemical phase equilibrium conditions are:

$$T^{(v)}=T^{(l)} \tag{2-1}$$

$$P^{(v)}=P^{(l)} \tag{2-2}$$

$$f_i^v = f_i^l \tag{2-3}$$

where, T and P are the temperature and pressure of the two phases at the equilibrium conditions, and f_i^v, f_i^l the fugacities of component i in the two phases. In practice, the solution of the phase equilibrium problem is given by equation 2-3, upon specifying the temperature, pressure and composition dependence of the fugacity of each phase.

At low to moderate pressures the activity-fugacity coefficient ($\gamma-\phi$) method was traditionally used, where different models are applied to the liquid and vapor phases. To apply this method, equation 2-3 is written:

$$y_i \phi_i^v P = x_i \gamma_i P_i^s \phi_i^s \exp[-\frac{v^l (P - P_i^s)}{RT}] \tag{2-4}$$

where the subscripts s, v and l refer to the saturated, vapor and liquid phases respectively. The mole fractions of component i in the liquid and vapor phase are denoted with x_i and y_i respectively. In equation 2-4 an equation of state (EoS) is employed to calculate the fugacity coefficient of the vapor phase and a solution model is used to derive the activity coefficient of the liquid phase.

At high pressures the $\phi-\phi$ methodology was traditionally used. In this approach an EoS capable of describing both the vapor and liquid phases over an extended range of conditions is used. The reasoning behind this methodology is that the vapor and liquid phases become indistinguishable at the critical point. Equation 2-3 is written:

$$y_i \phi_i^v = x_i \phi_i^l \tag{2-5}$$

The adjective high-pressure is relative, and according to Prausnitz et al (1986), in the area of vapor-liquid equilibria this adjective corresponds to values from about 20 to 1,000 bars. In any case, at high pressures the dependence of the fugacity on pressure can not be neglected.

In general, an expression for the chemical potential and an EoS for the pressure can be obtained from an expression for the total residual Helmholtz energy ($\underline{A}_r$) from the thermodynamic identities:

$$\mu_i = \left(\frac{\partial \underline{A}_r}{\partial N_i}\right)_{T,\underline{V},N_{j\neq i}} \tag{2-6}$$

$$P = -\left(\frac{\partial \underline{A}_r}{\partial \underline{V}}\right)_{T,N_i} \tag{2-7}$$

The residual Helmholtz energy model can in principle be derived from statistical mechanics or perturbation theories. The complexity involved in this approach however, forced the development of semiempirical models.

Two classes of semiempirical models that have been successfully applied to the fundamental phase equilibrium problem are the excess Gibbs energy (G^E) models and the cubic equations of state (EoS).

In the G^E models, the deviation of the mixture total Gibbs energy from an ideal state is described with a well-behaved function.

$$\Delta \underline{G}^E = \underline{G}(T,P,N_1,\ldots\ldots,N_n) - \underline{G}(T,P,N_1^o,\ldots\ldots,N_n^o) \tag{2-8}$$

where the superscript o denotes properties of the mixture at the reference state. From equation 2-8 the activity and fugacity coefficient can be calculated directly.

$$\ln \gamma_i = \left[\frac{\partial (nG^E / RT)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \tag{2-9}$$

$$\ln\frac{\phi_i}{\phi_i^p}=[\frac{\partial(nG^E/RT)}{\partial n_i}]_{T,P,n_{j\neq i}} \tag{2-10}$$

where the superscript p denotes a pure state at the mixture's temperature and pressure. Examples in this class of semiempirical models are the Wilson equation, and the NRTL and UNIQUAC expressions. The G^E models were traditionally used to provide the activity coefficients in the $\gamma-\phi$ methodology.

For high-pressure phase equilibria cubic EoS are mainly used, and usually in a two-parameter form:

$$P=\frac{RT}{v-b_m}-\frac{a_m}{v^2+uvb_m+wb_m^2} \tag{2-11}$$

where a_m and b_m are the mixture's energy and size parameters, while u and w are numerical constants. Commonly used two parameter EoS are based on the Redlich-Kwong (1949) EoS (RK-EoS) [u=1,w=0] or the Peng-Robinson (1976) EoS (PR-EoS) [u=2,w=-1]. These equations provide accurate representation of the volumetric behavior of pure components as well as mixtures with a suitable choice of mixing rules for the parameters a_m and b_m. The fugacity coefficient of component i in the mixture ($\hat{\phi}_i$) is given by:

$$RT\ln\hat{\phi}_i=\int_v^\infty[\frac{\partial P}{\partial n_i}-\frac{RT}{v}]dv-RT\ln Z \tag{2-12}$$

In this work, the $\phi-\phi$ methodology is used to solve the fundamental phase equilibrium (equation 2-3) over an extended range of conditions.

2.2 Cubic EoS

The cubic EoS chosen for this work is the Peng-Robinson-Stryjek-Vera (PRSV) EoS. For the PR-EoS the pressure explicit form is:

$$P=\frac{RT}{v-b}-\frac{a}{v^2+2bv-b^2} \tag{2-13}$$

The energy parameter is:

$$a = (0.457235)\frac{R^2T_c^2}{P_c}\alpha(T) \tag{2-14}$$

The size parameter is:

$$b = 0.077796\frac{RT_c}{P_c} \tag{2-15}$$

For the original PR-EoS the temperature dependent term is :

$$\alpha(T) = [1+\kappa(1-T_r^{0.5})]^2 \tag{2-16}$$

where T_r is the reduced temperature.

$$T_r = \frac{T}{T_c} \tag{2-17}$$

and κ is a pure component-dependent parameter that they correlated with the acentric factor.

Stryjek and Vera (1986b) modified the κ parameter to be:

$$\kappa = \kappa_o + [\kappa_1 + \kappa_2(\kappa_3 - T_r)(1-T_r^{0.5})](1+T_r^{0.5})(0.7-T_r) \tag{2-18}$$

with κ_0 given by:

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196544\omega^3 \tag{2-19}$$

and κ_1, κ_2 and κ_3 component dependent parameters.

In this form, the modified PR-EoS has been termed the PRSV2 EoS [Stryjek and Vera, (1986b)], and when κ_2 and κ_3 are set to zero it is reduced to the PRSV EoS of Stryjek and Vera, (1986a). This EoS, in either form, has been preferred for the Wong-Sandler mixing rule [Wong and Sandler, (1992), Orbey and Sandler (1995a, 1995b)] to other modern cubic EoS such as the Soave modification of the RK-EoS [Soave, (1972)].

2.3 Mixing Rules

Two classes of mixing rules can be distinguished: those mixing rules where the mixture parameters are semiempirically derived, and those whose they are derived from solution models. In this section, we will present models from each class of mixing rules that have been well studied.

2.3.1 Mixing Rules Based on Molecular Considerations

Van der Waals Mixing Rule.

The basis of the mixing rule development is the one-fluid van der Waals mixing rule. The energy a_m and size b_m EoS parameters are:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{2-20}$$

$$b_m = \sum_i x_i b_i \tag{2-21}$$

where, b_i is the pure ith component's size parameter and x_i, x_j are the mole fractions of components i and j respectively. The combining rule for the cross parameter a_{ij} is:

$$a_{ij} = \sqrt{a_i a_j}(1 - k_{ij}) \tag{2-22}$$

with a_i and a_j the pure component energy parameters and k_{ij} a binary interaction parameter. This mixing rule has been used by Soave (1972), and can be considered as an extension of the original mixing rules used for the van der Waals EoS. It has been mainly used for modeling nonpolar or slightly polar systems.

Panagiotopoulos and Reid (1986a) Composition Dependent Model (PRCD)

Panagiotopoulos and Reid (1986a), introduced a composition dependent binary interaction parameter in the combining rule of equation 2-22, merely to facilitate phase equilibria calculations of mixtures containing polar components. For this composition dependent model the energy parameter is:

$$a_m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij} + x_j l_{ij}) \tag{2-23}$$

Panagiotopoulos and Reid (1986b) Density Dependent Model (PRDD)

However, the PRCD model does not predict the correct quadratic composition dependence of the second virial coefficient at low pressures. An energy parameter that does give the correct composition dependence of the mixture second virial coefficient (discussed in section 2.4.1) at low pressures has been proposed by Panagiotopoulos and Reid (1986b).

$$a_m = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}(1 - k_{ij}) + \frac{b_m}{vRT} \sum_i \sum_j x_i x_j (x_i - x_j) l_{ij} \qquad (2\text{-}24)$$

This mixing rule is a density-dependent mixing rule, and although it treats each phase with a different model, it does predict a critical point. Both the PRCD and PRDD models use equation 2-21 for the mixture's size parameter.

2.3.2 Thermodynamically Derived Mixing Rules

Huron-Vidal Mixing Rule (1979)

A different approach for the development of multiparameter models, is the simple but ingenious work of Huron and Vidal (1979). The basis of the mixing rule is the requirement of equality between the G^E as derived from an EoS and the G^E calculated by a solution model (denoted by *), at a certain condition.

$$\left(\frac{G^E}{RT}\right)_{con}^{EoS} = \left(\frac{G^E}{RT}\right)_{con}^{*} \qquad (2\text{-}25)$$

Huron and Vidal (1979) used the Soave RK-EoS (1972), for which:

$$\frac{G^E}{RT} = -\{\ln[\frac{P(v_m - b_m)}{RT}] - \sum_i x_i \ln[\frac{P(v_i - b_i)}{RT}]]\} -$$

$$\frac{1}{RT}[\frac{a_m}{b_m}\ln(\frac{v_m + b_m}{v_m}) - \sum_i x_i \frac{a_i}{b_i}\ln(\frac{v_i + b_i}{v_i})] + \frac{P[v_m - \sum_i x_i v_i]}{RT} \qquad (2\text{-}26)$$

In the Huron-Vidal mixing rule, G^E values are equated at the infinite pressure limit where:

$$\lim_{p\to\infty} v_i = b_i$$

$$\lim_{p\to\infty} v_m = b_m \qquad (2\text{-}27)$$

If at the infinite pressure condition (equation 2-27), an ideal solution is assumed:

$$v_{\infty}^{E} = 0 \qquad (2\text{-}28)$$

These simplify equation 2-26 to:

$$\left(\frac{G^{E}}{RT}\right)_{P=\infty}^{EoS} = -\frac{1}{RT}\left[\frac{a_m}{b_m}\ln(2) - \sum_i x_i \frac{a_i}{b_i}\ln(2)\right] \qquad (2\text{-}29)$$

Combination of equations 2-27 and 2-28 results in the linear mixing rule for the size parameter (equation 2-21). The mixing rule for the energy parameter is obtained by combining equations 2-25 and 2-29 and solving for a_m.

$$a_m = b_m\left[\sum_i x_i \frac{a_i}{b_i} - \frac{(G_{P=\infty}^{E})^{*}}{\ln 2}\right] \qquad (2\text{-}30)$$

This approach can be used with any EoS; the resulting expression is:

$$a_m = b_m\left[\sum_i x_i \frac{a_i}{b_i} + \frac{(G_{P=\infty}^{E})^{*}}{C}\right] \qquad (2\text{-}31)$$

where the numerical constant C depends on the EoS used. For example it is equal to -1 for the van der Waals EoS, -0.62 for the PR-EoS, and -ln2 for the RK-EoS. The fugacity coefficient for the Huron-Vidal model (derived in Appendix A-1) is:

$$\ln\phi_i = -\ln\left[\frac{P(v-b)}{RT}\right] + \frac{b_i}{b_m}\left(\frac{Pv}{RT} - 1\right) + \frac{\dfrac{a_i}{b_i RT} + \dfrac{\ln\gamma_i}{C}}{2\sqrt{2}}\ln\left[\frac{v + b_m(1-\sqrt{2})}{v + b_m(1+\sqrt{2})}\right] \qquad (2\text{-}32)$$

Michelsen (1990) MHV1 Mixing Rule

As an alternative a zero pressure condition has been used by Michelsen (1990) in equation 2-25. Dimensionless energy and volume parameters are defined:

$$\alpha_m = \frac{a_m}{b_m RT} \qquad (2\text{-}33)$$

$$u_m = \frac{v}{b_m} \qquad (2\text{-}34)$$

and so the RK-EoS is written in dimensionless form as:

$$\frac{Pb_m}{RT} = \frac{1}{u_m - 1} - \frac{\alpha_m}{u_m(u_m + 1)} \qquad (2\text{-}35)$$

Equation 2-35 is solved at the zero pressure condition. The dimensionless volume parameter has solutions for the liquid phase density root if $\alpha > 3 + \sqrt{2}$. In the sense of equation 2-35, Michelsen (1990), defined the dimensionless zero pressure fugacity (q).

$$\ln \frac{f_o b_m}{RT} = q(u_m, \alpha_m) \qquad (2\text{-}36)$$

In the Modified-Huron-Vidal-1 model (MHV1) the parameter q is correlated linearly with only the parameter α_m, since u_m is defined by α_m at the zero pressure limit:

$$q(\alpha_m) = q_o + q_1 \alpha_m \qquad (2\text{-}37)$$

$$\left(\frac{G^E_{P=o}}{RT}\right)^{EoS} = \ln \frac{f_o}{RT} - \sum_i x_i \ln \frac{f_{io}}{RT} \qquad (2\text{-}38)$$

by definition and so combination of equations 2-36 to 2-38 gives:

$$\left(\frac{G^E_{P=o}}{RT}\right)^{EoS} + \sum_i x_i \ln \frac{b_m}{b_i} = q_1 (\alpha_m - \sum_i x_i \alpha_i) \qquad (2\text{-}39)$$

The numerical constant q_1 depends on the EoS used. For example q_1 is equal to -0.53 for the PR-EoS. Combination of equations 2-25, 2-33 and 2-39 gives:

$$\frac{a_m}{RTb_m} = \sum_i x_i \frac{a_i}{RTb_i} + \frac{1}{q_1}\left[\left(\frac{G^E_{P=0}}{RT}\right)^* + \sum_i x_i \ln \frac{b_m}{b_i}\right] \qquad (2\text{-}40)$$

For the mixture b_m parameter, equation 2-21 is again used.

Tochigi et al (1994) MHV1T Mixing Rule

Another model based on equation 2-40, is the work of Tochigi et al (1994). For this model (MHV1T) the mixture second virial coefficient is written as:

$$B_m = b_m - \frac{a_m}{RT} = b_m\left(1 - \frac{a_m}{b_m RT}\right) = \sum_i x_i\left(b_i - \frac{a_i}{RT}\right) \tag{2-41}$$

Combination of equations 2-40 and 2-41 gives for the size parameter:

$$b_m = \frac{\sum_i x_i\left(b_i - \frac{a_i}{RT}\right)}{1 - \sum_i x_i \frac{a_i}{RTb_i} - \frac{1}{q_1}\left[\left(\frac{G^E_{P=0}}{RT}\right)^{*} + \sum_i x_i \ln\frac{b_m}{b_i}\right]} \tag{2-42}$$

Wong-Sandler (1992) Mixing Rule

The idea of using equation 2-41 in mixing rule development was first introduced by Wong and Sandler (1992). The Wong-Sandler mixing rule derives the mixture parameters from a set of two boundary conditions at the zero and infinite pressure limits. For the zero pressure limit the second virial coefficient condition is used, and the excess Helmholtz energy A^E is used for the infinite pressure limit. For example, the A^E for the van der Waals EoS is:

$$\begin{aligned}(A^E)^{EoS} &= -\frac{a_m}{v_m} + \sum_i x_i \frac{a_i}{v_i} - \\ &-RT\ln\left[\frac{p(v_m - b_m)}{RT}\right] + RT\sum_i x_i \ln\left[\frac{p(v_i - b_i)}{RT}\right]\end{aligned} \tag{2-43}$$

and at the infinite pressure limit (equation 2-27):

$$(A^E_{P=\infty})^{EoS} = -\frac{a_m}{b_m} + \sum_i x_i \frac{a_i}{b_i} \tag{2-44}$$

For any two-parameter cubic EoS equation 2-44 is written as:

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{(A^E_{P=\infty})^{EoS}}{C} \tag{2-45}$$

where the values of the parameter C are as reported previously for the Huron-Vidal model. The second virial coefficient condition is written as:

$$B_m = b_m - \frac{a_m}{RT} = \sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij} \qquad (2\text{-}46)$$

with the combining rule for the cross second virial coefficient condition:

$$(b - \frac{a}{RT})_{ij} = \frac{(b_i - \frac{a_i}{RT}) + (b_j - \frac{a_j}{RT})}{2}(1 - k_{ij}) \qquad (2\text{-}47)$$

where k_{ij} is a binary interaction parameter.

Combination of equations 2-45 and 2-46 gives the mixing rule for the mixture parameters.

$$\frac{a_m}{RT} = Q\frac{D}{1-D} \qquad (2\text{-}48)$$

$$b_m = \frac{Q}{1-D} \qquad (2\text{-}49)$$

where,

$$Q = \sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij} \qquad (2\text{-}50)$$

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{(A^E_{P=\infty})^*}{CRT} \qquad (2\text{-}51)$$

Wong and Sandler (1992) noted that the A^E is not dependent strongly on pressure, and so they have used the approximation:

$$(A^E_{P=\infty})^{EoS} \approx (A^E_{P=low})^{EoS} \qquad (2\text{-}52)$$

For a solution model at low pressures we also have the approximation:

$$(G^E_{P=low})^* = (A^E_{P=low})^* + P(v^E_{P=low})^* \approx (A^E_{P=low})^* \qquad (2\text{-}53)$$

Combination of equations 2-25 (written for A^E), 2-52 and 2-53 gives:

$$(A^E_{P=\infty})^{EoS} \approx (G^E_{P=low})^* \qquad (2\text{-}54)$$

Equation 2-54 is utilized in equations 2-48, 2-49 and 2-51 to solve for the mixture parameters from available experimental information at low pressures

2.4 Discussion on Mixing Rules

In this section we will discuss the mixing rules of section 2.3, and try to show points in their development, that are of general interest.

2.4.1 Mixing Rules Based on Molecular Considerations

The mixing rule of equations 2-20 to 2-22 is based on the one-fluid approach, first proposed by van der Waals in 1890, [Malanowski and Anderko, (1992)]. One-fluid theory treats a binary mixture as a hypothetical pure fluid at the same temperature and pressure, but with mixture parameters that are averages of the pure component parameters weighted by the mole fractions. The van der Waals mixing rule has been used by Redlich and Kwong (1949). The form of the combining rule 2-22 incorporates the idea of multicomponent mixture behavior prediction from only binary data. The binary interaction parameter k_{ij} has been introduced into the combining rule to match physical properties of a mixture. Graboski and Daubert (1979) have set the k_{ij} parameter equal to zero for binary hydrocarbon mixtures of equal size.

The mixing rule of equation 2-23 does not satisfy the condition that the mixture second virial coefficient should be quadratic in composition (equation 2-46). This condition has been derived from statistical mechanics. The virial expansion in pressure holds for dilute to moderately dense gases and vapors, since it is an expansion of the compressibility in powers of pressure about a pressure value equal to zero, [Abbott and van Ness, (1989)]. For this reason, the condition of equation 2-46 is expected from a mixing rule at low pressures. This idea prompted the density dependent mixing rule of equation 2-24 where the molar volume is incorporated into the mixture energy parameter. At low densities the energy parameter reduces to equation 2-20 with the combining rule of equation 2-22, and at high densities the model of equation 2-23 is recovered.

A significant problem that has to be avoided in the area of mixing rule development has been pointed by Michelsen and Kistenmacher (1990). In the Michelsen-Kistenmacher invariance problem the second component of a binary mixture is divided into two other components sharing the same properties, and with the same overall mole fraction as component two of the binary mixture. The EoS parameters for both mixtures have to be the same in this thought experiment. This invariance problem is not merely of academic interest as Michelsen and Kistenmacher (1990) pointed out, but also of practical interest. In several industrial applications, mixtures contain similar components, whether isomers or associating fluids, and an arbitrary number of pseudocomponents is used.

The two mixing rules, PRCD and PRDD, show the Michelsen-Kistenmacher invariance problem; the result depends on the number of pseudocomponents used in the multicomponent mixture of the thought experiment of Michelsen and Kistenmacher (1990).

A problem called the "dilution effect" has been pointed out by Michelsen and Kistenmacher (1990) as well, for the PRCD and PRDD models. The "dilution effect" relates to the diminishing of the parameter l_{ij} upon introduction of more components in the binary mixture i-j. This is due to the fact that the l_{ij} parameter takes significant part in the correlation of data since double summation terms contain the product of three mole fractions. Thus in multicomponent mixtures the effect of this parameter diminishes.

We note here, that mixing rules with the Michelsen-Kistenmacher invariance problem will break the one-fluid character of the van der Waals mixing rule since the hypothetical binary and ternary fluids will result in two different mixture critical conditions. While equations 2-14 and 2-15 hold for pure fluids only, a pseudocritical temperature and pressure can be defined which depend on the mixture equation of state parameters, [Reid et al, (1987)]. The Michelsen-Kistenmacher invariance problem is one possible reason why the one-fluid theory approach is used in EoS mixing rule development and not the two fluid theory approach. The mixture critical properties for the one-fluid theory treatment depend on the pure component critical properties and on the overall composition. On the other hand, the properties for the two-fluid theory treatment also depend on the number of the components used, since summation terms are involved.

2.4.2 Mixing Rules Based on Thermodynamic Formalism

In this section, discussion will follow on the mixing rules presented in section 2.3.2.

Equation 2-25 is the basis of the new generation of mixing rules, the so-called G^E-EoS models. The Huron-Vidal model has been used for correlating experimental data, since as it has been stated, it cannot utilize available information of a solution model given at low pressures [Michelsen, (1990), Wong and Sandler, (1992)]. Moreover, the model does not satisfy the second virial coefficient condition. Huron and Vidal (1979) defended the inability of the model to satisfy the second virial coefficient condition, since they believed that the experimental data at high densities require a higher order mixing rule in composition. Note here that if a density independent mixing rule satisfies this condition, it does so not only at low pressures but at all conditions. In the Huron-Vidal model, equation 2-28 is necessary so that the value of G^E will not be infinity at the infinite pressure limit.

While the mixing rules of Huron and Vidal (1979), and Michelsen (1990) will not result in any divergence of a state function at the infinite pressure state, the Wong-Sandler (1992) and the Tochigi (1994) models will do so, since they do not employ equation 2-21. On the other hand, the last two models do satisfy the second virial coefficient condition, while the first two do not.

Although MHV1 was criticized by Wong and Sandler (1992), in that it uses ad hoc extensions of the zero pressure fugacity, and that it does not satisfy the second virial coefficient condition, the MHV1T did not show any significant differences in the results compared to the MHV1 model, [Tochigi et al, (1994)].

2.5 Solution Models

Mainly solution models that are based on the two-fluid theory have been used with the G^E-EoS methodology.

Two-fluid theory has been introduced into G^E models by Wilson (1964), along with the local composition concept. This theory treats the binary mixture as two hypothetical fluids with each one having its own properties and local ordering. The NRTL and UNIQUAC equations are both based on two-fluid theory.

Besides the two-fluid theory models, the van Laar expression has been used as well [Wong et al, (1992)], but holds only for binary mixtures:

$$\left(\frac{G^E}{RT}\right)^* = \frac{1}{\frac{1}{A_{12}x_1} + \frac{1}{A_{21}x_2}} \tag{2-55}$$

A solution model that is widely used nowadays is the NRTL expression for which:

$$\left(\frac{G^E}{RT}\right)^* = \sum_{i=1}^{n} x_i \frac{\sum_{j=1}^{n} x_j G_{ji} \tau_{ji}}{\sum_{k=1}^{n} x_k G_{ki}} \tag{2-56}$$

where,

$$G_{ji} = \exp\left(-\alpha_{ji} \frac{\tau_{ji}}{RT}\right) \tag{2-57}$$

In the NRTL expression there are two energy parameters (τ_{ij} and τ_{ji}) and a non randomness parameter α_{ij} for each binary i-j pair. For the nonrandomness parameter the following assumption is used:

$$\alpha_{ij}=\alpha_{ji} \tag{2-58}$$

Although it is difficult to assign any physical meaning to the model parameters, the NRTL expression has excellent correlative abilities. A modification of equation 2-57 used by Huron and Vidal (1979) is:

$$G_{ji} = b_j \exp(-\alpha_{ji} \frac{\tau_{ji}}{RT}) \qquad (2\text{-}59)$$

The activity coefficients at infinite dilution for a binary mixture (for later reference), are related to the parameters of the modified NRTL expression [Orbey and Sandler, (1995b)] through the equations:

$$\tau_{21} = \ln \gamma_1^\infty - \tau_{12} \frac{b_1}{b_2} \exp(-\alpha_{12}\tau_{12})$$

$$\tau_{12} = \ln \gamma_2^\infty - \tau_{21} \frac{b_2}{b_1} \exp(-\alpha_{21}\tau_{21}) \qquad (2\text{-}60)$$

Comparisons of the mixing rules based on molecular considerations with those based on thermodynamic formalism are shown in Figure 2-1. While the classical, PRCD and PRDD models can not correlate the experimental data for the systems presented, the G^E-EoS models can predict their behavior with van Laar parameters taken at low pressures, as given in Wong et al (1992). Note that the MHV1T model has one parameter less than the Wong-Sandler model. The parameters for the molecular based mixing rules are given in Table 2-1.

Table 2-1 Parameters for acetone-water/2-propanol-water (Figure 2-1)

Mixing Rule	k_{ij}	l_{ij}
Classical	-0.167/-0.142	
PRCD	-0.404/-0.270	-0.015/-0.050
PRDD	-0.152/-0.139	5.556/1.099

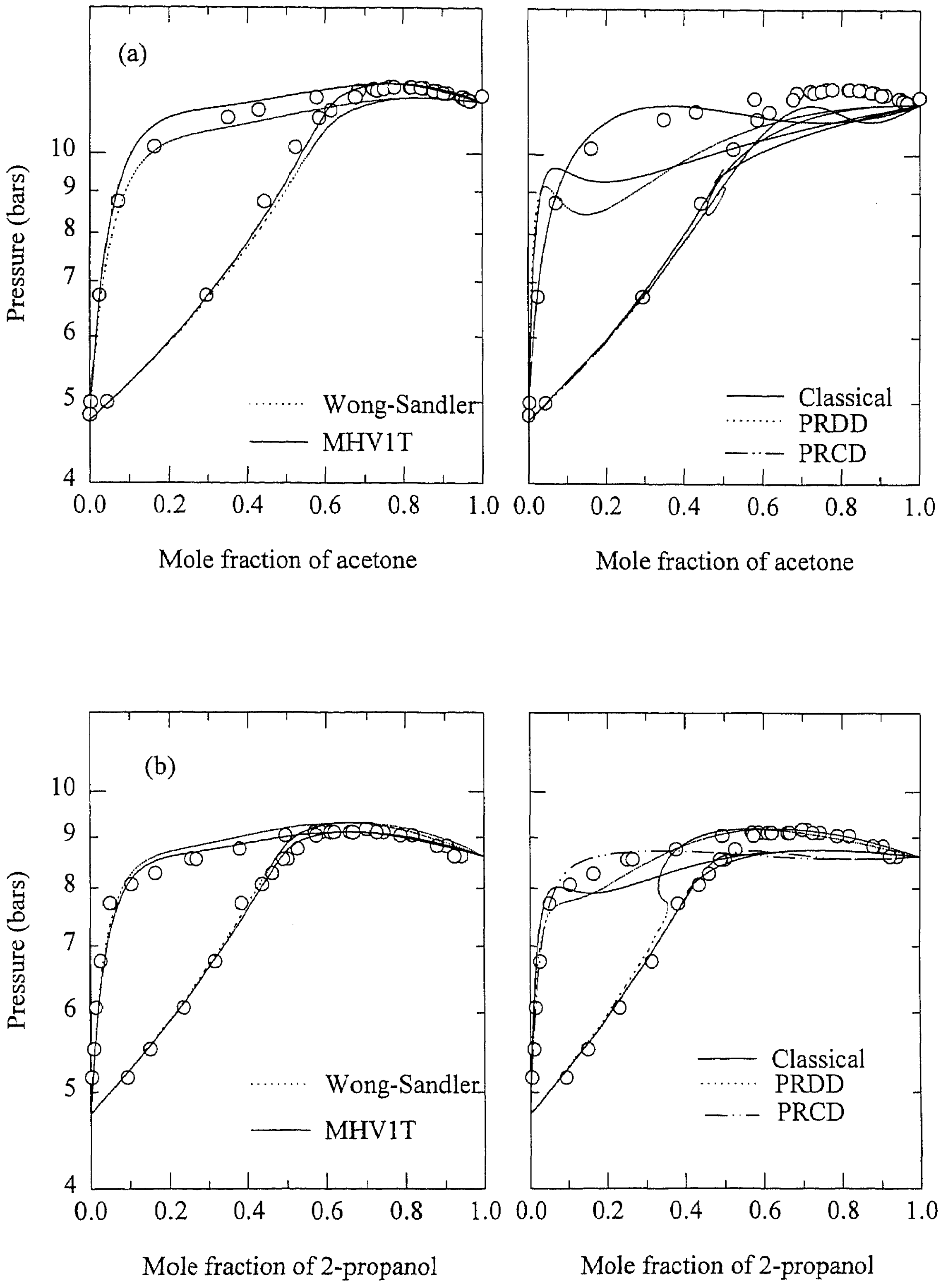

Figure 2-1 Comparisons of different models for the system (a) acetone-water, and (b) 2-propanol-water at 150°C.

CHAPTER 3

LITERATURE REVIEW

This study delved into a number of different issues. These issues involve modeling of high pressure nonideal systems with parameters obtained from systems at low pressure, equation of state (EoS) modeling of hydrogen containing systems with weight on ternary systems, as well as modeling of refrigerant mixtures. Due to the diversity of these various issues, the literature review has been organized in three different sections.

3.1 Vapor-Liquid Equilibria Predictions of High Pressure Systems

The first predictive model for high pressure equilibrium calculations from available G^E information at low pressures is the MHV1 model of Michelsen (1990) (presented in section 2.3.2). The MHV1 model was able to describe qualitative experimental data over a range of temperatures. Another version of this model (MHV2) developed by Dahl and Michelsen (1990) provided more accurate representation of high pressure vapor-liquid equilibria.

The thermodynamic formalism presented by Wong and Sandler (1992) has been applied successfully as a predictive tool to a variety of nonideal systems [Wong et al, (1992)]. A comprehensive study of the Wong-Sandler and the MHV2 models on a set of high-low pressure systems (test problems), by Huang and Sandler (1993), proved the superiority of the Wong-Sandler mixing rule over the MHV1 model for both the PRSV EoS and the Soave modification of the RK-EoS [Soave, (1992)]. That work included comparisons for vapor-liquid predictions of ternary systems.

Tochigi et al (1994) revised the MHV1 model so that it will be consistent with the second virial coefficient condition. They have not noticed any significant change in the results as compared to the MHV1 model. Moreover, they showed that the Wong-Sandler model does not always reproduce accurately G^E information at low pressures. They attributed this to the infinite pressure formalism on which the Wong-Sandler model is based.

Eubank et al (1995) extended the Wong-Sandler mixing rule, and proposed the use of the regular solution assumption for the liquid phase. This results for the van Laar model, for example, in an inverse relationship of the parameters with temperature so that the excess free energy model would be independent of temperature. They also revised the gas phase procedure, to take into account experimental values of cross second virial coefficients.

Orbey and Sandler (1995b), suggested the use of an excess free energy model of a special form with the Wong-Sandler mixing rule, so that it can be reduced to the 1-fluid mixing rule for systems where it is appropriate. For the nonideal systems they decided to have a predictive model, where the energy parameters of the NRTL expression [Renon and Prausnitz, (1968)] are obtained from the infinite dilution activity coefficients of a group contribution model, the nonrandomness is set to 0.1 and the binary interaction parameter in the combining rule is set to zero. As the NRTL model was originally developed, the nonrandomness parameter related to the reciprocal of the coordination number in the mixture, [Walas, (1985)].

Group contribution solution models with parameters obtained from experimental data reduction at low pressures can be incorporated into G^E-EoS models as well. Dahl et al (1991) used the MHV2 model with the modified UNIFAC model [Larsen et al, (1987)] for multicomponent vapor-liquid equilibria of complex systems and gas solubility predictions at low and high pressures. Orbey et al (1993), used the UNIFAC model at a low temperature to calculate the UNIQUAC parameters, which was the G^E model used with the Wong-Sandler mixing rule, to predict vapor-liquid and liquid-liquid equilibria over a great range of pressures and temperatures. To obtain the binary interaction parameter in the combining rule for the mixture second virial coefficient, they used the mixing rule at a low temperature and at an equimolar composition point of the binary mixture. In another work, Kolar and Kojima (1993) used an infinite dilution activity coefficient model to match it with the one derived from the EoS and so they defined the value of the cross second virial coefficient which in turn defined the value of the binary interaction parameter. They used their model with group contribution methods such as the modified UNIFAC [(Larsen et al, (1987)], and the modified ASOG method [Tochigi et al, (1993)]. Soave et al (1994), used another modified UNIFAC specific for infinite dilution activity coefficient prediction, which was subsequently used for the calculation of the activity coefficients at the infinite pressure state, and phase equilibria predictions followed with a Huron-Vidal mixing rule.

3.2 Modeling of Hydrogen Containing Mixtures

The phase behavior of hydrogen containing mixtures is of major importance in the chemical industry, as for example for the development of hydrotreating processes (coal liquefaction area) or cryogenic recovery of methane from synthetic gas. Mixtures containing hydrogen show such complex phase equilibria behavior as gas-gas demixing, and density inversions for mixtures of light gases. The description of the phase equilibria of these high pressure systems, was traditionally done with the use of charts specific for each system, that provided the equilibrium ratio for each component, and the equations of state that were at hand. In the following we will provide a short review of the work in the area of hydrogen containing systems.

Sagara et al (1972), provided equilibrium data of binary and ternary systems. In particular, they studied the ternary systems hydrogen-ethylene-methane (ethane). They concluded that the addition of a heavier hydrocarbon than methane raises the relative volatility of the hydrogen to methane, and that upgrades the purity of hydrogen in the recovery gas. The Benedict-Webb-Rubin (1951) EoS (BWR) was fair for the description of the experimental data. In another work Sagara et al (1975) studied the ternary mixtures hydrogen - methane - propylene, hydrogen - propane - propylene, and hydrogen - propane - ethylene. The accuracy in the predictions of the equilibrium values of the hydrocarbons decreased at lower temperatures with the BWR EoS. They especially observed that, when the system was below the normal boiling points of the hydrocarbons, the errors of those components exceeded 10%. Besides, they applied the regular solution theory for Henry's constant predictions and they concluded that their method could be successfully applied for predictions of the Henry's coefficients of simple gases in nonpolar mixed solvents. Nieto and Thodos (1978), studied the polar-nonpolar system ethanol-propane over an extended range of conditions and they used the BWR EoS, and also the Soave RK-EoS (Soave, 1972) to describe the phase properties of the mixture. The results were fair, with somewhat better predictions of the cubic EoS for the equilibrium values of the polar component. They suggested that the improvement in the system representation can result from the mixing rule improvement, and the better understanding of the interactions between unlike molecules.

Graboski and Daubert (1979) developed the Penn State EoS which was applied to both defined and undefined systems containing hydrogen. They concluded that there is no need for binary interaction parameters for systems of hydrocarbons, but for mixtures of nonhydrocarbons the binary interaction parameter improves the predictions significantly. Moreover, they correlated the interaction parameter with the solubility parameter difference between the hydrogen and the nonhydrocarbon. Gray et al (1983), examined a variety of cubic EoS for multicomponent systems containing hydrogen, and concluded that a version of the RK-EoS, with a temperature dependent size parameter, can facilitate the phase equilibria correlations of the binary systems, but not necessarily for the multicomponent mixtures.

Vetere (1986) applied the γ–ϕ method with the symmetric convention for all mixture components, for vapor-liquid equilibria of mixtures with supercritical gases. He correlated the NRTL parameters of the binary polar and nonpolar systems with temperature. The results showed good representation of multicomponent systems. Wang and Zhong (1989), studied several hydrogen containing mixtures and suggested the use of the Panagiotopoulos and Reid (1986a) mixing rule for the cohesive mixture parameter, and a similarly modified form for the mixture covolume parameter. In another work Grevel and Chatterjee (1992), studied vapor-liquid equilibria of the hydrogen-water system, over an extended range of conditions with a modified form of the RK-EoS. They assumed pressure dependent size and energy parameters for the pure components, and they used the one fluid mixing rule for the mixture. These assumptions involved a numerical integration into the phase equilibrium problem.

Promising results into this difficult problem of phase predictions of mixtures involving supercritical gases, came from the work of Huang et al (1994), who employed the G^E-EoS methodology with the Wong-Sandler (1992) mixing rule and the NRTL model, for hydrogen-hydrocarbon mixtures. Moreover, they correlated the model's parameters with temperature and the acentric factor of the hydrocarbon. Their work proves the usefulness of a G^E model for phase predictions for the highly asymmetric class of hydrogen-hydrocarbon systems.

3.3 Modeling of Refrigerant Mixtures

The most important application of chlorofluorocarbons (CFCs), and hydrochlorofluorocarbons (HCFCs) is refrigeration. The phase behavior prediction of refrigerant mixtures and pure components has been addressed through the EoS approach. A review of the recent literature involving cubic EoS which have been most commonly used for modeling of the refrigerant systems will follow.

Wright (1985), applied the Soave-RK-EoS (Soave, 1972), for several binary mixtures and the ternary nonazeotropic system R13b1-R12-R152a. A limited amount of experimental data on binary mixtures was correlated to provide the value of the single interaction parameter per pair of components which gave good predictions for the systems tried. Abu-Eishah (1991), used the PR-EoS with a single interaction parameter for a variety of CFC mixtures and CFC-gas mixtures. His model did not work with the same accuracy for all systems tried, as for example it predicted a false phase splitting at low temperature for the system R14-R23. Moreover, he concluded that the binary interaction parameter is not always easily correlated with temperature for all systems with a single equation. Nevertheless, Lee and Sun (1992), by using the Patel-Teja (1982) EoS with a single mixture parameter, managed to correlate it with the acentric and the critical compressibility factors of the pure components. The predictive model worked satisfactorily for phase equilibria predictions of a variety of refrigerant mixtures including azeotropes. Moshfegian et al (1992), recommended the use of the PR-EoS with classical mixing rules for calculating thermodynamic properties of refrigerant mixtures including azeotropic ones, except for liquid densities, where the predictions were not so accurate. Gow (1993) used a Clausius type EoS, with one parameter for each pure component and one interaction parameter per binary pair, for modeling the phase equilibria properties of pure refrigerants and mixtures. Additionally, he correlated the interaction parameter with temperature for each binary pair with the use of a second degree polynomial. Reasonable model predictions followed for the ternary mixture R14-R23-R13 at 199.8 K and 6.895 bars, with parameters correlated from the constituent binaries at the same temperature. Laugier et al (1994), presented experimental data and modeling of binary and ternary mixtures of HCFCs and CFCs. They concluded that either the Trebble-Bishnoi-Salim EoS or its generalized form [Salim and Trebble, (1991)], are best suited for the representation of saturated pressures and liquid molar volumes of the mixtures studied. In the generalized Trebble-Bishnoi-Salim EoS pure component parameters are correlated with the acentric factor and the critical compressibility factor. For the mixing rule, after trials with a temperature dependent size parameter, they settled on the one parameter classical mixing rule to avoid erroneous results for derivative properties predicted from their model. Kleiber (1994), studied vapor-liquid equilibria of sixteen binary refrigerant mixtures with propylene or R134a with the PR-EoS as modified by Stryjek and Vera (1986a). He concluded that a two-parameter van Laar type of mixing rule gave only slightly better results than the one parameter van der Waals mixing rule. He also noted, the inability of the UNIFAC group contribution method to deal with halogenated refrigerant mixtures.

Noncubic EoS have also been used for refrigerant mixtures. For example, Blindenbach et al (1994) applied the Perturbed Anisotropic Chain Theory, a closed-form EoS, to model vapor pressures and liquid densities of pure CFC and HCFC components, as well as mixtures of CFCs with HCFCs and CFCs/HCFCs with hydrocarbons. Their model performed successfully as a predictive tool, especially for mixtures with polar components, while they suggested the use of a cubic EoS such as the PR-EoS as a correlative tool. An extended BWR EoS has been proposed by Nishiumi et al (1995) for mixtures of HCFCs and CFCs. This EoS is not in a closed form and includes in the compressibility factor of each pure component, five parameters for polar contributions in addition to fifteen nonpolar parameters. The mixing rule for their model has one binary interaction parameter which was correlated for each system with temperature through a quadratic equation.

The problem of the description of the temperature dependence of the binary interaction parameters involved in the models presented, passed with the use of the G^E-EoS models. These models provide temperature-dependent mixture parameters through the built-in temperature dependence of the G^E model. Orbey and Sandler (1995a), suggested the use of the Wong-Sandler mixing rule with a cubic EoS for unconventional refrigerant mixtures. For the G^E model they used the NRTL theory [Renon and Prausnitz, (1968)] which along with the combining rule, constitutes a three parameter thermodynamic model. As they have shown, it is possible to obtain the model's parameters from experimental data regression at a single temperature, and then use the same parameters for phase equilibria predictions at other temperatures. In another work by Peng et al (1995), an excess enthalpy-EoS (H^E-EoS) model was derived from the infinite pressure limit of the excess enthalpy (H^E). The H^E function has been shown to be independent of pressure. An explicit expression of the EoS mixture energy parameter resulted only after they isolated the absolute temperature from the pure component EoS energy parameter. A polynomial expression with two to four parameters was used for the direct correlation of available H^E experimental data, along with the Soave RK-EoS (Soave, 1972), and simple linear mixing rules with no adjustable parameters. The model was applied to vapor-liquid equilibria property predictions for a variety of hydrocarbon and halogenated refrigerant mixtures with fair results.

CHAPTER 4

MODEL DEVELOPMENT

4.1 Density Dependent Mixing Rule

In order to relax the vapor phase model from the free energy model traditionally used for the liquid phase, and also use the ideal solution assumption at the infinite pressure limit (equation 2-28), we developed a density dependent mixing rule. Note that the mixing rule of equation 2-21 is a good assumption for the EoS approach, [Walas, (1985)]. Besides, a temperature dependent mixture size parameter will result in a divergent value of $U^E_{P=\infty}$ [Eubank et al, (1995)]. In Appendix A-2 we show the steps for the mixing rule derivation. The mixing rule that results is:

$$a_m = (\frac{(G^E_{P=\infty})^*}{C} + \sum_i x_i \frac{a_i}{b_i})bF + RT[b - \sum_i x_i(b_i - \frac{a_i}{RT})](1-F) \qquad (4\text{-}1)$$

where F is a density dependent interpolation function.

In this work we considered an interpolation function with the general form:

$$F = \frac{rb}{v+(r-1)b} \Rightarrow 1-F = \frac{v-b}{v+(r-1)b} \qquad (4\text{-}2)$$

where r a composition dependent separation parameter:

$$r = \sum_i \sum_j x_i x_j r_{ij} \qquad (4\text{-}3)$$

Equation 4-3 is needed so that calculation of multicomponent systems will be possible from only binary parameters. When all r_{ij} parameters in this equation are equal to one, we get for the interpolation function:

$$F = \frac{b}{v} \qquad (4\text{-}4)$$

and for the fugacity coefficient:

$$\ln\phi_i = -\ln[\frac{P(v-b)}{RT}] + \frac{b_i}{b}[\frac{Pv}{RT}-1] + \frac{\partial nD/\partial n_i}{2\sqrt{2}}\ln[\frac{v+(1-\sqrt{2})b}{v+(1+\sqrt{2})b}] +$$

$$\frac{b_i Q - 2b\sum_j x_j (b_{ij} - \frac{\sqrt{a_i a_j}}{2RT}) - b^2(\frac{\partial nD}{\partial n_i} - 1)}{2b^2}\ln(\frac{v^2}{v^2+2bv-b^2}) \quad (4\text{-}5)$$

where Q and D are defined in equations 2-50 and 2-51 respectively. For the mixture size parameter we employed equation 2-21. The only model parameters are those from the G^E model. A study of more than forty ethanol-water systems from the Dechema Data Series, [Gmehling and Onken, (1977)] revealed that a system at 4.137 bars gives the best van Laar parameters for overall predictions with the Wong-Sandler mixing rule. We used the same system to obtain the van Laar parameters for mixing rule 4-1. For comparison, we also used a data set at 50°C to obtain the van Laar parameters.

Comparisons of the model of equation 4-5 (DD model) with the Wong-Sandler (W-S) mixing rule is given in Table 4-1. The table reports the sum-of-squared residuals obtained for predicting data sets at eight different temperatures. Note that the Wong-Sandler approach uses not only the two van Laar parameters but also a k_{ij} parameter (equation 2-47).

Table 4-1 $DP = \sum_N (P - P_{exp})^2$ and $Dy = \sum_N (y - y_{exp})^2$ for the system ethanol-water, with the Wong-Sandler (W-S) and the density dependent (DD) mixing rule.

	W-S (4.137 b)		DD (4.137 b)		DD (50°C)	
T (°C)	DP	Dy	DP	Dy	DP	Dy
120	$1.207\ 10^{0}$	$2.215\ 10^{-2}$	$1.154\ 10^{0}$	$1.683\ 10^{-2}$	$5.475\ 10^{-1}$	$6.632\ 10^{-3}$
150	$1.825\ 10^{0}$	$8.399\ 10^{-3}$	$2.392\ 10^{1}$	$1.105\ 10^{-2}$	$9.040\ 10^{-1}$	$4.931\ 10^{-3}$
200	$5.805\ 10^{0}$	$1.157\ 10^{-3}$	$1.430\ 10^{1}$	$3.618\ 10^{-3}$	$5.157\ 10^{0}$	$2.295\ 10^{-3}$
250	$1.108\ 10^{1}$	$2.073\ 10^{-3}$	$4.995\ 10^{1}$	$2.127\ 10^{-3}$	$1.868\ 10^{1}$	$1.376\ 10^{-3}$

Table 4-1 (continued)

	W-S (4.137 b)		DD (4.137 b)		DD (50°C)	
T (°C)	DP	Dy	DP	Dy	DP	Dy
275	$6.509\ 10^{1}$	$7.413\ 10^{-3}$	$3.825\ 10^{1}$	$1.373\ 10^{-3}$	$2.834\ 10^{1}$	$1.419\ 10^{-3}$
300	$5.835\ 10^{1}$	$2.166\ 10^{-3}$	$2.307\ 10^{0}$	$5.703\ 10^{-4}$	$1.785\ 10^{1}$	$7.288\ 10^{-4}$
325	$2.733\ 10^{2}$	$5.509\ 10^{-3}$	$3.934\ 10^{1}$	$1.144\ 10^{-3}$	$5.788\ 10^{1}$	$1.288\ 10^{-3}$
350	$9.328\ 10^{0}$	$8.488\ 10^{-5}$	$1.209\ 10^{1}$	$3.173\ 10^{-6}$	$9.257\ 10^{0}$	$2.864\ 10^{-6}$

Although the results for the ethanol-water system were good, that was not the case for other high pressure systems. The main problem encountered was the difficulty with tuning the binary r_{ij} parameters, which implies that it is not possible to separate the vapor and liquid phases when both phases are at high densities. Besides, the DD model has been implicitly derived from the G^E-EoS formalism. So the idea of using different models for each phase and matching them at the critical point with a density dependent mixing rule did not work well in this sense of a predictive tool, and it was difficult to extend to multicomponent mixtures.

4.2 Utilization of Low Pressure Data for the Huron-Vidal Model

It is preferable to use the infinite pressure limit, since information from the structure of the EoS can be directly incorporated in the mixing rule. Moreover, these limiting cases can reveal theoretical weaknesses of a model.

Since the excess internal energy can not be divergent at any condition (including the infinite pressure state, [Eubank et al, (1995)]), and the A^E is not divergent as well at the infinite pressure limit (equation 2-44), we get for the excess entropy (S^E):

$$S^E_{P=\infty} = \frac{U^E_{P=\infty} - A^E_{P=\infty}}{T} \neq \infty \qquad (4\text{-}6)$$

Two approaches can be followed at this point. In the first approach equation 2-28 holds. For this case the G^E at the infinite pressure state is not divergent due to the relationship:

$$v^E_{P=\infty} = 0 = \left(\frac{\partial G^E}{\partial P}\right)_{T,x} \tag{4-7}$$

Besides,

$$H^E_{P=\infty} = U^E_{P=\infty} + Pv^E_{P=\infty} = U^E_{P=\infty} \tag{4-8}$$

Also,

$$A^E_{P=\infty} = U^E_{P=\infty} - TS^E_{P=\infty} \tag{4-9}$$

$$G^E_{P=\infty} = H^E_{P=\infty} - TS^E_{P=\infty} \tag{4-10}$$

Combining equations 4-8 to 4-10 we get:

$$A^E_{P=\infty} = G^E_{P=\infty} \tag{4-11}$$

In the second approach [as used by Wong and Sandler (1992)] in lieu of equation 2-28 we have:

$$v^E_{P=\infty} \neq 0 \tag{4-12}$$

Consequently the $G^E_{P=\infty}$ is divergent as well as $H^E_{P=\infty}$ from equation 4-8. Also, for cases where the EoS energy parameter does not depend on temperature, [Eubank et al (1995)]:

$$S^E_{P=\infty} = 0 \tag{4-13}$$

For these cases where equation 4-13 holds we get from equation 4-9:

$$A^E_{P=\infty} = U^E_{P=\infty} \tag{4-14}$$

We note that while the approach based on equation 2-28 (ideal solution) would work for both the athermal and regular solution models at the infinite pressure state, the approach based on equation 4-10 would work only with the regular solution model.

Equation 4-9, based on the ideal solution assumption at the infinite pressure limit (equation 2-28), along with equations 2-52 to 2-54 provide the basis for the utilization of low pressure information for the Huron-Vidal mixing rule.

4.3 One Fluid Excess Gibbs Energy (1FG^E) Model

The following model that we will present is not based on two-fluid theory and so it can be incorporated in equation 2-25 in a consistent way. Note that we do not need just a value from the solution model, but we incorporate its structure to the G^E-EoS model.

Rigorous development from statistical mechanics and proper use of molecular thermodynamic considerations have been combined with the local composition concept established by Wilson (1964) to provide the total Gibbs energy of mixing for a liquid solution [Knox et al, (1984)]:

$$\frac{\Delta G^t}{kT} = \frac{(\Delta G^t)^{ath}}{kT} - \sum_i \frac{z_i N_i}{2} \ln \frac{z_i N_i / 2}{I} + \sum_i \sum_j N_{ij} \left(\frac{\varepsilon_{ij}}{kT} + \ln \frac{N_{ij}}{z_i N_i / 2} \right) - \sum_i \frac{z_i N_i \varepsilon_{ii}}{2kT} \qquad (4\text{-}15)$$

The interaction energy of an i-j pair is ε_{ij} and the number of i-j pair interactions is N_{ij}. The Boltzmann factor is denoted with k. The number of component i molecules is N_i and z_i is the characteristic number of pair interactions for a molecule i with other molecules.

The counting of the number of pair interactions assigned to species i is:

$$\frac{z_i N_i}{2} = \sum_j N_{ij} \qquad (4\text{-}16)$$

The i-j pair interactions are assigned half to species i and half to species j:

$$N_{ij} = N_{ji} \qquad (4\text{-}17)$$

The total number of interactions in the mixture is:

$$I = \sum_i \frac{z_i N_i}{2} \tag{4-18}$$

So we can define the local composition around an i species:

$$x_{ij} = \frac{N_{ij}}{z_i N_i / 2} \tag{4-19}$$

and a molecular z-area fraction as:

$$\vartheta_i = \frac{z_i N_i / 2}{I} \tag{4-20}$$

The maximum sum of the model's partition function results when:

$$\frac{N_{ij} N_{ji}}{N_{ii} N_{jj}} = \exp[\frac{-(2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj})}{kT}] \tag{4-21}$$

For the athermal solution model, Knox et al (1984) used the Guggenheim model for which:

$$\frac{(\Delta G)^{ath}}{RT} = \sum_i x_i \ln \varphi_i + \sum_i \frac{z_i x_i}{2} \ln \frac{\vartheta_i}{\varphi_i} \tag{4-22}$$

From the definition of G^E:

$$\frac{G^E}{RT} = \frac{\Delta G}{RT} - \sum_i x_i \ln x_i \tag{4-23}$$

we get:

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\varphi_i}{x_i} + \sum_i \frac{z_i x_i}{2} \ln \frac{x_{ii}}{\varphi_i} \tag{4-24}$$

where φ_i is a volume fraction of component i:

$$\varphi_i = \frac{x_i r_i}{\sum_j x_j r_j} \tag{4-25}$$

where r_i a volume parameter defined in Bondi (1968).

The model's activity coefficient is:

$$\ln\gamma_k = 1 - \frac{\varphi_k}{x_k} + \ln\frac{\varphi_k}{x_k} + \frac{z_k}{2}\left(\frac{\varphi_k}{\vartheta_k} - 1 + \ln\frac{x_{kk}}{\varphi_k}\right) \qquad (4\text{-}26)$$

Originally the model was used for correlating vapor-liquid equilibria under the assumption:

$$\frac{x_{ij}x_{ji}}{x_{ii}x_{jj}} = C_{ij} \qquad (4\text{-}27)$$

Knox et al (1984) applied the model for vapor-liquid equilibria of binary systems, with the use of three parameter z_1, z_2 and C_{12}. The results showed that different values of the same species had to be assigned to improve the correlations. Replacement of the z_i values with the q_i values did not produce accurate results.

In order to fix this problem and since we noted that z_i counts the pair interactions, we made the modification that:

$$z_i = \sum_j p_{ij}\frac{N_j}{N} \qquad (4\text{-}28)$$

where p_{ij} is a binary parameter correlated to the pure component area parameter q_i as set from Bondi (1968). Note here that as in the original model the i-j pair interactions are averaged in the mixture, it is not proper to treat the p_{ij} parameter as an adjustable one, under the assumption:

$$p_{ij} \neq p_{ji} \qquad (4\text{-}29)$$

Of course it can be treated as fitted parameter under the assumption:

$$p_{ij} = p_{ji} \qquad (4\text{-}30)$$

This requirement is necessary so that physical information on the system can be captured with the use of the parameter. Otherwise, the predictive ability will be defeated, in lieu of the correlative ability. This is a crucial point in a model development, since if we can find a model which relates the p_{ij} parameter to pure component properties in a functional form, of course then we can have equation 4-29, but then the functional form of the p_{ij} parameter should be invariant under the change of the subscripts of the components in the mixture.

We thus managed to modify the model of Knox et al (1984), so that it will be consistent with the idea of phase behavior predictions of multicomponent mixtures with only binary parameters.

Upon application of the activity coefficient definition:

$$\ln\gamma_k = (\partial\frac{\Delta G^t / kT}{\partial N_k})_{T,P,N_j} - \ln x_k \qquad (4\text{-}31)$$

we get:

$$\ln\gamma_k = 1 - \frac{\varphi_k}{x_k} + \ln\frac{\varphi_k}{x_k} + \frac{z_k}{2}(\frac{\varphi_k}{\vartheta_k} - 1 + \ln\frac{x_{kk}}{\varphi_k}) + \sum_i \frac{x_i(p_{ik} - z_i)}{2}\ln\frac{x_{ii}}{\varphi_i} \qquad (4\text{-}32)$$

The working equations of our model are 4-24, 4-32 along with:

$$\vartheta_i = \frac{z_i x_i}{\sum_j z_j x_j} \qquad (4\text{-}33)$$

$$\frac{x_{ij} x_{ji}}{x_{ii} x_{jj}} = \exp[\frac{-10^4}{RT}\lambda_{ij}] \qquad (4\text{-}34)$$

$$\vartheta_i x_{ij} = \vartheta_j x_{ji} \qquad (4\text{-}35)$$

$$\sum_j x_{ij} = 1 \qquad (4\text{-}36)$$

$$z_i = \sum_j x_j p_{ij} \qquad (4\text{-}37)$$

Note here that since this model is to be used for phase behavior predictions over a range of temperatures, equation 4-34 is needed, while for single temperature correlations, equation 4-27 could be used very well.

If we assume in equation 4-32:

$$p_{ik} = z_i \qquad (4\text{-}38)$$

our model reduces to the original model of Knox et al (1984). Equations 4-24 and 4-32 are derived in Appendix A-3.

With inspection of equations 1-1 to 1-4 it is clear that this model (termed as $1FG^E$) is based on one fluid theory, consistent with the one-fluid character of G^E as derived from an EoS.

4.4 Predictive Tools (Case Three)

In this section we will give a short discussion on a main point that this work tackles in chapter seven.

As we already mentioned, the needs in Applied Thermodynamics have recently changed. A predictive tool is needed where a minimum amount of experimental information can be used to tune the model parameters so that predictions can be made at higher and lower temperatures.

Multiparameter models are not in general suitable for this reason. For example we need at least four experimental data points to obtain the parameters of the NRTL expression when it is combined with the Huron-Vidal mixing rule, or five points for the Wong-Sandler mixing rule. Note here that in order to fit model parameters with the Marquardt-Levenberg algorithm, used in this work, we need at least one degree of freedom [(number of points) - (number of parameters)].

Another point related to the numerical solution of the problem, is the encounter of local minima for the objective function [Walas, (1985)]. This implies that the number of parameters in the nonlinear model are too many, and they should be reduced.

In the phase equilibrium problem with the $\phi-\phi$ methodology, it is required that the correct dependence of the fugacity coefficient, on the temperature, pressure, and composition can be captured from the model. Moreover, it is sought that the model parameters, as tuned to meet the correct dependence of the fugacity coefficient on the problem variables, can be related to physical properties of the mixture such as its polarity and asymmetricity (size differences of the molecules). In a sense this would prove the usefulness of the model as a predictive tool.

This problem as tackled by a predictive model is not trivial at all, due to the extreme range of the conditions involved. A heuristic rule is set in this work to develop such a predictive model. The overall correlation of all the temperature sets should result in model parameters, that are within the ranges defined from the correlation of the individual temperature sets. We can imagine that for a fixed temperature and a binary system we look at a surface of the fugacity coefficient [$\phi(P,x_1)$]. As the results of chapter seven will show, the description of the model can be mapped to a single parameter. For a range of temperatures these surfaces can define in the parameter space a polynomial of various degrees (first, third, etc.). The difficulty comes when we consider the hypersurface of the fugacity coefficient, where the temperature varies. For this case the rule that we set can accommodate the need that this hypersurface (four dimensions) will reduce to the individual surfaces defined earlier.

Two-fluid theory models in particular, are not good candidates for such a predictive tool, since it is difficult to assign physical meaning to the parameters. This can be seen for the NRTL model, where the nonrandomness parameter can be set to different values for different classes of systems [Orbey and Sandler, (1995a), Orbey and Sandler, (1995b)]. Of course the behavior of the model is different for different values of the nonrandomness parameter, and very different to the behavior of the original NRTL model, where all three parameters are fitted simultaneously.

CHAPTER 5

CASE STUDY ONE

5.1 Introduction

In this chapter we will present high pressure vapor-liquid equilibria predictions with the $1FG^E$-EoS model under the thermodynamic formalism of the Huron-Vidal model. Low pressure experimental data will provide the single energy parameter of the $1FG^E$ model. The justification of our approach is given in section 4.2. The systems modeled are "test systems", tried for most of the research work presented in section 3.1

The cross binary parameter p_{ij} (equation 4-37) for the $1FG^E$ model has been replaced by the simple relation:

$$p_{ij} = \frac{q_i + q_j}{2} \tag{5-1}$$

The fugacity coefficient for the Huron-Vidal model has been given in equation 2-32.

One alternative to the $1FG^E$-EoS model presented recently for these "test systems", is the reformulated Wong-Sandler mixing rule [Orbey and Sandler, (1995b)]. This model can draw information from infinite dilution activity coefficients as given by a solution model, such as UNIFAC [Fredenslund et al, (1975)]. For the class of nonideal systems tried in this chapter the binary interaction parameter needed in equation 2-46 is set to zero. In this form the model becomes fully predictive. In contrast the $1FG^E$-EoS model requires a limited amount of available experimental information at low pressures. The difference between a group contribution model and the $1FG^E$-EoS model is that the group contribution model can be used for modeling of systems where there are no experimental data available. The reformulated Wong-Sandler model will be presented in section 5.1. Predictions for binary and ternary systems from both of these models will be presented in section 5.2.

5.2 Reformulated Wong-Sandler Mixing Rule (RWS)

The idea behind the model's formulation is its ability to describe fluids in a multicomponent mixture which are good candidates for the one-fluid van der Waals mixing rule as well as highly nonideal fluids.

Orbey and Sandler (1995b), substituted the classical mixing rule in equation 2-45 to solve for the excess Helmholtz energy as:

$$A_\infty^E = \frac{Cx_1x_2}{x_1b_1 + x_2b_2}(2a_{12} - a_1\frac{b_2}{b_1} - a_2\frac{b_1}{b_2}) = \frac{\delta x_1x_2}{x_1b_1 + x_2b_2} \qquad (5\text{-}2)$$

For example if the choice of the excess Helmholtz energy model is the van Laar expression which is given by:

$$A_\infty^E = \frac{\beta x_1x_2}{x_1b_1 + x_2b_2} \qquad (5\text{-}3)$$

we get for the binary interaction parameter:

$$\frac{[b_m - \sum\limits_i\sum\limits_j x_ix_j(b - \frac{a}{RT})_{ij}]RT}{b_m} - \sum_i x_i\frac{a_i}{b_i} = \frac{\beta x_1x_2}{x_1b_1 + x_2b_2} \Rightarrow$$

$$k_{12} = 1 - \frac{1}{2\sqrt{a_1a_2}}[a_1\frac{b_2}{b_1} + a_2\frac{b_1}{b_2} + \frac{\beta}{C}] \qquad (5\text{-}4)$$

where the combining rule (equation 2-47) is written as:

$$(b - \frac{a}{RT})_{ij} = \frac{b_i + b_j}{2} - \frac{\sqrt{a_ia_j}(1 - k_{ij})}{RT} \qquad (5\text{-}5)$$

which ensures the van der Waals, classical mixing rule recovery.

Besides the van Laar model the modified NRTL model (section 2.5) can also be reduced in a similar manner. If we also set the nonrandomness parameter (in equation 2-59) equal to zero, then:

$$A_{\infty}^{E} = \frac{x_1 x_2 (b_1 \tau_{12} + b_2 \tau_{21})}{x_1 b_1 + x_2 b_2} \tag{5-6}$$

and with the substitution of the classical mixing rule into equation 2-45, the binary interaction parameter is given as follows:

$$k_{12} = 1 - \frac{1}{2\sqrt{a_1 a_2}}[a_1 \frac{b_2}{b_1} + a_2 \frac{b_1}{b_2} + \frac{RT}{C}(b_1 \tau_{12} + b_2 \tau_{21})] \tag{5-7}$$

Since the excess Helmholtz energy models that have been derived from statistical mechanics cannot be reduced to the form of the equation 5-2 (for example the ideal gas mixture contains the term $x_i \ln x_i$), Orbey and Sandler (1995b), suggested the use of a predictive model for nonideal mixtures, where the binary interaction parameter k_{ij} (equation 5-5) is set to zero, the nonrandomness parameter α_{ij} (equation 2-59) is set to 0.1, and the set of equations 2-60 is solved for the energy parameters τ with the infinite dilution activity coefficients given from a predictive model such as UNIFAC, or any other excess free energy model. In the case where we want to use the van der Waals mixing rule we set the nonrandomness parameter equal to zero and use a known value of the binary interaction parameter k_{ij} to solve for the energy parameters τ. In this case the authors reduced equation 5-7 as:

$$2\sqrt{a_i a_j}(1 - k_{ij}) = [(\frac{a_i}{b_i} + \frac{a_j}{b_j})b_{ij} + \frac{RT}{C} b_{ij}(\tau_{ij} + \tau_{ji})] =$$

$$[2\frac{a_i}{b_i} b_{ij} + \frac{RT}{C} b_{ij} 2\tau_{ji}] \Rightarrow \tau_{ji} = \frac{C}{RT}[\frac{\sqrt{a_i a_j}(1 - k_{ij})}{b_{ij}} - \frac{a_i}{b_i}] \tag{5-8}$$

since equation 5-7 does not result in a unique solution for the energy parameters, which are needed to calculate the activity coefficients. In the above equation b_{ij} denotes an average value of the pure component size parameters b. Note that in this way (τ_{ij}=τ_{ji}) the two-fluid theory based NRTL model, reduces to the one-fluid theory based van der Waals model.

The systems tried in this chapter as being highly nonideal are modeled with the modified NRTL model, where the nonrandomness parameter is set to 0.1 following the suggestions of Orbey and Sandler (1995b), along with the UNIFAC model as the source of the infinite dilution activity coefficients. Examples of the infinite dilution activity coefficient derivation for the systems methanol-water, acetone-methanol and acetone-water are presented in Appendix A-4, with a general program given in Appendix D-1. For the energy parameters τ of equation 2-60, we employ a Newton algorithm from the IMSL software package to solve the system of the nonlinear equations. The energy parameters τ for some of the binary systems we tried are given in Table 5-1 along with the infinite dilution activity coefficients.

Table 5-1 Infinite dilution activity coefficients and energy parameters for several binary systems with the reformulated Wong-Sandler mixing rule

System (1-2)	$\ln\gamma_{12}^{\infty}$	$\ln\gamma_{21}^{\infty}$	τ_{12}	τ_{21}
acetone-methanol	0.6739	0.6735	4.282	-4.095
acetone-water	2.4399	1.9962	11.069	-11.072
methanol-water	0.8086	0.4729	5.862	-6.239
ethanol-water	1.4990	0.8180	8.293	-8.824
methanol-chloroform	2.1730	0.8970	-4.370	6.541
acetone-chloroform	-1.0000	-0.8520	5.610	-4.532
			-0.730	-0.133
			-3.321	4.109

As we see from the system acetone-chloroform in Table 5-1 multiple solutions for the energy parameters could result, depending on the initial estimates given to solve the nonlinear set of equations 2-60. As Walas (1985) states this phenomenon is common for the NRTL equation for cases where the infinite dilution activity coefficient is less than one. Moreover, this is expected for other solution models based on two-fluid theory. For binary mixtures there are heuristic approaches to find the best set of parameters, for the original NRTL, depending either on the sum of the absolute values of the energy parameters, or their product, [Walas, (1985)]. These approaches were not successful for the modified NRTL, and it is difficult to extend to multicomponent mixtures.

5.3 Results

In section 5.2.1 we present results for low-high pressure vapor-liquid equilibria of the "test systems" (references reported in Table 5-2), along with the few low pressure binary systems used for predictions for ternary systems. In section 5.2.2 we present vapor-liquid equilibria predictions of the ternary system methanol-acetone-water at low and high pressures, and the system chloroform-acetone-methanol at low pressures. The last ternary system involves multiple solutions for the energy parameters of the NRTL expression for the binary mixture chloroform-acetone. This ternary system has been chosen to test for the sensitivity of the results on the choice of the parameter set for the RWS model (Wong-Sandler formalism). Results for the ternary systems with the 1FG^E-EoS model (Huron-Vidal formalism) are given for two different parameters for the methanol-acetone system, obtained from fit of two different low pressure systems.

5.3.1 Binary Mixtures

The area and volume parameters for the components involved in the systems we have tried are given in Table A-5-1. All of them were set from Bondi (1968), except for the area parameter for water, which was set as the best suited value for the systems tried.

In Table 5-2 we report absolute average deviations in pressure and vapor phase composition for several binary systems [$\text{AADM} = \sum_{i=1}^{n} \frac{|M - M^{exp}|}{M^{exp}}$ where M stands for pressure or vapor phase mole fraction]. A general purpose program for bubble and dew point vapor-liquid equilibria has been developed for this work. The program listing is given in Appendix D-2. The model parameters in this work are obtained from the nonlinear optimization Marquardt-Levenberg algorithm. The objective function used is $\sum_{i=1}^{N} (P - P_{exp})^2$.

Table 5-2 AAD(%) in pressure and vapor phase composition, and binary parameter for several binary systems with the $1FG^E$ model.

System 1-2	Temperatures (K)	Number of points/ Data sets/ λ_{12}	(%)AAD(P-Y_1-Y_2)
Methanol-benzene(1)	308.15,328.15,363.15, 373.15-493.15	94/10/4.41	4.37-5.49-11.01
Methanol-water(2)	298.15, 373.15-523.15	70/5/-0.37	3.36-5.79-8.01
Acetone-methanol(2)	308.15,328.15 373.15-473.15	78/5/2.88	1.84-3.74-7.68
Acetone-water(2)	308.15 373.15-523.15	100/5/0.69	2.54-3.54-5.33

Table 5-2 (continued)

System 1-2	Temperatures (K)	Number of points/ Data sets/ λ_{12}	(%)AAD(P-Y_1-Y_2)
Ethanol-water⁽³⁾	298.14,323.15,348.15 423.15-623.15	110/10/0.13	2.19-3.35-2.46
2-propanol-water⁽³⁾	308.16,318.29,328.18,338.19 423.15-573.15	109/9/0.29	2.45-5.39-1.07

(1) High pressure data from Butcher & Medani (1968),(2) Griswold & Wong (1952),(3) Barr-David & Dodge (1959)

The low pressure system used to fit the energy parameter is taken from the Dechema Data Series, Gmehling and Onken (1977), and its temperature is reported first, in the second column of Table 5-2. We can see that the one parameter model we presented can successfully utilize low pressure data for phase equilibria predictions over an extended temperature range. The systems that we have tried are highly nonideal and are presented in a graphical form in Appendix A-5. The choice of the excess Gibbs energy model is of much importance, since a model with more parameters might give worse results for systems that are predicted with the parameters fitted at other conditions. For example the system acetone-water has been modeled in Wong et al (1992) with the original Wong-Sandler mixing rule with the van Laar expression as the choice of the G^E model. The van Laar parameters were taken from a system at 100 °C and the binary interaction parameter (equation 2-47) set at 0.27. The absolute average deviations in pressure and vapor phase compositions of acetone and water for the system at 35 °C with this three parameter model are (6.69,2.08,16.92) respectively, while for the one parameter 1FG^E model they are: (4.09,1.62,12.15).

In Table 5-3 we compare results for the binary systems that are involved in the low pressure ternary system methanol-chloroform-acetone taken from Goral et al (1985), with the 1FG^E model and with the RWS model. Additionally, we report predictions for the ethanol-water binary system with the RWS mixing rule, for which we see that the pressure deviation is two times larger than our model and the vapor phase composition three times larger. For the chloroform-acetone binary system the three sets of parameters do not show significant variation in the pressure or vapor composition absolute average deviation values. For the system methanol -acetone reported in Goral et al (1985) at 40°C we obtained a different value of the energy parameter than the value 2.88 that had resulted from the system taken from the Dechema Data Series and reported in Table 5-2. We thus list the predictions with both values of the energy parameter. We see that the results are acceptable for the case with the value of the energy parameter set to 2.88, but of course, the fitted value 3.49 is superior for the error in pressure, since it has been specifically fitted to one of the two chloroform-acetone binary systems.

Table 5-3 AAD(%) in pressure and vapor phase compositions for the constituent binaries of the system methanol-chloroform-acetone at 313.15 and 323.15 K with models 1F^{G}E-EoS and the RWS models, and the ethanol-water system with the RWS model.

System 1-2	Data sets/ No of points	(%)AAD(P-Y_1-Y_2)	λ_{12} 1FG^E-EoS	τ_{12},τ_{21} RWS
Methanol-chloroform	2/55	3.23-7.45-7.63	7.26	
		5.52-6.06-4.86		-4.37,6.54
Methanol-acetone	2/48	0.74-2.73-1.27	3.49	
		2.22-3.57-3.68	2.88	
		3.28-4.30-3.83		-4.10,4.28

Table 5-3 (continued)

System 1-2	Data sets/ No of points	(%)AAD(P-Y_1-Y_2)	λ_{12} 1FG^E-EoS	τ_{12},τ_{21} RWS
Chloroform-acetone	2/30	0.88-3.10-2.03	-2.02	
		2.14-3.19-3.59		4.11,-3.32
		2.35-3.55-4.00		-0.13,-0.73
		1.63-2.31-2.93		-4.53,5.61
Ethanol-water	10/110	6.35-7.86-5.98		8.24,-8.82

5.3.2 Ternary Mixtures

Two ternary systems have been tried with the 1FG^E-EoS and compared to the RWS model. In Table 5-4 we report the results for the system acetone-methanol-water at two different temperatures. The data were taken from Griswold and Wong (1952).

It can be observed from Table 5-4 that the error in pressure for the 1FG^E model, is more sensitive at the lower temperature (100°C), to the low pressure parameter used. However, the vapor phase compositions with our model are insensitive to the system taken to fit the binary parameter, and the errors are consistently less than the errors from the RWS model. Nevertheless, the data for the system at 100 °C are much more difficult to predict with either of the models.

Table 5-4. Absolute average deviations (AAD%) in pressure and vapor phase composition for the ternary system acetone(1)-methanol(2)-water(3) at 100 & 250 °C

T (°C)	(%)AAD(P-Y_1-Y_2-Y_3)	$\lambda_{12}/\lambda_{13}/\lambda_{23}$	$\tau_{12}/\tau_{21},\tau_{13}/\tau_{31},\tau_{23}/\tau_{32}$
		1FG^E-EoS	RWS
100	3.04-8.22-19.55-6.39	2.88/0.69/-0.37	
250	3.64-5.25-5.75-3.96	“	
100	3.81-8.36-20.44-7.06	3.49/0.69/-0.37	
250	4.04-5.60-5.72-4.02	"	
100	4.18-11.44-22.51-6.86		4.28/-4.10, 11.07/-11.07, 5.86/-6.24
250	2.01-6.92-7.87-5.16		"

A point of interest is that while for the 1FG^E model the error in pressure for the higher temperature is larger than for the lower temperature system (as we would expect when using a low pressure parameter and extrapolating to higher temperatures), this is not the case for the RWS model.

In a similar approach by Huang and Sandler (1993), an average of several low pressure data systems was used to model the ternary system acetone-methanol-water, at the two temperatures of 100 and 250 °C, with the UNIQUAC equation. They report a value of ($\sum_{i=1}^{N} \frac{\Delta P}{P}\%$) equal to 2.49 while for our model and with the parameters of Table 5-2 we get 0.53, which shows that our model results in more sign changes. This is an indication that for these high pressure binary and ternary "test systems", the assumption of the linear mixing rule for the size parameter (equation 2-21) is performing better than the temperature dependent rule (equation 2-49) assumed in the Wong-Sandler (1992) model.

In Table 5-5 we report results for the ternary system methanol-chloroform-acetone at 40 and 50 °C taken from Goral et al (1985). For the RWS model we present the results for the three different parameter combinations as given in Table 5-3. It can be seen from the results in Table 5-5 that the 1FG^E model is less sensitive to the change of the low pressure parameter. Moreover, the small variations in the vapor phase composition of one component are compensated with variations in the composition of the other, so that the summation of the errors in vapor composition of all three components does not vary significantly.

Table 5-5 Absolute average deviations (AAD%) in pressure and vapor phase composition for the ternary system methanol(1)-chloroform(2)-acetone(3) at 40 & 50 ^oC

T (^oC)	(%)AAD(P-Y_1-Y_2-Y_3)	$\lambda_{12}/\lambda_{13}/\lambda_{23}$	$\tau_{12}/\tau_{21},\tau_{13}/\tau_{31},\tau_{23}/\tau_{32}$
		1FG^E-EoS	RWS
40	2.24-7.24-4.18-9.41	7.26/3.49/-2.02	
50	1.72-5.81-3.44-6.32	"	
40	1.84-5.32-5.63-9.30	7.26/2.88/-2.02	
50	1.41-4.71-4.81-6.80	"	
40	2.76-11.41-3.83-9.79		-4.37/6.54, -4.10/4.28, 4.11/-3.32
50	2.98-9.25-2.87-6.71		"
40	2.38-5.84-6.63-14.58		-4.37/6.54, -4.10/4.28, -0.13/-0.73
50	2.00-4.63-5.58-10.47		"
40	4.58-17.13-6.94-7.06		-4.37/6.54,-4.10/4.28, -4.53/5.61
50	5.11-13.93-8.53-5.45		"

The RWS model shows small variations in the pressure predictions for the first two set of parameters, but the vapor phase composition predictions show large variations for methanol and acetone (up to two times). The pressure predictions as well as the vapor phase composition predictions for methanol and chloroform are less accurate for the last set of parameters, compared to all model variations tried in Table 5-5. While for this last case the results are two to three times less accurate than the other models, the same model predicts the vapor composition of acetone more accurately than all the other models.

This sensitivity of the results to the choice of the parameters for the RWS model, is an issue concerning the use of the model as a predictive tool for multicomponent mixtures. On the other hand, the good performance of the 1FG^E-EoS on the predictions of the binary and ternary systems along with its robustness on the change of the parameter set, adds to its reliability when used as a predictive model for these high-low binary and ternary "test systems" based on available low-pressure experimental information.

CHAPTER 6

CASE STUDY TWO

6.1 Introduction

In this part of our work the Huron-Vidal thermodynamic formalism is combined with the $1FG^E$-EoS model for vapor-liquid equilibria correlations of hydrogen containing ternary systems along with their constituent binary systems. Both phases in the systems studied are at high densities, and so we do not have any compliance problem with the second virial coefficient condition. Trials with the density dependent mixing rule presented in Appendix A-2 gave poor results, since the model could not distinguish between the two phases at high pressures. The systems tried provide the basis for examining our model's potential to describe highly asymmetric systems, where the ratio of the molecular volumes of the components is far away from unity.

For these systems there are two parameters in the $1FG^E$ model. One energy related (λ_{ij} in equation 4-34) and one size related parameter (p_{ij} in equation 4-37). As we mentioned in section 4.3, a consistent way to treat p_{ij} as an adjustable parameter is to combine equation 4-37 with equation 4-30.

As Gray et al (1983) suggested, for accurate prediction for the ternary systems, we might need to weight the binary parameters accordingly. An alternative, of course, would be to introduce ternary interaction parameters in an empirical way, but this would have complicated the model and would be inconsistent with the idea of multicomponent mixture behavior prediction from only binary parameters.

In order to obtain conclusive results on the correlative abilities of the $1FG^E$ model we have included four ternary along with 15 binary systems in our list of systems. The area and volume related parameters of the pure components are taken from Bondi (1968), except for the area parameters for hydrogen, carbon monoxide and ethylene, which were regressed from all the systems in which they were involved. These parameters along with the acentric factor of each component are given in Table B-1. The cubic EoS that we have used is the PRSV EoS (section 2.2).

An alternative G^E-EoS model that has been recently presented by Huang et al (1994), uses the PRSV EoS along with the Wong-Sandler mixing rule, for modeling hydrogen-hydrocarbon mixtures. Their choice for the G^E model was the NRTL expression (section 2.5).

Huang et al (1994) set the nonrandomness parameter (equation 2-57) to 0.36 for this class of systems, and temperature independent parameters were used in equation 2-57:

$$G_{ji} = \exp(-\alpha_{ji} A_{ji}) \qquad (6\text{-}1)$$

This model assigns three parameters to each binary pair. There is one binary interaction parameter k_{ij} in the combining rule (equation 2-47) and two energy parameters in the G^E model, A_{ij} and A_{ji} (equation 6-1). They have correlated the vapor-liquid equilibrium data at each temperature set independently. Although all binary parameters showed variation with temperature for each system, the authors decided to correlate the binary interaction parameter k_{ij} with temperature, and the energy parameters with the acentric factor of the hydrocarbon, so that the model could be used as a predictive tool. In Table 6-1 we report the values of the energy parameters as given by Huang et al (1994), for both the correlative and predictive models, for two representative systems.

Table 6-1. Energy parameters for the NRTL model [as reported by Huang et al (1994)]

System	T (K)	Correlation		Prediction	
1-2		A_{12}	A_{21}	A_{12}	A_{21}
H_2-Ethane	283	0.134	0.456	0.69	0.39
	255	-0.150	0.500	"	"

Table 6-1. (continued)

System 1-2	T (K)	Correlation A_{12}	 A_{21}	Prediction A_{12}	 A_{21}
H_2-Ethane	227	0.499	0.499	0.69	0.39
	199	-0.359	1.569	"	"
H_2-Decane	583	0.208	0.448	0.24	0.24
	543	-0.029	0.550	"	"
	503	-0.188	0.604	"	"
	462	-0.275	0.600	"	"

Although the values of the k_{ij} parameter were close to one for most of the systems and could be correlated to temperature, the energy parameter values in Table 6-1 suggest that it is difficult to correlate them not only with temperature but with the acentric factor of the hydrocarbon as well. Note that the predictive model will not be able to deal with multicomponent mixtures, since it is based only on hydrogen containing binaries. Nonetheless it is of extreme importance for a good model to be able to use the acentric factor of the hydrocarbon to correlate hydrogen-hydrocarbon binaries, since this parameter can be used to characterize the asymmetricity of the mixture.

The good results that the authors obtained for several systems dictated the significance of the binary interaction parameter k_{ij} in their model, while several sets of energy parameters could be used with no significant effect on the calculations. So it is the number of parameters responsible for the good correlations of these systems. Huang et al (1994), have also showed that the one parameter van der Waals mixing rule, with the parameter fitted at each isotherm, gave only fair results.

In section 6.2 we present results for the binary and ternary systems from the $1FG^E$-EoS model. Moreover, we will investigate the ability of the model to assign physical significance on the parameters, since this could implicitly add value to the character of the model as a predictive tool.

6.2 Results and Discussion

6.2.1 Binary Mixtures

In Table 6-2 the energy and size parameters, as well as the hydrocarbon acentric factor, for a block of seven hydrogen-hydrocarbon pairs (more results are given in Table B-2) are reported. These results are directly obtained from the optimization algorithm used to fit a large number of data sets.

Table 6-2 Mixture size and energy parameters

System (1-2)	λ_{ij}	p_{ij}	ω_2
H_2-C_2H_6	3.14	1.61	0.098
H_2-C_3H_8	1.58	2.22	0.154
H_2-n C_4H_{10}	-0.49	3.48	0.201
H_2-n C_6H_{14}	-0.64	3.74	0.301
H_2-n C_7H_{16}	-0.83	3.85	0.350
H_2-n $C_{10}H_{22}$	-1.84	4.44	0.491
H_2-n $C_{16}H_{34}$	-3.07	5.34	0.744

Table 6-2 indicates that as the size of the hydrocarbon increases the unlike interactions are favored. This means that in equation 4-21 the cross parameter $2\varepsilon_{12}$ has larger absolute value than the sum of the interaction energies measuring the size of the like interactions.

Note that since the interaction energy measures the depth of the potential well it has a negative value. Also, a larger number for the p_{ij} parameter translates to a larger number of interactions (like and unlike). Our observations for this block of hydrogen-hydrocarbon systems are translated with an excellent correlation of the p_{ij} parameter with the acentric factor of the hydrocarbon, as well as of the energy parameter λ_{ij} with the p_{ij} parameter. these two correlations are:

$$p_{ij} = 1.77 + 5.26\omega_i \qquad (6\text{-}2)$$

$$\lambda_{ij} = 5.49 - 1.64 p_{ij} \qquad (6\text{-}3)$$

In Table 6-3 we report the absolute average deviations in pressure and vapor phase mole fraction for the first component for all temperatures.

Table 6-3. AAD(%) in pressure and vapor phase composition of component 1 for binary systems.

Components 1-2	Temperature sets	Temperature range (K)	Number of points	%AADP	%AADY$_1$
H_2-CO	2	83.30-100.00	18	4.6653	2.9514
CH_4-CO	5	91.60-123.90	22	3.7066	8.6238
H_2-CH_4	4	103.15-173.05	26	3.3856	2.8454
H_2-C_2H_6	4	148.15-223.15	16	5.3152	0.7070
CH_4-C_2H_6	12	130.37-199.93	129	2.3571	0.8433
H_2-C_2H_4	6	158.15-255.35	34	3.3520	3.5024
C_2H_6-C_2H_4	4	199.82-263.15	43	2.9594	3.4851
CH_4-C_2H_4	10	148.09-248.37	144	1.3171	0.6175
H_2-C_3H_8	7	173.15-323.15	41	5.6585	1.0705
H_2-n C_4H_{10}	5	327.65-394.25	60	1.8740	2.5029
H_2-n C_6H_{14}	6	277.59-444.26	94	4.2338	1.2643

Table 6-3. (continued)

Components 1-2	Temperature sets	Temperature range (K)	Number of points	%AADP	$\%AADY_1$
H_2-n C_7H_{16}	3	424.15-498.85	32	8.0101	2.4906
H_2-n $C_{10}H_{22}$(a)	4	462.45-583.45	26	3.9801	1.7174
H_2-n $C_{16}H_{34}$(b)	4	461.65-664.05	28	14.0701	0.6260
H_2-C_7H_8	3	461.85-542.15	20	1.5651	1.6983

(a) Data from Sebastian et al (1980), (b) Data from Lin et al (1980).

Several of the systems reported in Table 6-3 are given in a graphical form in Figures B-1 to B-10. We see that the systems are well represented, but for some series the pressure deviation is either positive or negative. As Kolbe and Gmehling (1985) suggested, this is due to the fact that the model must be able at the same time to reproduce the temperature dependence of the fugacity coefficient, and also the measurements across the whole concentration range. They had modeled the ethanol-water system over a great span of temperatures.

Another important issue in the $1FG^E$ model is the description of the local ordering in the mixture, although we cannot verify the results either from a lab or a molecular simulation experiment. For example, for the hydrogen n-hexadecane binary and for the high temperature set, we have the local composition of the hydrocarbon around the hydrogen molecule to be 0.41 and the hydrogen local composition around the hydrocarbon to be 0.72 for an equimolar mixture. This which means that the hydrogen is surrounded by more molecules of hydrogen most probably due to steric effects from the size difference of the molecules of the components in the mixture.

Since the errors in pressure for the systems hydrogen-heptane and hydrogen-n-hexadecane in Table 6-3 are higher than for the other systems, it is tempting to investigate the use of the assumption 4-29, which adds one additional parameter in the model.

Table 6-4 Predictions with the three parameter model for two hydrogen-hydrocarbon binaries.

System (1-2)	λ_{ij}	p_{ij}	p_{ji}	(%)AADP	(%)AADY1
H_2-n C_7H_{16}	1.24	2.94	5.21	4.4804	3.0425
H_2-n $C_{16}H_{34}$	-0.75	4.01	6.09	3.0931	0.8188

The results in Table 6-4 are not hard to interpret since both of the size parameters have perturbed around the size parameter reported in Table 6-2, with the hydrocarbon molecule to show larger of pair interactions. This result suggests the possibility of a judicious introduction of an extra size parameter to improve the correlation without loss of physical meaning.

In contrast, the same formalism (Huron-Vidal) with two-fluid theory based G^E models is not sensitive to the variation of the parameters in the fitting procedure, as Yoon et al (1993) reports, and without significant variance in the results from the choice of the G^E model. They have worked with the ternary system carbon dioxide-water-methanol.

Results for each individual isotherm are reported in Table B-3 . The high error value for the vapor mole fraction of the hydrocarbon, is due to the small experimental values.

6.2.2 Ternary Mixtures

Results for the ternary systems are presented in Table 6-5. The ternary mixtures were regressed along with the binary mixtures with the use of only binary parameters (given in Table B-2). We thus get the best predicted results for both the binary and ternary mixtures. Our model predictions for the ternaries H_2-CH_4-C_2H_6 and H_2-CO-CH_4 are compared with the results from the Dechema Data Series [Knapp et al, (1982)] on exactly the same data set. In the Dechema Data Series the experimental data are modeled with the PR-EoS and the classical one-fluid mixing rule. The results for the ternaries H_2-CH_4-C_2H_4 and H_2-C_2H_6-C_2H_4 are compared with the BWR equation on the same data set as reported from Sagara et al (1972).

Table 6-5 Absolute average deviations in pressure and vapor phase mole fractions for the ternary systems.

Components 1-2-3	Temperature sets Number of points	Temperature span (K) Pressure span (bars)	(%)AAD(P-Y_1-Y_2-Y_3)
H_2-CO-CH_4	12-95	120.00-173.25 28.9-103.42	2.85-6.29-2.65-3.64
Dechema			6.32-15.41-4.04-3.57
H_2-CH_4-C_2H_6	4-15	144.26-199.82 34.47-68.95	3.61-3.21-4.35-12.66
Dechema			6.03-8.55-7.55-20.41
H_2-C_2H_4-CH_4	20-98	123.15-248.15 20.26-81.04	4.67-5.72-9.27-17.86
BWR			13.55-5.66-13.43-37.38
H_2-C_2H_4-C_2H_6	16-80	148.15-223.15 20.26-81.04	4.69-0.92-16.21-11.98
BWR			17.60-1.44-21.15-31.60

The large percentage errors in the mole fraction of the vapor phase of ethylene, methane, and ethane in the last two ternary systems of Table 6-5 are due to the small numerical values involved. Deletion of only five points for the system H_2-CH_4-C_2H_4 brings the absolute average deviation of methane down by more than 4 percent. Also, as Sagara et al (1972) implied, the experimental compositions in the high dilution region may have large errors.

Figure 6-1 illustrates the ternary mixture hydrogen-methane-ethane at 144.26 K and 68.95 bars. We see that at the conditions given, the methane-ethane system is completely miscible and well described with our model. A few other indicative ternary diagrams for each of the ternary systems are given in Figures B-11 to B-13.

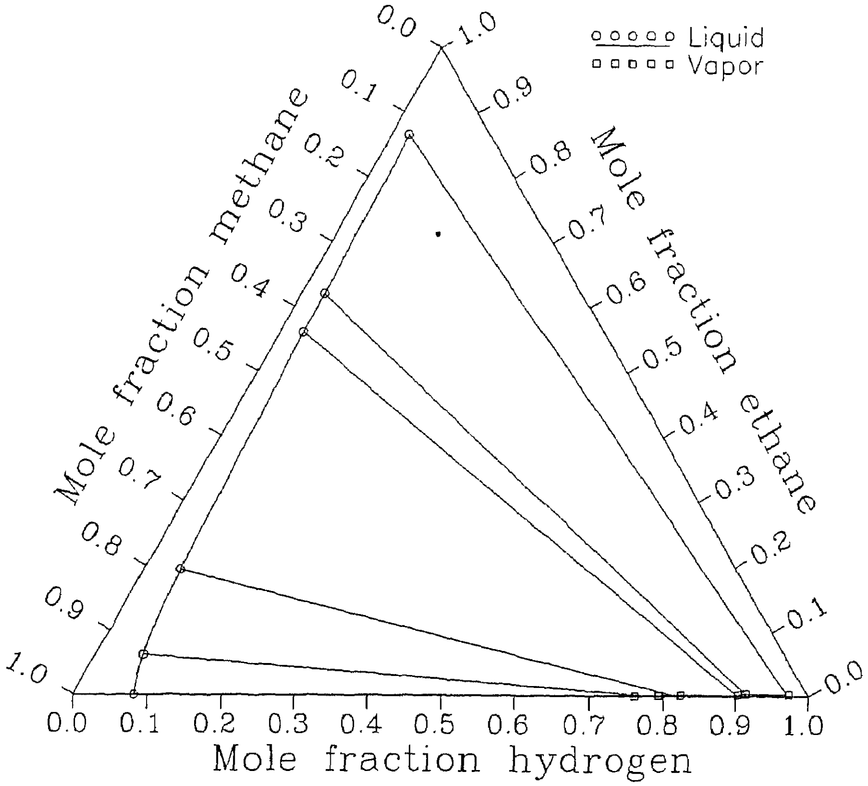

Figure 6-1 Vapor-liquid equilibria for the ternary system hydrogen-methane-ethane at 144.26 K and 68.95 bars

In the case where the vapor phase mostly contains hydrogen, the excess Helmholtz function term is close to zero, so that basically this term corrects for nonidealities in the liquid phase. In Tables B-4 to B-7, we report the error averages for each data set, at each of the various temperatures.

It is obvious that our approach decreased the absolute average deviation significantly for these so-called "difficult" systems. In general, the results in Appendix B indicate the ability of the model to describe the vapor composition of these systems at high pressure even though the vapor composition is not included in the objective function for the regression. This gives us confidence in the description of both phases with the 1FG^E-EoS model we proposed.

CHAPTER 7

CASE STUDY THREE

7.1 Significance

The study of the "ozone hole" above the Antarctic has established the relationship between the chlorine and ozone content in the stratospheric zone, and has also shown that the chlorine oxide (ClO^-) radical is mainly responsible for the ozone destruction. This radical is formed by chlorine atoms released by chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs).

CFCs are not water soluble and they rise to the stratosphere where upon the action of UV rays they release chlorine atoms. These transform ozone molecules to oxygen, while the hydrogen atom facilitates hydrolytic reactions in HCFCs and lowers their life expectancy in the atmosphere.

The ozone depletion potential (ODP), defined as reduction of ozone per unit mass of gas emitted per year, and compared with that for a unit mass of CFC-11, are given in Table 7-1 for some CFCs and HCFCs along with their life expectancy in the atmosphere [Clodic and Sauer, (1994)].

Besides their ozone destruction capabilities, CFCs and HCFCs are also contributors to the greenhouse effect, mainly by the release of carbon dioxide in the energy production cycles for cooling.

The Montreal Protocol (1987), which was followed up by the London Revision (1990), grouped the six CFCs of Table 7-1 and their mixtures as Class I along with carbon tetrachloride and methyl chloroform, and halons 1211, 1301 (R13B1), 2402 as Class II, and required that these two classes have to be phased out by the year 2000 in stages. The required reductions targeted all applications; namely for CFCs: refrigerants, blowing agents in polymer foam manufacture, solvents for electronics and propellant gases for aerosols; and for halons: extinguishers and refrigeration products.

Table 7-1 ODP values of CFCs and HCFCs.

Component	Life in atmosphere (years)	ODP
CFC-11	60	1
CFC-12	130	1
CFC-13	400	1
CFC-113	90	1.07
CFC-114	130	0.8
CFC-115	400	0.52
HCFC-22	15	0.055
HCFC-123	2	0.02
HCFC-124	7	0.022
HCFC-141b	8	0.11
HCFC-142b	19	0.065

The Copenhagen Revision (1992) accelerated the phase out in stages of CFCs by the year 1996, and of halons by 1994. The phase out date for HCFCs was set in the year 2030, while in the USA, the Environmental Protection Agency (EPA) accelerated the phase out date of the products HCFC-141b, HCFC-142b and HCFC-22 as well as hydrobromofluorocarbons, by the year 1996. Later in 1993, a proposal by the European Community Commission followed, which suggested as the phase out date of HCFCs the year 2015. For each country the phase out of the CFCs is based on its consumption (production + import - export) in the year 1989, while for the other products is based on their consumption, as well as the CFCs consumption, for the same year.

The need for thermodynamic predictions of mixtures containing CFCs and HCFCs starting from accurate information of the properties of the pure components will facilitate their replacement procedure according to the environmental regulations recently imposed, and with a minimum cost of necessary modifications performed to the existing refrigeration equipment. Besides, since alternatives to current ozone depleting refrigerant fluids were found to be several hydrofluorocarbons (HFCs) and HCFCs, the study of mixture properties could alleviate bad properties of some single component refrigerants such as inflammability, or insolubility in oil which hinders their recovery.

7.2 Thermodynamic Framework

As explained in section 3.3, previous researchers have established the good correlative ability of the simple van der Waals one parameter model for phase equilibria calculations of many refrigerant mixtures, as well as its poor predictive abilities. For this reason we examine a one-parameter version of the $1FG^E$-EoS model on representative fluorocarbon (FC), CFC, and HCFC mixtures and CFC/HCFC-hydrocarbon mixtures.

In particular we were interested in deriving a predictive model in the sense noted by Orbey and Sandler (1995a). Phase equilibrium experimental data, in a limited amount, can be used to obtain the value of the parameter at a single temperature. Then phase equilibria predictions can follow at higher, or lower temperatures.

Orbey and Sandler (1995a) used the Wong-Sandler mixing rule along with the NRTL expression (equations 2-56 to 2-58). A limited amount of experimental data were used for each binary system at a single temperature to fit the two NRTL parameters τ_{12} and τ_{21} along with the binary interaction parameter k_{ij} (equation 2-47). The nonrandomness parameter (equation 2-57) set to 0.40 for most of the systems, but they had to set it equal to 0.35 to improve the correlation for the system R14-R23 at 145 K.

This model will be designated as 3PWS (three-parameter Wong-Sandler) and will be used for comparisons with the $1FG^E$ model (incorporated to the Wong-Sandler mixing rule) for ternary systems.

For the $1FG^E$ model equation 4-29 is used where p_{ij} is given by:

$$p_{ij} = \frac{q_i^{\alpha_{ij}}}{q_j^{\alpha_{ij}-1}} \tag{7-1}$$

The area parameter q_i is used in other local composition models as well; for example, the UNIQUAC model, developed by Abrams and Prausnitz (1975). It is worth noting that with the form of the equation 7-1 we have the choice of getting back the original model of Knox et al (1984) by setting the α_{ij} parameter equal to one, or having the interactions per molecular components equal to each other by setting this parameter equal to zero. The α_{ij} parameter could be compared with the non-randomness parameter of the NRTL model, except that for our model the parameter has more theoretical background since it is connected implicitly to the number of interactions per molecule through the surface area parameters.

This framework can be treated as a three parameter model (α_{ij}, λ_{ij}, k_{ij}), or upon suitable assumptions its parameters could be reduced. A major problem which we find for multiparameter models is that the values of the parameters depend on the initial estimates, and especially for systems with few data points there exist a range of parameter values which can give accurate correlation at a single temperature. The problem then would be to choose the most appropriate set of parameters for predictions of binary and ternary systems. The difficulty with the overcorrelation of experimental data and the encounters (dependent on the initial estimates) with local minima of the objective function, is more prominent as the number of parameters in the model increases.

To be able to establish a method to screen among various versions of the $1FG^E$-EoS model while defining a suitable predictive model we set a heuristic rule. We required the simultaneous fitting of all the temperature sets of a system (overall fit), to result in model parameters that are in the range defined by the parameters obtained from the fittings of each individual temperature separately. A sample program for an overall fit case (R134a-propane) is given in Appendix D-3.

A suitable predictive model in the sense of this work, should have parameters that do not vary significantly with the temperature. The temperature dependence of the model extrapolations should be described from the structure of the G^E-EoS model.

In order to appreciate the value of our heuristic rule, we note that a correlation of a system at a single temperature set, treats the system under the athermal solution assumption, while for the overall fitting the temperature dependence of a parameter is of importance to the results. This in a sense justifies the use of an overall fitting to validate the model's ability to assign the correct parameter value with a single temperature set.

Basically we expect to map the highly nonlinear problem of the dependence of the fugacity coefficients, to a temperature-parameter coordinate system, where for small parameter variations with temperature, the parameter is considered to be constant. Moreover, it is highly desirable to connect the model parameters with physical properties of the systems studied, such as the polarity of the mixture.

For an initial model screening we have chosen five binary refrigerant systems to test for this purpose: R134a-Propane, Propylene-R134a, R23-R13, Propylene-R22, and R134a-R152a.

The cubic EoS used is the PRSV or PRSV2 EoS (section 2.2). Pure component parameters are given in Table C-1. The EoS parameters for R123 (equation 2-18) were optimized in this work, from saturated pressure data of Nishiumi et al (1995). The r and q parameters of the $1FG^E$ model (section 4.3) for the components R13, R134a, R152a, R22, R23, propane, and propylene were taken from Kleiber (1994) and for the other components from Bondi (1968).

7.3 Model Parametric Forms

Initially we looked at the general three parameter model, α_{ij}, λ_{ij}, k_{ij} (3PM). The results from this model for the five binary systems are reported in Table C-2. A few are shown in Table 7-2. We report the absolute average deviations in pressure and vapor phase composition of the first component for each system.

Table 7-2 AAD(%) in pressure and vapor phase composition of component (1) for the 3PM model

System (1-2)	Fitting temperature (K)	Parameters $\alpha/\lambda/k$	Δp-Δy_1
R134a-Propane	Overall	1.755/4.520/0.217	1.660-2.353
	255	0.446/3.369/0.378	0.236-2.916
	275	0.776/3.409/0.339	0.099-1.562
	298	1.497/3.912/0.254	0.394-0.994
R134a-R152a	Overall	-4.971/-0.430/-0.088	0.387-0.516
		-3.974/-0.292/-0.067	0.424-0.458
	255	-5.236/-0.514/-0.102	0.155-0.482
	275	-0.994/0.095/-0.058	0.071-0.592
	298	-2.594/0.001/-0.067	0.125-0.383

Obviously, for the 3PM model the encounters with local minima are an issue. Moreover, we see that the model parameters for the system R134a-propane are not within the range defined from the individual data sets.

One possible reduction to a two-parameter model is to set the α_{ij} parameter equal to zero which is equivalent to the assumption of having the same number of interactions for each molecule in the mixture. In Table C-3 we report results for this two parameter model with adjustable parameters the λ_{ij}, k_{ij} (2PMa). A few of the results are shown in Table 7-3.

Table 7-3 AAD(%) in pressure and vapor phase composition of component (1) for the 2PMa model

System (1-2)	Fitting temperature (K)	Parameters λ/k	Δp-Δy_1
R134a-Propane	Overall	3.556/0.299	1.997-2.027
	255	3.150/0.399	0.298-2.068
	275	3.048/0.373	0.292-2.323
	298	3.001/0.334	0.495-1.484
Propylene-R134a	Overall	1.391/0.316	1.200-1.520
	251	0.948/0.410	0.634-1.888
	275	0.754/0.401	0.631-1.264
	298	0.733/0.376	0.463-1.337

The results in Table 7-3 indicate that the 2PMa model does not satisfy our heuristic rule.

In another version of a two-parameter model where we assumed that the k_{ij} parameter has been replaced by a linear average of the acentric factors of the pure components. This assumption will result in k_{ij} values of about 0.2. The results for this model (2PMb) are reported in Table C-4 and a few shown in Table 7-4.

The results in Table 7-4 suggest that the idea to fix the k_{ij} parameter, makes the model parameters less sensitive to temperature variations. In total the 2PMb model satisfied our heuristic rule for three systems, the 2PMa for none, and the 3PM for one system. We have chosen to use the 2PMb model to try to reduce the number of its parameters. The reduction to a one-parameter model is based on the conclusion of the review made in section 3.3, where we showed that the one parameter classical van der Waals is an adequate model for predicting properties of refrigerant mixtures, while multiparameter mixing rules gave only slightly better results.

Table 7-4 AAD(%) in pressure and vapor phase composition of component (1) for the 2PMb model.

System (1-2)	Fitting temperature (K)	Parameters α/λ	ΔP-Δy_1
R134a-Propane	Overall	1.658/4.252	1.691-2.147
	255	1.274/4.940	0.762-1.528
	275	1.229/4.571	0.489-1.226
	298	1.585/4.098	0.388-1.015
Propylene-R134a	Overall	1.389/2.112	0.664-1.155
	251	1.394/2.323	0.127-1.552
	275	1.503/2.179	0.169-0.693
	298	1.344/2.068	0.125-0.366

Results for the correlative capabilities of the 2PMb model for 14 binary mixtures and for an overall fit, are given in Table C-5. It is inevitable that upon reduction in the number of parameters we lose in accuracy of the pressure predictions, but not necessarily in vapor phase composition predictions, since the objective function used is $\sum_{i=1}^{N} (P - P_{exp})^2$. The error in the vapor composition for the system R23-R22 is based on the predictions by the Trebble-Bishnoi EoS given in Laugier et al (1994), since the authors do not report the experimental values.

Note that as Figure 7-1 indicates the energy parameter should be adjustable. Even two parameters α_{ij} and k_{ij} can not recover the system when λ_{ij} is set to -5. For the 2PMb model (k_{ij}=0.46) for the energy λ_{ij} values: 1,2,3 the α_{ij} parameter correlated is: -5, 1.847, 0.594. For the 3PM model for the energy λ_{ij} values: -5,2,6 the α_{ij}/k_{ij} values obtained are: 1.112/1.023, 1.416/0.248, 1.596/-0.098.

7.4 Athermal Solution

In this section we investigate the so-called athermal solution assumption. For an athermal solution the G^E/RT function should be independent of temperature. This definition translates to the temperature dependence of the parameters. If temperature independent parameters are to be used with the $1FG^E$ model then the right hand side of equation 4-34 is replaced by: $\exp(-\lambda_{ij})$. The results for the system R14-R13 were the same as given in Table C-5, with the values in the parentheses of the exponential term based on the data given at a single temperature. Results for the system R14-R23, for which the data cover a great temperature span, are reported in Table 7-5. For this system all temperature sets were correlated simultaneously. It is obvious that a temperature dependent parameter help to correlate the experimental data more accurately than the case where the athermal solution assumption is used.

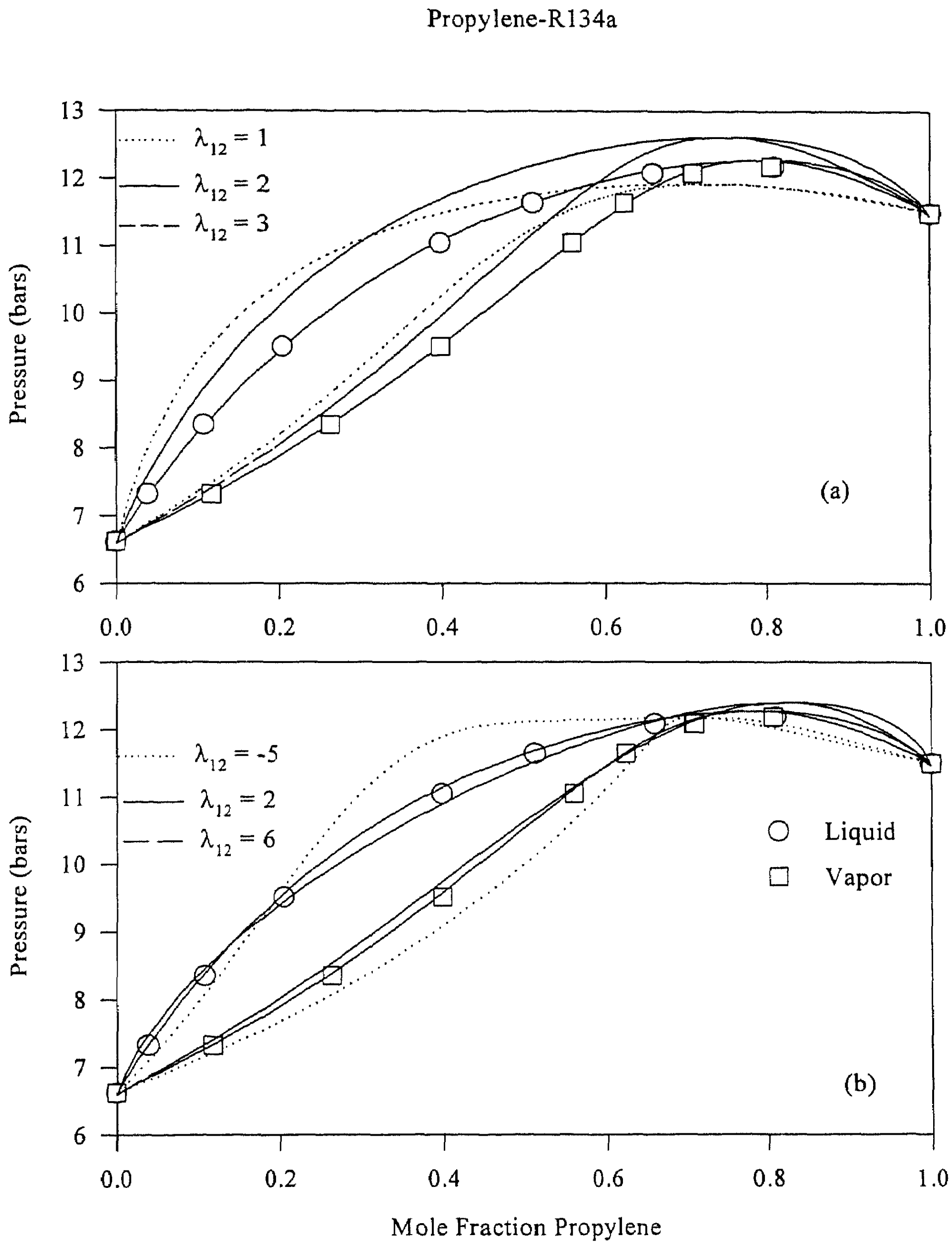

Figure 7-1 2PMb (a) and 3PM (b) model predictions for the system propylene-R134a at 298 K

Table 7-5 AAD(%) in pressure and vapor composition of R14 for the system R14-R23 for the cases of temperature dependent and independent λ parameter

T (K)	T dependent (α/λ:-0.919/3.135)	T independent (α/λ:-1.613/-1.490)
145	9.421-0.455	21.424-1.719
172	4.712-0.581	11.573-2.569
200	0.824-2.153	4.200-6.260
225	1.018-1.078	1.221-0.789
255	1.614-4.081	1.534-4.037
283	0.572-3.454	0.364-3.100

7.5 One-Parameter Model and Results

As we have discussed in section 7-3 upon fixing the value of the k_{ij} parameter rather than treating it as an adjustable one, the other model parameters show less temperature dependence. More importantly, the parameters taken from the overall fit are close to the parameters from the individual fit of the higher pressure system, since it carries more weight in the fitting routine.

While this is true for the 2PMb model this is not the case for the other two models 2PMa, and 3PM, where it seems impossible to predict the expected values of the overall fit parameters. For this reason we use the 2PMb model for further reduction in the number of its parameters.

In Table C-6 we calculated the p_{12} and p_{21} values for all binary pairs from the α_{ij} values of Table C-5 and then fit them to the one parameter equation 7-1. By doing this we get a value of α_{ij} close to 1.5. The values obtained from the fitting routine are given in Table C-6. The functional form of equation 7-1 results in two symmetric functions p_{12} and p_{21} around a value 0.5 of the α_{ij} parameter. This point induced us to examine whether if the order of these functions (p_{12} , p_{21}) is of importance to the accuracy of the error predictions. For example, we see from the Table C-6 that for the systems R14-R13, R23-R13, R14-R23 and R13-nButane the order of these functions (p_{12} , p_{21}) has been reversed. We have chosen five systems to investigate this point further. We compare the results of having an α_{ij} parameter with value 1.5 to the case where the parameter equals to 0.5. The results in Table C-7 suggest that the simplified assumption of the geometric average of the pure components is satisfactory. The area parameters used with this assumption result in the p_{ij} parameter values given in the last column of Table C-6. As we see, all the parameters fall within the range defined by the parameters given in Table C-5.

For the 1PM model we have also tried the five systems that we had tried with the previous two models to check if the parameters from the overall fit fall within the range defined by the individual temperature fits. The results are given in Table 7-6 and they indeed verify that the 1PM model satisfies our heuristic rule. Similar results are obtained for the rest of the systems, as shown in Table C-8.

Table 7-6 AAD(%) in pressure and vapor phase composition of component (1) for the 1PM model.

System (1-2)	Fitting temperature (K)	Parameters λ	ΔP-Δy_1
R134a-Propane	Overall	4.257	1.824-2.111
	255	4.953	0.740-2.047
	275	4.584	0.535-1.413
	298	4.095	0.722-0.940
Propylene-R134a	Overall	2.164	0.964-1.464
	251	2.367	1.119-1.374
	275	2.251	0.842-1.492
	298	2.117	0.590-1.180

Table 7-6 (continued)

System (1-2)	Fitting temperature (K)	Parameters λ	ΔP-Δy_1
R23-R13	Overall	1.857	2.074-1.987
	273	1.750	0.362-0.725
	255	1.975	0.381-0.767
	225	2.265	0.541-0.921
	199	2.646	0.642-1.084
Propylene-R22	Overall	-0.099	0.334-0.929
	258	-0.033	0.307-0.920
	263	-0.049	0.290-0.862
	268	-0.079	0.274-0.897
	273	-0.102	0.280-1.086
	278	-0.107	0.266-0.547
	283	-0.143	0.277-1.018
R134a-R152a	Overall	-2.049	1.101-1.002
	255	-1.805	0.178-0.876
	275	-1.911	0.081-0.473
	298	-2.107	0.139-0.465

It is obvious that with the simplifying assumptions we introduced, we lose in accuracy of the correlations. Nevertheless, the one parameter 1FG^E-EoS model we propose show, promise for use as a predictive model. Moreover, the results of Table 7-6 show that temperature dependence of the energy parameter could be correlated with a straight line. For some of the systems in Table C-8 we have two straight lines to be correlated with a cubic polynomial.

For the model 1PM we tested the idea of having the binary parameter fitted at a single temperature near 273 K temperature, and then predict vapor-liquid equilibria over a range of temperatures. The results of this model are given in Table C-9, where the highlighted temperature is the one used to obtain the energy parameter. We can see that for most of the systems, the performance of the model is good. For comparison, in Table C-10 we give the results for the systems R14-R23 and R13-R113 using the same approach, for the classical one-fluid van der Waals mixing rule (vdW). We can see that the vdW model predicts poorly the pressure at low temperature for R14-R23 and at high temperature for R13-R113. In Table 7-7 we report the results for the ternary system R14-R23-R13 taken from Proust and Stein (1979b) from the models 1PM, vdW and 3PWS. The binary parameters of the 3PWS model for the system R14-R13 were obtained from Orbey and Sandler (1995). The values of Table 7-7 show better results for the G^E-EoS models than for the classical (vdW) rule. Also, the 1PM model gives up to two times smaller error for the pressure, and four times for the vapor phase composition predictions, than the 3PWS model for the high pressure system. We note that the predictions at low pressure for the system R14-R23 deteriorate, while at about seven bars all binaries are represented very accurately.

From the overall results of Table 7-7 it can be seen that the vdW model predicts the phase composition worse as the component's polarity increases, while for the two other models based on the Wong-Sandler mixing rule this is not the case. The dipole moments for these components [Blindenbach et al, (1994)] are: 0, 1.65, and 0.50 for the molecules R14, R23, and R13 respectively.

In order to derive some conclusions as to the significance of the parameters, we note that the system R14-R13 favors the unlike interactions more than the other two binaries, since there is less polarity and less size difference in the components (one chlorine replaces one fluorine). The system R14-R23 favors the like interactions more than the other two systems, since one component is polar and the other nonpolar. Also, there are size differences, since one hydrogen atom replaces one fluorine atom. For the system R23-R13 the two phenomena (size-polarity differences) bring the parameter in between the parameters of the other two binary systems. It is interesting to note that the van der Waals parameter shows the same order in magnitude, while it is difficult to assign any physical meaning to he NRTL parameters.

Table 7-7 AAD% in pressure and vapor phase compositions of components 1, 2 and 3 for the ternary system R14-R23-R13 and parameters for the models vdW, 1PM, and 3PWS (R14-R23/R14-R13/R23-R13).

System (1-2-3)	vdW k	1PM λ	3PWS $k/\tau_{12}/\tau_{21}$
Parameters	0.143	3.143	0.201/542/95
	0.028	0.079	0.106/617/-40
	0.1032	1.750	-0.109/588/588
R14-R23-R13 (3.447 bars)	6.53-4.71-5.97-3.60	2.47-3.27-3.36-7.71	1.15-4.22-2.31-6.12
R14-R23-R13 (6.895 bars)	4.51-1.36-8.16-4.68	0.78-0.67-3.76-6.02	1.97-2.90-6.56-13.15
Overall (35 points)	5.66-3.27-6.91-4.06	1.74-2.15-3.53-6.99	1.50-3.65-4.13-9.13

In Figure 7-2 we show this ternary system at two different pressures with the two models 1PM and 3PWS. It is obvious that for the high pressure system our model's predictions are within the data points while for the low pressure system the NRTL model underpredicts the vapor phase composition of R14, and our model overpredicts it. In Figures C-1 to C-12 we present predictions for the binary systems that we have analyzed with the 1FG^E model.

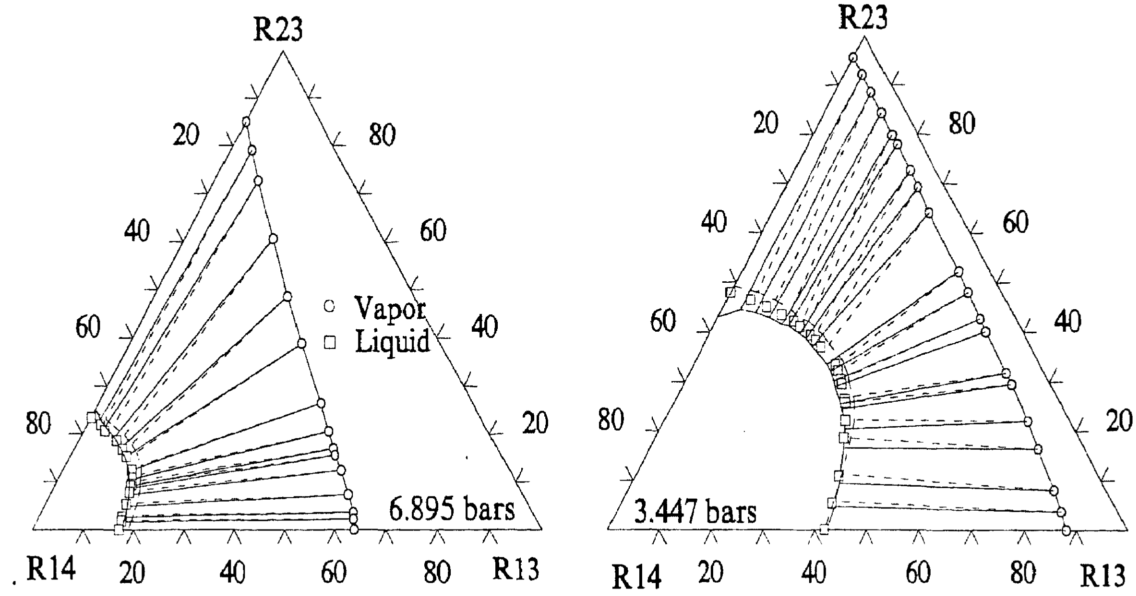

Figure 7-2 1PM model (—) predictions and 3PWS 2 (---) for the ternary system R14-R23-R13 at 3.447 bars and 6.895 bars.

A point of importance here, is that it is difficult to recognize how the NRTL model can treat a ternary mixture with two similar components as essentially a binary, since for the binary and ternary mixtures we write:

$$A^E = x_1 \frac{x_2 A_{12} G_{12}}{x_1 + x_2 G_{12}} + x_2 \frac{x_1 A_{21} G_{21}}{x_1 G_{21} + x_2} \tag{7-2}$$

$$A^E = x_1 \frac{x_2' A_{12} G_{12} + x_3' A_{13} G_{13}}{x_1 + x_2' G_{12} + x_3' G_{13}} + x_2' \frac{x_1 A_{21} G_{21} + x_3' A_{23} G_{23}}{x_1 G_{21} + x_2' + x_3' G_{23}} + x_3' \frac{x_1 A_{31} G_{31} + x_2' A_{32} G_{32}}{x_1 G_{31} + x_2' G_{32} + x_3'} \tag{7-3}$$

where,

$$A_{ij} = \frac{\tau_{ij}}{RT} \tag{7-4}$$

As Michelsen and Kistenmacher (1990) pointed out, in a multicomponent mixture treated with pseudocomponents we could expect for example, to treat the R14-R13 (2' and 3') system as the second component of the binary mixture (equation 7-2). Nevertheless, we can see from Table 7-7 that the energy parameters for the R14-R13 system have values away from zero. For this reason two-fluid theory based models can not be safely extended to multicomponent mixtures, treated with a number of pseudocomponents.

On the other hand the 1FG^E model characterizes this system as an athermal one with small positive deviations from Raoult's law.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

The $1FG^E$ model is presented in this work. The model shares the features of the G^E model of Knox et al (1984), on which it is established. The $1FG^E$ model is able to predict multicomponent mixture phase equilibria from only binary interaction parameters. A feature of the $1FG^E$ model is that its binary parameters have physical significance, as they are connected with the number of interactions and the local ordering of the molecules in the mixture. This model is incorporated into G^E-EoS mixing rules based on the infinite pressure state, in order to address the need of phase equilibrium thermodynamics for a predictive as well as a correlative model, for use over an extended range of temperatures and pressures.

Moreover, from the study of the nonideal mixtures of chapter five we have established the adequacy of the Huron-Vidal (1979) mixing rule as connected to the $1FG^E$ model, to predict vapor-liquid equilibrium behavior using only a few experimental data. The one energy parameter of the $1FG^E$ model could be very well obtained from available experimental information at low pressures. In contrast the theoretical pitfalls of the G^E model presented for the reformulated Wong-Sandler mixing rule [Orbey and Sandler, (1995b)], renders it inadequate to be connected with the one-fluid character inherent to an EoS.

In chapter six we prove the correlative abilities of our model as applied to a variety of hydrogen containing ternaries and their constituent binaries under the thermodynamic formalism of the Huron-Vidal mixing rule. The only parameters involved are those of the $1FG^E$ model, one size and one energy related parameters, and they are able to represent the data very well. The errors in the predictions of pressure and vapor phase composition drop down significantly with respect to previous models. More importantly, for binary hydrogen-hydrocarbon mixtures the parameters can be correlated with the acentric factor of the hydrocarbon which means that our model can describe the highly asymmetric character of these so-called "difficult systems".

In chapter seven we have provided a flexible cross interaction parameter able to provide an average number of interactions for different limiting cases. With simple assumptions, we provide a one parameter version of the $1FG^E$-EoS model, based on the Wong-Sandler (1992) mixing rule. The study of multiparameter models showed that more than one parameter models tend to overcorrelate few experimental data given at a single temperature, and so make it more difficult to predict the values of the parameters at other conditions. It has been shown, through the heuristic rule that we have established in this work, that the structure of the $1FG^E$ model can describe the temperature dependence of the fugacity coefficient, which makes it a unique candidate to be used as a predictive tool for the highly nonideal class of refrigerant mixtures.

Also, in chapter seven we have studied the athermal (temperature-independent C parameter of equation 4-27) solution assumption for the $1FG^E$ model, and it has been shown to be in discord with the idea of phase equilibria predictions over a range of temperatures. Thus, the temperature-dependent equation 4-34 should be used. In addition, the results for the ternary system R14-R23-R13 proved the model capable of predictions of multicomponent mixtures with only a single binary parameter per pair of components. Additionally, the $1FG^E$ model parameters have the potential to be related to characteristic constants of the systems, such as the pure component acentric factors or dipole moments. In contrast, the Non-Random-Two-Liquid theory [Renon and Prausnitz, (1968)] chosen by Orbey and Sandler (1995a) on the same thermodynamic formalism as ours, shows much higher errors in both pressure and vapor phase composition predictions.

8.2 Recommendations

Future work could include computer simulations employing the Gibbs ensemble method able to provide the local ordering of the molecules of both phases at high pressures.

Although the predictive model we have presented is a competitor to the group contribution methods, there are classes of systems for which there are not available experimental data. So, for the important class of refrigerant mixtures, we recommend developing a one-parameter group contribution model, using several binary and multicomponent mixtures. This model could test the use of two global parameters in equation 7-1, namely two different exponents in the nominator and denominator. An overall correlation of the many experimental data could provide the energy interaction parameters between the groups. This may be an improvement over the existing group contribution models that are based on two-fluid theory.

Two more points that we can suggest, is to incorporate the athermal solution of Florry-Huggins theory into the $1FG^E$ model, for predictions of the volumetric properties of polymer solutions. Also the model could be tested for the prediction of infinite dilution activity coefficients.

APPENDIX A

A-1 Derivation of the Fugacity Coefficient for the Huron-Vidal Mixing Rule

A-2 Derivation of the Fugacity Coefficient for the Density Dependent Mixing Rule

A-3 Derivation of the Excess Gibbs Energy and the Activity Coefficient for the $1FG^E$ Model

A-4 Derivation of Infinite Dilution Activity Coefficients with the UNIFAC Model

A-5 Results with the $1FG^E$/Huron-Vidal Mixing Rule

APPENDIX A-1

Derivation of the Fugacity Coefficient for the Huron-Vidal Mixing Rule

The mixture parameters are given by:

$$\frac{a}{RT} = bD \qquad \text{(A-1-1)}$$

$$b = \sum_i x_i b_i \qquad \text{(A-1-2)}$$

where,

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{CRT} \qquad \text{(A-1-3)}$$

and,

$$C = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1) \qquad \text{(A-1-4)}$$

The volume cubic form of the EoS is:

$$v^3 + (b - \frac{RT}{P})v^2 - (3b^2 + RTb\frac{2-D}{P})v + (b^3 - RTb^2\frac{D-1}{P}) = 0 \quad \text{(A-1-5)}$$

The EoS is written as:

$$\frac{P}{RT} = \frac{1}{v-b} - \frac{bD}{v^2 + 2bv - b^2} = \frac{n}{\underline{v} - nb} - \frac{nbnD}{\underline{v}^2 + 2nb\underline{v} - (nb)^2} \qquad \text{(A-1-6)}$$

The compositional derivative of the pressure is:

$$\frac{\partial(P/RT)}{\partial n_i} = \frac{1}{\underline{v} - nb} + \frac{n}{(\underline{v} - nb)^2} b_i - b_i \frac{nD}{\underline{X}} -$$

$$\frac{nb(\partial nD/\partial n_i)}{\underline{X}} + \frac{n^2 bD}{\underline{X}^2} 2b_i[\underline{v} - nb] \qquad \text{(A-1-7)}$$

The terms in equation A-1-7 upon integration will give:

$$\ln(\underline{v} - nb) - \frac{nb_i}{\underline{v} - nb} - \frac{[b_i nD + nb(\partial nD/\partial n_i)]}{2\sqrt{2}nb} \ln[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}] +$$

$$n^2 bD2b_i\{\frac{\underline{v} - nb}{4nb\underline{X}} + \frac{1}{8\sqrt{2}(nb)^2} \ln(\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}) +$$

$$nb[\frac{\underline{v} + nb}{4(nb)^2\underline{X}} + \frac{1}{8\sqrt{2}(nb)^3} \ln(\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})})]\} =$$

$$\ln(\underline{v}-nb)-\frac{nb_i}{\underline{v}-nb}-\frac{[b_i nD+nb(\partial nD/\partial n_i)]}{2\sqrt{2}nb}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]+$$

$$n^2bD2b_i\{\frac{\underline{v}}{2nb\underline{X}}+\frac{1}{4\sqrt{2}(nb)^2}\ln(\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})})\}=$$

$$\ln(\underline{v}-nb)-\frac{nb_i}{\underline{v}-nb}-\frac{[b_i nD+nb(\partial nD/\partial n_i)-b_i nD]}{2\sqrt{2}nb}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]+$$

$$\frac{n^2bD2b_i\underline{v}}{2nb\underline{X}}=$$

$$\ln(\underline{v}-nb)-\frac{nb_i}{\underline{v}-nb}-\frac{(\partial nD/\partial n_i)}{2\sqrt{2}}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]+\frac{nDb_i\underline{v}}{\underline{X}} \tag{A-1-8}$$

$$\ln\phi_i=-\int_{\infty}^{\underline{v}}[\frac{1}{RT}(\frac{\partial P}{\partial n_i})_{T,\underline{v},n_j}-\frac{1}{\underline{v}}]d\underline{v}-\ln Z=-\ln[\frac{P(\underline{v}-b)}{RT}]+$$

$$\frac{b_i}{v-b}+\frac{(\partial nD/\partial n_i)}{2\sqrt{2}}\ln[\frac{v+b(1-\sqrt{2})}{v+b(1+\sqrt{2})}]-\frac{Db_iv}{v^2+2bv-b^2}=$$

$$-\ln[\frac{P(\underline{v}-b)}{RT}]+\frac{b_i}{b}(\frac{Pv}{RT}-1)+\frac{(\partial nD/\partial n_i)}{2\sqrt{2}}\ln[\frac{v+b(1-\sqrt{2})}{v+b(1+\sqrt{2})}] \tag{A-1-9}$$

where we have used the relationship:

$$\frac{Pv}{RT}-1=\frac{b}{v-b}-\frac{Dbv}{v^2+2bv-b^2}$$

APPENDIX A-2

Derivation of the Fugacity Coefficient for the Density Dependent Mixing Rule

For the development of the density dependent mixing rule we consider the expression:

$$\frac{a}{RT} = \frac{a}{RT}^{(l)} F + \frac{a}{RT}^{(v)} (1 - F) \tag{A-2-1}$$

where,

$$\frac{a}{RT}^{(l)} = bD \tag{A-2-2}$$

$$\frac{a}{RT}^{(v)} = b - Q \tag{A-2-3}$$

For the density dependent interpolation function F we consider the expression:

$$F = \frac{rb}{v + (r-1)b} \Rightarrow 1 - F = \frac{v - b}{v + (r-1)b} \tag{A-2-4}$$

Since we consider multicomponent mixtures r should be composition dependent and quadratic in composition:

$$r = \sum_i \sum_j x_i x_j r_{ij} \tag{A-2-5}$$

For b we use the simple linear mixing rule (equation 2-21) and Q and D are given by equations 2-50 and 2-51 respectively with the combining rule given by equation 2-47. The volume roots of the cubic EoS are given by solving the expression:

$$\begin{aligned} &v^4 + v^3[rb - \frac{RT}{P}] + v^2[b^2(r-4) - \frac{RT}{P}(rb + Q)] + \\ &v[b^3(4 - 3r) - \frac{RT}{P} b[(2r-1)b - Drb - 2Q]] + \\ &[(r-1)b^4 - \frac{RT}{P} b^2 (rDb - rb + Q)] = 0 \end{aligned} \tag{A-2-6}$$

For the compositional derivatives we have:

$$\frac{\partial b}{\partial n_i} = b_i \tag{A-2-7}$$

$$\frac{1}{n} \frac{\partial n^2 r}{\partial n_i} = 2 \sum_j x_j r_j \tag{A-2-8}$$

$$\frac{1}{n}\frac{\partial n^2Q}{\partial n_i} = 2\sum_j x_j[\frac{b_i + b_j}{2} - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij})] \qquad \text{(A-2-9)}$$

$$\frac{\partial nD}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln\gamma_{\infty i}}{C} \qquad \text{(A-2-10)}$$

Besides,

$$\frac{n^2 a}{RT} = (nD)(nb)\frac{\frac{n^2 r}{n^2}(nb)}{\underline{v} + (\frac{n^2 r}{n^2} - 1)(nb)} + n^2(b - Q)\frac{\underline{v} - nb}{\underline{v} + (\frac{n^2 r}{n^2} - 1)(nb)} \qquad \text{(A-2-11)}$$

where, $\underline{v}$ denotes the total volume of the system. So, we get for the compositional derivative of the energy parameter:

$$\frac{\partial n^2 a}{\partial n_i} = \frac{\partial nD}{\partial n_i}nbF + nD\frac{\partial nb}{\partial n_i}F +$$

$$nDnb\{\frac{[Anb + r\frac{\partial nb}{\partial n_i}][\underline{v} + (r-1)nb] - rnb[Anb + (r-1)\frac{\partial nb}{\partial n_i}]}{[\underline{v} + (r-1)nb]^2}\} +$$

$$(nb + n\frac{\partial nb}{\partial n_i} - \frac{\partial n^2 Q}{\partial n_i})(1 - F) +$$

$$n^2(b - Q)\{\frac{-\frac{\partial nb}{\partial n_i}[\underline{v} + (r-1)nb] - [\underline{v} - nb][Anb + (r-1)\frac{\partial nb}{\partial n_i}]}{[\underline{v} + (r-1)nb]^2}\} =$$

$$\frac{\partial nD}{\partial n_i}nbF + nD\frac{\partial nb}{\partial n_i}F +$$

$$nDnb\frac{[Anb(\underline{v} - nb) + r\frac{\partial nb}{\partial n_i}\underline{v}]}{[\underline{v} + (r-1)nb]^2} + (nb + n\frac{\partial nb}{\partial n_i} - \frac{\partial n^2 Q}{\partial n_i})(1 - F) -$$

$$n^2(b - Q)\frac{[Anb(\underline{v} - nb) + r\frac{\partial nb}{\partial n_i}\underline{v}]}{[\underline{v} + (r-1)nb]^2} =$$

$$(nb + n\frac{\partial nb}{\partial n_i} - \frac{\partial n^2 Q}{\partial n_i}) +$$

$$(\frac{\partial nD}{\partial n_i}nb + nD\frac{\partial nb}{\partial n_i} - nb - n\frac{\partial nb}{\partial n_i} + \frac{\partial n^2Q}{\partial n_i})F +$$

$$n^2(bD - b + Q)\frac{[Anb(\underline{v} - nb) + r\frac{\partial nb}{\partial n_i}\underline{v}]}{[\underline{v} + (r-1)nb]^2} \qquad \text{(A-2-12)}$$

where:

$$A = \frac{\frac{\partial n^2 r}{\partial n_i} - 2rn}{n^2} \qquad \text{(A-2-13)}$$

and so we derive:

$$\frac{\partial P}{RT\partial n_i} = \frac{1}{(\underline{v} - nb)} + \frac{n}{(\underline{v} - nb)^2}\frac{\partial nb}{\partial n_i} - \frac{\partial n^2 a}{RT\partial n_i}\frac{1}{\underline{X}} + \frac{2n^2 a}{RT\underline{X}^2}[\underline{v} - nb]\frac{\partial nb}{\partial n_i} =$$

$$\frac{1}{(\underline{v} - nb)} + \frac{n}{(\underline{v} - nb)^2}\frac{\partial nb}{\partial n_i} - (nb + n\frac{\partial nb}{\partial n_i} - \frac{\partial n^2 Q}{\partial n_i})\frac{1}{\underline{X}} -$$

$$(\frac{\partial nD}{\partial n_i}nb + nD\frac{\partial nb}{\partial n_i} - nb - n\frac{\partial nb}{\partial n_i} + \frac{\partial n^2 Q}{\partial n_i})\frac{F}{\underline{X}} -$$

$$n^2(bD - b + Q)\frac{[Anb(\underline{v} - nb) + r\frac{\partial nb}{\partial n_i}\underline{v}]}{[\underline{v} + (r-1)nb]^2\underline{X}} +$$

$$2\frac{\partial nb}{\partial n_i}n^2[\frac{b - Q}{\underline{X}^2} + \frac{bD - b + Q}{\underline{X}^2}F](\underline{v} - nb) \qquad \text{(A-2-14)}$$

where we defined: $\underline{X} = \underline{v}^2 + 2nb\underline{v} - (nb)^2$

Now we will make use of the following relations:

$$\frac{1}{\underline{X}}\frac{1}{[\underline{v} + (r-1)nb]^2} = \frac{-1}{(nb)^3(r^2 - 4r + 2)^2}$$

$$\{\frac{2(r-2)\underline{v} - nb(r^2 - 6r + 10)}{\underline{X}} - \frac{2(r-2)}{\underline{v} + (r-1)nb} - \frac{nb(r^2 - 4r + 2)}{[\underline{v} + (r-1)nb]^2}\} \qquad \text{(A-2-15)}$$

$$\frac{1}{\underline{X}}\frac{1}{[\underline{v} + (r-1)nb]} = \frac{-1}{(nb)^2(r^2 - 4r + 2)}$$

$$[\frac{\underline{v}-nb(r-3)}{\underline{X}}-\frac{1}{\underline{v}+(r-1)nb}] \qquad \text{(A-2-16)}$$

$$\frac{1}{\underline{X}^2}\frac{1}{[\underline{v}+(r-1)nb]}=\frac{1}{(nb)^4(r^2-4r+2)^2}$$

$$[\frac{-(nb)^2(r^2-4r+2)\underline{v}+(nb)^3(r^3-7r^2+14r-6)}{\underline{X}^2}+$$

$$\frac{1}{\underline{v}+(r-1)nb}+\frac{nb(r-3)-\underline{v}}{\underline{X}}] \qquad \text{(A-2-17)}$$

$$\frac{\partial P}{RT\partial n_i}=\frac{1}{(\underline{v}-nb)}+\frac{n}{(\underline{v}-nb)^2}\frac{\partial nb}{\partial n_i}-(nb+n\frac{\partial nb}{\partial n_i}-\frac{\partial n^2Q}{\partial n_i})\frac{1}{\underline{X}}-$$

$$(\frac{\partial nD}{\partial n_i}nb+nD\frac{\partial nb}{\partial n_i}-nb-n\frac{\partial nb}{\partial n_i}+\frac{\partial n^2Q}{\partial n_i})$$

$$[\frac{-r}{r^2-4r+2}]\frac{1}{nb}[\frac{\underline{v}-nb(r-3)}{\underline{X}}-\frac{1}{\underline{v}+(r-1)nb}]+$$

$$n^2(bD-b+Q)\frac{[Anb(\underline{v}-nb)+r\frac{\partial nb}{\partial n_i}\underline{v}]}{(nb)^3(r^2-4r+2)^2}$$

$$\{\frac{2(r-2)\underline{v}-nb(r^2-6r+10)}{\underline{X}}-\frac{2(r-2)}{\underline{v}+(r-1)nb}-\frac{nb(r^2-4r+2)}{[\underline{v}+(r-1)nb]^2}\}+$$

$$2\frac{\partial nb}{\partial n_i}n^2\frac{b-Q}{\underline{X}^2}(\underline{v}-nb)+2\frac{\partial nb}{\partial n_i}n^2(bD-b+Q)\frac{(\underline{v}-nb)r}{(nb)^3(r^2-4r+2)^2}$$

$$[\frac{-(nb)^2(r^2-4r+2)\underline{v}+(nb)^3(r^3-7r^2+14r-6)}{\underline{X}^2}+$$

$$\frac{1}{\underline{v}+(r-1)nb}+\frac{nb(r-3)-\underline{v}}{\underline{X}}]=$$

$$\frac{1}{(\underline{v}-nb)}+\frac{n}{(\underline{v}-nb)^2}\frac{\partial nb}{\partial n_i}-$$

$$(nb+n\frac{\partial nb}{\partial n_i}-\frac{\partial n^2Q}{\partial n_i})\frac{1}{\underline{X}}+(\frac{\partial nD}{\partial n_i}nb+nD\frac{\partial nb}{\partial n_i}-nb-n\frac{\partial nb}{\partial n_i}+\frac{\partial n^2Q}{\partial n_i})$$

$$[\frac{r}{r^2-4r+2}]\frac{1}{nb}[\frac{\underline{v}-nb(r-3)}{\underline{X}}-\frac{1}{\underline{v}+(r-1)nb}]-$$

$$\frac{n^2(bD-b+Q)A}{(nb)(r^2-4r+2)^2}$$

$$\{\frac{2(r-2)\underline{v}-nb(r^2-6r+10)}{\underline{X}}-\frac{2(r-2)}{\underline{v}+(r-1)nb}-\frac{nb(r^2-4r+2)}{[\underline{v}+(r-1)nb]^2}\}+$$

$$\frac{n^2(bD-b+Q)(Anb+r\frac{\partial nb}{\partial n_i})}{(nb)^3(r^2-4r+2)^2}$$

$$\{\frac{2(r-2)\underline{v}^2-nb(r^2-6r+10)\underline{v}}{\underline{X}}-\frac{2(r-2)\underline{v}}{\underline{v}+(r-1)nb}-\frac{nb(r^2-4r+2)\underline{v}}{[\underline{v}+(r-1)nb]^2}\}+$$

$$2\frac{\partial nb}{\partial n_i}n^2(b-Q)\frac{\underline{v}}{\underline{X}^2}-2\frac{\partial nb}{\partial n_i}n^2(b-Q)\frac{nb}{\underline{X}^2}-$$

$$2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^2(r^2-4r+2)^2}$$

$$[\frac{-(nb)^2(r^2-4r+2)\underline{v}+(nb)^3(r^3-7r^2+14r-6)}{\underline{X}^2}+$$

$$\frac{1}{\underline{v}+(r-1)nb}+\frac{nb(r-3)-\underline{v}}{\underline{X}}]+2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^3(r^2-4r+2)^2}$$

$$[\frac{-(nb)^2(r^2-4r+2)\underline{v}^2+(nb)^3(r^3-7r^2+14r-6)\underline{v}}{\underline{X}^2}+$$

$$\frac{\underline{v}}{\underline{v}+(r-1)nb}+\frac{nb(r-3)\underline{v}-\underline{v}^2}{\underline{X}}] \tag{A-2-18}$$

To get the fugacity we have to integrate the terms in equation A-2-18 and for that we use the relationships:

$$\int\frac{d\underline{v}}{\underline{X}}=\frac{1}{2\sqrt{2}nb}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}] \tag{A-2-19}$$

$$\int\frac{\underline{v}d\underline{v}}{\underline{v}+(r-1)nb}=\underline{v}-(r-1)nb\ln[\underline{v}+nb(r-1)] \tag{A-2-20}$$

$$\int\frac{d\underline{v}}{\underline{X}^2}=-\frac{\underline{v}+nb}{4(nb)^2\underline{X}}-\frac{1}{8\sqrt{2}(nb)^3}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}] \tag{A-2-21}$$

$$\int\frac{\underline{v}d\underline{v}}{\underline{X}^2}=\frac{\underline{v}-nb}{4(nb)\underline{X}}+\frac{1}{8\sqrt{2}(nb)^2}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}] \tag{A-2-22}$$

$$\int \frac{\underline{v}^2 d\underline{v}}{\underline{X}} = \underline{v} - nb \ln \underline{X} + \frac{3(nb)}{2\sqrt{2}} \ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right] \qquad \text{(A-2-23)}$$

$$\int \frac{\underline{v} d\underline{v}}{\underline{X}} = \frac{1}{2}\left[\ln \underline{X} - \frac{1}{\sqrt{2}} \ln\left(\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right)\right] \qquad \text{(A-2-24)}$$

$$\int \frac{\underline{v}^2 d\underline{v}}{\underline{X}^2} = \frac{-3\underline{v} + nb}{4\underline{X}} + \frac{1}{8\sqrt{2}(nb)} \ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right] \qquad \text{(A-2-25)}$$

$$\int \frac{\underline{v}^3 d\underline{v}}{\underline{X}^2} = \frac{1}{2}\left\{\ln \underline{X} - \frac{5}{4\sqrt{2}} \ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right] + \frac{7(nb)\underline{v} - 3(nb)^2}{2\underline{X}}\right\} \qquad \text{(A-2-26)}$$

$$\int \frac{\underline{v}^3 d\underline{v}}{\underline{X}} = \frac{5}{2}(nb)^2 \ln \underline{X} + \frac{\underline{v}^2}{2} - 2nb\underline{v} -$$

$$\frac{7}{2\sqrt{2}}(nb)^2 \ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right] \qquad \text{(A-2-27)}$$

$$\int \frac{\underline{v}^2 d\underline{v}}{\underline{v} + (r-1)nb} = \frac{[\underline{v} + (r-1)nb]^2}{2} -$$

$$2(r-1)nb[\underline{v} + (r-1)nb] + (r-1)^2(nb)^2 \ln[\underline{v} + nb(r-1)] \qquad \text{(A-2-28)}$$

$$\int \frac{\underline{v} d\underline{v}}{[\underline{v} + (r-1)nb]^2} = \frac{(r-1)nb}{\underline{v} + (r-1)nb} + \ln[\underline{v} + nb(r-1)] \qquad \text{(A-2-29)}$$

The terms of equation A-2-18 upon integration will give:

$$\ln[\underline{v} - nb] - \frac{n\partial nb / \partial n_i}{\underline{v} - nb} - \left(nb + n\frac{\partial nb}{\partial n_i} - \frac{\partial n^2 Q}{\partial n_i}\right) \frac{\ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right]}{2\sqrt{2}nb}$$

$$\left(\frac{\partial nD}{\partial n_i} nb + nD\frac{\partial nb}{\partial n_i} - nb - n\frac{\partial nb}{\partial n_i} + \frac{\partial n^2 Q}{\partial n_i}\right)\left[\frac{r}{r^2 - 4r + 2}\right]\frac{1}{nb}$$

$$\left\{\frac{1}{2}\left[\ln \underline{X} - \frac{\ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right]}{\sqrt{2}}\right] - \frac{r-3}{2\sqrt{2}} \ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right] - \ln[\underline{v} + (r-1)nb]\right\} -$$

$$\frac{n^2(bD - b + Q)A}{(nb)(r^2 - 4r + 2)^2}\left\{(r-2)\left[\ln \underline{X} - \frac{\ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right]}{\sqrt{2}}\right] -\right.$$

$$\frac{r^2 - 6r + 10}{2\sqrt{2}} \ln\left[\frac{\underline{v} + nb(1-\sqrt{2})}{\underline{v} + nb(1+\sqrt{2})}\right] - 2(r-2)\ln[\underline{v} + (r-1)nb] +$$

$$\frac{(nb)(r^2-4r+2)}{[\underline{v}+(r-1)nb]}\}+\frac{n^2(bD-b+Q)(Anb+r\frac{\partial nb}{\partial n_i})}{(nb)^3(r^2-4r+2)^2}\{2(r-2)[\underline{v}-nb\ln\underline{X}+$$

$$\frac{3}{2\sqrt{2}}nb\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]-\frac{nb(r^2-6r+10)}{2}[\ln\underline{X}-\frac{1}{\sqrt{2}}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]-$$

$$2(r-2)[\underline{v}-(r-1)nb\ln[\underline{v}+(r-1)nb]]-(nb)(r^2-4r+2)[\frac{(r-1)nb}{\underline{v}+(r-1)nb}+$$

$$\ln[\underline{v}+(r-1)nb]]\}+$$

$$2\frac{\partial nb}{\partial n_i}n^2(b-Q)[\frac{\underline{v}-nb}{4nb\underline{X}}+\frac{1}{8\sqrt{2}(nb)^2}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]+$$

$$2\frac{\partial nb}{\partial n_i}n^2(b-Q)(nb)[\frac{\underline{v}+nb}{4(nb)^2\underline{X}}+\frac{1}{8\sqrt{2}(nb)^3}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]-$$

$$2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^2(r^2-4r+2)^2}\{-\frac{1}{2}[\ln\underline{X}-\frac{1}{\sqrt{2}}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]+$$

$$\frac{(r-3)}{2\sqrt{2}}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]-(nb)^2(r^2-4r+2)[\frac{\underline{v}-nb}{4(nb)\underline{X}}+$$

$$\frac{1}{8\sqrt{2}(nb)^2}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]-(nb)^3(r^3-7r^2+14r-6)[\frac{\underline{v}+nb}{4(nb)^2\underline{X}}+$$

$$\frac{1}{8\sqrt{2}(nb)^3}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]+\ln[\underline{v}+(r-1)nb]\}+$$

$$2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^3(r^2-4r+2)^2}\{-[\underline{v}-nb\ln\underline{X}+\frac{3}{2\sqrt{2}}nb\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]+$$

$$(r-3)\frac{nb}{2}[\ln\underline{X}-\frac{1}{\sqrt{2}}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]-(nb)^2(r^2-4r+2)[\frac{nb-3\underline{v}}{4\underline{X}}+$$

$$\frac{1}{8\sqrt{2}nb}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]+(nb)^3(r^3-7r^2+14r-6)[\frac{\underline{v}-nb}{4(nb)\underline{X}}+$$

$$\frac{1}{8\sqrt{2}(nb)}\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]]+[\underline{v}-(r-1)nb\ln[\underline{v}+(r-1)nb]]\}=$$

$$\ln[\underline{v}-nb]-\frac{n\partial nb/\partial n_i}{\underline{v}-nb}+\frac{\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]}{2\sqrt{2}}\{\frac{-(nb+n\frac{\partial nb}{\partial n_i}-\frac{\partial n^2Q}{\partial n_i})}{(nb)}+$$

$$(\frac{\partial nD}{\partial n_i}nb + nD\frac{\partial nb}{\partial n_i} - nb - n\frac{\partial nb}{\partial n_i} + \frac{\partial n^2 Q}{\partial n_i})[\frac{r(2-r)}{r^2-4r+2}]\frac{1}{nb} -$$

$$\frac{n^2(bD-b+Q)A}{(nb)(r^2-4r+2)^2}[-2(r-2)-(r^2-6r+10)]+$$

$$\frac{n^2(bD-b+Q)(Anb + r\frac{\partial nb}{\partial n_i})}{(nb)^2(r^2-4r+2)^2}[6(r-2)+(r^2-6r+10)]+$$

$$2\frac{\partial nb}{\partial n_i}\frac{n^2(b-Q)}{4(nb)^2}+2\frac{\partial nb}{\partial n_i}\frac{n^2(b-Q)}{4(nb)^2}-2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^2(r^2-4r+2)^2}$$

$$[(r-2)-\frac{(r^2-4r+2)}{4}-\frac{(r^3-7r^2+14r-6)}{4}]+$$

$$2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^2(r^2-4r+2)^2}[-r-\frac{(r^2-4r+2)}{4}-\frac{(r^3-7r^2+14r-6)}{4}]\}+$$

$$\ln\underline{X}\{\frac{r}{2(r^2-4r+2)(nb)}(\frac{\partial nD}{\partial n_i}nb + nD\frac{\partial nb}{\partial n_i} - nb - n\frac{\partial nb}{\partial n_i} + \frac{\partial n^2 Q}{\partial n_i}) -$$

$$\frac{n^2(bD-b+Q)A}{(nb)(r^2-4r+2)^2}(r-2)+\frac{n^2(bD-b+Q)(Anb + r\frac{\partial nb}{\partial n_i})}{(nb)^2(r^2-4r+2)^2}$$

$$[-2(r-2)-\frac{(r^2-6r+10)}{2}]+\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^2(r^2-4r+2)^2}+$$

$$+\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^2(r^2-4r+2)^2}(r-1)\}+\ln[\underline{v}+(r-1)nb]$$

$$\{\frac{-r}{(r^2-4r+2)(nb)}(\frac{\partial nD}{\partial n_i}nb + nD\frac{\partial nb}{\partial n_i} - nb - n\frac{\partial nb}{\partial n_i} + \frac{\partial n^2 Q}{\partial n_i}) +$$

$$\frac{n^2(bD-b+Q)A}{(nb)(r^2-4r+2)^2}2(r-2)+\frac{n^2(bD-b+Q)(Anb + r\frac{\partial nb}{\partial n_i})}{(nb)^2(r^2-4r+2)^2}$$

$$[2(r-2)(r-1)-(r^2-4r+2)]-2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)^2(r^2-4r+2)^2}-$$

$$2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r(r-1)}{(nb)^2(r^2-4r+2)^2}\}+\{-\frac{n^2(bD-b+Q)A}{[\underline{v}+(r-1)nb](r^2-4r+2)}+$$

$$\frac{n^2(bD-b+Q)(Anb+r\frac{\partial nb}{\partial n_i})}{(nb)^2(r^2-4r+2)}[-\frac{(r-1)nb}{\underline{v}+(r-1)nb}]+2\frac{\partial nb}{\partial n_i}n^2(b-Q)\frac{\underline{v}-nb}{4nb\underline{X}}+$$

$$+2\frac{\partial nb}{\partial n_i}n^2(b-Q)\frac{\underline{v}+nb}{4nb\underline{X}}+2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)(r^2-4r+2)^2}[(r^2-4r+2)\frac{\underline{v}-nb}{4\underline{X}}+$$

$$(r^3-7r^2+14r-6)\frac{\underline{v}+nb}{4\underline{X}}]+2\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r}{(nb)(r^2-4r+2)^2}[-(r^2-4r+2)\frac{nb-3\underline{v}}{4\underline{X}}$$

$$+(r^3-7r^2+14r-6)\frac{\underline{v}-nb}{4\underline{X}}]\}=$$

$$\ln[\underline{v}-nb]-\frac{n\partial nb/\partial n_i}{\underline{v}-nb}+\frac{\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]}{2\sqrt{2}}$$

$$\{\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r(r-2)}{(nb)^2(r^2-4r+2)}+\frac{2n^2(bD-b+Q)A}{(nb)(r^2-4r+2)^2}(r^2-2r+2)+$$

$$\frac{\partial nb}{\partial n_i}\frac{n^2(b-Q)}{(nb)^2}+(\frac{\partial nD}{\partial n_i}nb+nD\frac{\partial nb}{\partial n_i})[\frac{r(2-r)}{r^2-4r+2}]\frac{1}{nb}+(nb+n\frac{\partial nb}{\partial n_i}-\frac{\partial n^2Q}{\partial n_i})$$

$$[\frac{2(r-1)}{r^2-4r+2}]\frac{1}{nb}\}+\ln\frac{\underline{X}}{[\underline{v}+(r-1)nb]^2}\{\frac{\partial nb}{\partial n_i}\frac{n^2(bD-b+Q)r(-\frac{1}{2})}{(nb)^2(r^2-4r+2)}-$$

$$\frac{(r^2-2)}{2}\frac{n^2(bD-b+Q)A}{(nb)(r^2-4r+2)^2}+\frac{r}{2(r^2-4r+2)nb}(\frac{\partial nD}{\partial n_i}nb+nD\frac{\partial nb}{\partial n_i})-$$

$$\frac{r}{2(r^2-4r+2)}\frac{1}{)nb}(nb+n\frac{\partial nb}{\partial n_i}-\frac{\partial n^2Q}{\partial n_i})\}+\frac{\frac{\partial nb}{\partial n_i}}{(nb)}\{\frac{n^2(bD-b+Q)r}{(r^2-4r+2)\underline{X}}$$

$$[\underline{v}(r-1)-nb]+\frac{n^2(b-Q)}{\underline{X}}\underline{v}-\frac{r(r-1)n^2(bD-b+Q)r}{(r^2-4r+2)[\underline{v}+(r-1)nb]}\}-$$

$$\frac{n^2(bD-b+Q)Ar}{[\underline{v}+(r-1)nb](r^2-4r+2)}=$$

$$\ln[\underline{v}-nb]-\frac{n\partial nb/\partial n_i}{\underline{v}-nb}+$$

$$\{\frac{2(r-1)[n^2Q\frac{\partial nb}{\partial n_i}-(nb)\frac{\partial n^2Q}{\partial n_i}+(nb)^2]-r(r-2)(nb)^2\frac{\partial nD}{\partial n_i}}{(nb)^2(r^2-4r+2)}+$$

$$\frac{2(r^2-2r+2)}{(r^2-4r+2)^2}\frac{n^2(bD-b+Q)A}{nb}\}\frac{\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]}{2\sqrt{2}}+$$

$$\{\frac{r[nb\frac{\partial n^2Q}{\partial n_i}-(nb)^2+(nb)^2\frac{\partial nD}{\partial n_i}-n^2Q\frac{\partial nb}{\partial n_i}]}{2[r^2-4r+2](nb)^2}-(\frac{r^2-2}{2})\frac{n^2[bD-b+Q]A}{(nb)(r^2-4r+2)^2}\}$$

$$\ln\frac{\underline{X}}{[\underline{v}+(r-1)nb]^2}+\frac{\frac{\partial nb}{\partial n_i}}{(nb)}\{\frac{n^2(b-Q-bD)r(r-1)}{(r^2-4r+2)}\frac{1}{[\underline{v}+(r-1)nb]}+n^2(b-Q)$$

$$\frac{(2-3r)\underline{v}+rnb}{(r^2-4r+2)\underline{X}}+\frac{(r-1)\underline{v}-nb}{\underline{X}(r^2-4r+2)}rn^2bD\}$$

$$-\frac{n^2(bD-b+Q)Ar}{[\underline{v}+(r-1)nb](r^2-4r+2)} \qquad \text{(A-2-30)}$$

$$\ln\phi_i=-\int_{\infty}^{\underline{v}}[\frac{1}{RT}(\frac{\partial P}{\partial n_i})_{T,\underline{v},n_j}-\frac{1}{\underline{v}}]d\underline{v}-\ln Z=-\ln[\frac{P(\underline{v}-b)}{RT}]+$$

$$\{-\frac{2(r-1)[n^2Q\frac{\partial nb}{\partial n_i}-(nb)\frac{\partial n^2Q}{\partial n_i}+(nb)^2]-r(r-2)(nb)^2\frac{\partial nD}{\partial n_i}}{(nb)^2(r^2-4r+2)}-$$

$$\frac{2(r^2-2r+2)}{(r^2-4r+2)^2}\frac{n^2(bD-b+Q)}{nb}\frac{\frac{\partial n^2r}{\partial n_i}-2rn}{n^2}\}\frac{\ln[\frac{\underline{v}+nb(1-\sqrt{2})}{\underline{v}+nb(1+\sqrt{2})}]}{2\sqrt{2}}-$$

$$\{\frac{r[nb\frac{\partial n^2Q}{\partial n_i}-(nb)^2+(nb)^2\frac{\partial nD}{\partial n_i}-n^2Q\frac{\partial nb}{\partial n_i}]}{2[r^2-4r+2](nb)^2}-(\frac{r^2-2}{2})\frac{n^2[bD-b+Q]A}{(nb)(r^2-4r+2)^2}\}$$

$$\ln\frac{\underline{X}}{[\underline{v}+(r-1)nb]^2}+\frac{\partial nb/\partial n_i}{b}(Z-1)+\frac{n^2(bD-b+Q)Ar}{[\underline{v}+(r-1)nb](r^2-4r+2)} \text{(A-2-31)}$$

Note that we have used the relationship:

$$\frac{\partial nb/\partial n_i}{(nb)}\{\frac{n(nb)}{\underline{v}-nb}-\frac{n^2(b-Q-bD)r(r-1)}{(r^2-4r+2)}\frac{1}{[\underline{v}+(r-1)nb]}-n^2(b-Q)$$

$$\frac{(2-3r)\underline{v}+rnb}{(r^2-4r+2)\underline{X}}-\frac{(r-1)\underline{v}-nb}{\underline{X}(r^2-4r+2)}rn^2bD\}=\frac{\partial nb/\partial n_i}{(nb)}(Z-1) \qquad \text{(A-2-32)}$$

since,

$$-r(r-1)n^2[b-Q-bD]\underline{X}-[(2-3r)\underline{v}+rnb]n^2(b-Q)[\underline{v}+(r-1)nb]-$$

$$[(r-1)\underline{v}-nb]rn^2bD[\underline{v}+(r-1)nb]=n^2(b-Q)\{\underline{v}^2(-r^2+4r-2)+$$

$$\underline{v}nb[r^2-4r+2]\}+n^2bD\{\underline{v}nb[-r(r^2-4r+2)]\} \qquad \text{(A-2-33)}$$

So we have:

$$\frac{\partial nb/\partial n_i}{(nb)}\{\frac{n(nb)}{\underline{v}-nb}-\frac{n^2(b-Q-bD)r(r-1)}{(r^2-4r+2)}\frac{1}{[\underline{v}+(r-1)nb]}-n^2(b-Q)$$

$$\frac{(2-3r)\underline{v}+rnb}{(r^2-4r+2)\underline{X}}-\frac{(r-1)\underline{v}-nb}{\underline{X}(r^2-4r+2)}rn^2bD\}=\frac{\partial nb/\partial n_i}{(nb)}\{\frac{n(nb)}{\underline{v}-nb}+$$

$$\frac{1}{[\underline{v}+(r-1)nb]\underline{X}}[n^2(b-Q)\underline{v}(nb-\underline{v})-rn^2bDnb\underline{v}]\} \qquad \text{(A-2-34)}$$

and,

$$\frac{P\underline{v}}{RT}-1=\{\frac{(nb)n}{\underline{v}-nb}-$$

$$\frac{1}{[\underline{v}+(r-1)nb]\underline{X}}[rb^2D\underline{v}n^3-(b-Q)b\underline{v}n^3+(b-Q)n^2\underline{v}^2]\}\frac{1}{n} \qquad \text{(A-2-35)}$$

The fugacity expression on a molar basis is:

$$\ln\phi_i=-\ln[\frac{P(\underline{v}-b)}{RT}]+\frac{\partial nb/\partial n_i}{b}(Z-1)+\frac{(bD-b+Q)(\frac{1}{n}\frac{\partial n^2r}{\partial n_i}-2r)r}{[v+(r-1)nb](r^2-4r+2)}$$

$$+\{-\frac{2(r-1)[Q\frac{\partial nb}{\partial n_i}-b(\frac{1}{n}\frac{\partial n^2Q}{\partial n_i})+b^2]-r(r-2)b^2\frac{\partial nD}{\partial n_i}}{b^2(r^2-4r+2)}-$$

$$\frac{2(r^2-2r+2)}{(r^2-4r+2)^2}\frac{(bD-b+Q)}{b}(\frac{1}{n}\frac{\partial n^2r}{\partial n_i}-2r)\}\frac{\ln[\frac{v+b(1-\sqrt{2})}{v+b(1+\sqrt{2})}]}{2\sqrt{2}}+$$

$$\{\frac{-r[b(\frac{1}{n}\frac{\partial n^2Q}{\partial n_i})-b^2+b^2\frac{\partial nD}{\partial n_i}-Q\frac{\partial nb}{\partial n_i}]}{2[r^2-4r+2]b^2}+(\frac{r^2-2}{2})\frac{[bD-b+Q]}{b(r^2-4r+2)^2}$$

$$(\frac{1}{n}\frac{\partial n^2r}{\partial n_i}-2r)\}\ln\frac{v^2+2bv-b^2}{[v+(r-1)b]^2} \qquad \text{(A-2-36)}$$

APPENDIX A-3

Derivation of the Excess Gibbs Energy and the Activity Coefficient for the 1FG^E Model

The total Gibbs energy of mixing is given by Knox et al (1984):

$$\frac{\Delta G^t}{kT} = \frac{(\Delta G^t)^{ath}}{kT} - \sum_i \frac{z_i N_i}{2} \ln \frac{z_i N_i / 2}{I} + \sum_i \sum_j N_{ij} \left(\frac{\varepsilon_{ij}}{kT} + \ln \frac{N_{ij}}{z_i N_i / 2} \right) - \sum_i \frac{z_i N_i \varepsilon_{ii}}{2kT} \qquad \text{(A-3-1)}$$

where the total number of interactions for the mixture are:

$$I = \sum_i \frac{z_i N_i}{2} \qquad \text{(A-3-2)}$$

An important distinction with the two fluid theory is that the i-j pair interactions are assigned half to species i and half to species j and so:

$$N_{ij} = N_{ji} \qquad \text{(A-3-3)}$$

So we get the total number of interactions of species-i molecules:

$$\frac{z_i N_i}{2} = \sum_j N_{ij} \qquad \text{(A-3-4)}$$

with a total area fraction:

$$\vartheta_i = \frac{z_i N_i / 2}{I} \qquad \text{(A-3-5)}$$

Besides, the local composition of molecules j around a molecule i is:

$$x_{ij} = \frac{N_{ij}}{z_i N_i / 2} \qquad \text{(A-3-6)}$$

The local compositions will take values so that the partition function will be maximized and they will be solved as [Knox et al (1984)]:

$$\frac{N_{ij} N_{ji}}{N_{ii} N_{jj}} = \exp\left(\frac{-(2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj})}{kT} \right) \qquad \text{(A-3-7)}$$

where ε_{ij} is the interaction energy for the pair i-j.

As explained in Knox et al (1984), (pg. 282):

$$\sum_i \sum_j N_{ij} \left(\frac{\varepsilon_{ij}}{kT} + \ln \frac{N_{ij}}{z_i N_i / 2} \right) = \sum_i \frac{z_i N_i}{2} \left(\frac{\varepsilon_{ii}}{kT} + \ln \frac{N_{ii}}{z_i N_i / 2} \right) \qquad \text{(A-3-8)}$$

So equation A-3-1 becomes:

$$\frac{\Delta G^t}{kT} = \frac{(\Delta G^t)^{ath}}{kT} - \sum_i \frac{z_i N_i}{2} \ln \frac{z_i N_i / 2}{I} + \sum_i \frac{z_i N_i}{2} \ln \frac{N_{ii}}{z_i N_i / 2} \qquad \text{(A-3-9)}$$

written in molar basis as:

$$\frac{\Delta G}{RT} = \frac{(\Delta G)^{ath}}{RT} - \sum_i \frac{z_i x_i}{2} \ln \vartheta_i + \sum_i \frac{z_i x_i}{2} \ln x_{ii} \qquad \text{(A-3-10)}$$

with the Guggenheim's model as the choice of the athermal solution:

$$\frac{(\Delta G)^{ath}}{RT} = \sum_i x_i \ln \varphi_i + \sum_i \frac{z_i x_i}{2} \ln \frac{\vartheta_i}{\varphi_i} \qquad \text{(A-3-11)}$$

and with the definition of the excess Gibbs energy:

$$\frac{G^E}{RT} = \frac{\Delta G}{RT} - \sum_i x_i \ln x_i \qquad \text{(A-3-12)}$$

we get:

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\varphi_i}{x_i} + \sum_i \frac{z_i x_i}{2} \ln \frac{x_{ii}}{\varphi_i} \qquad \text{(A-3-13)}$$

The activity coefficient is defined as:

$$\partial \frac{\Delta G^t / kT}{\partial N_k})_{T,P,N_j} - \ln x_k = \ln \gamma_k \qquad \text{(A-3-14)}$$

We will use the expression :

$$z_i = \sum_j p_{ij} \frac{N_j}{N} \qquad \text{(A-3-15)}$$

So,

$$\frac{\partial(z_i N_i)}{\partial N_k} = \frac{\partial(\sum_j p_{ij} \frac{N_j}{N})}{\partial N_k} = p_{ik}\frac{N_i}{N} - \sum_j p_{ij}\frac{N_j}{N^2}N_i + (\sum_j p_{ij}\frac{N_j}{N})\delta_{ik}$$

$$= p_{ik}x_i - z_i x_i + z_i \delta_{ik} \qquad \text{(A-3-16)}$$

Also,

$$\frac{\partial I}{\partial N_k} = \frac{\partial \sum_i z_i N_i / 2}{\partial N_k} = [\sum_i \frac{\partial \sum_i z_i}{\partial N_k}\frac{N_i}{2} + \sum_i z_i \frac{\partial N_i / 2}{\partial N_k}] =$$

$$\sum_i [\frac{p_{ik}}{N} - \frac{\sum_j p_{ij} N_j}{N^2}]\frac{N_i}{2} + \sum_i \frac{z_i}{2}\delta_{ik} = \sum_i [\frac{p_{ik}x_i}{2} - \frac{z_i x_i}{2} + \frac{z_i}{2}\delta_{ik}] \qquad \text{(A-3-17)}$$

Now from equation A-3-1 and A-3-14 we have:

$$\ln\gamma_k = \ln\gamma_k^{ath} -$$

$$\sum_i [\frac{\partial z_i N_i}{\partial N_k}\frac{\ln \vartheta_i}{2} + \frac{z_i N_i}{2}\frac{I}{z_i N_i / 2}(\frac{1}{2})\frac{\frac{\partial z_i N_i}{\partial N_k} I - z_i N_i \frac{\partial I}{\partial N_k}}{I^2}]$$

$$+\sum_i \sum_j [\frac{\partial N_{ij}}{\partial N_k}(\frac{\varepsilon_{ij}}{kT} + \ln\frac{N_{ij}}{z_i N_i / 2}) + N_{ij}\frac{z_i N_i / 2}{N_{ij}}(2)\frac{\frac{\partial N_{ij}}{\partial N_k} z_i N_i - N_{ij}\frac{\partial z_i N_i}{\partial N_k}}{(z_i N_i)^2}]$$

$$-\sum_i \frac{\varepsilon_{ii}\frac{\partial z_i N_i}{\partial N_k}}{2kT} \Rightarrow \ln\gamma_k = \ln\gamma_k^{ath} - \sum_i [\frac{\partial z_i N_i}{\partial N_k}\frac{\ln\vartheta_i}{2} + \frac{1}{2}\frac{\partial z_i N_i}{\partial N_k} - \frac{z_i N_i}{2I}\frac{\partial I}{\partial N_k}]$$

$$\sum_i \sum_j [\frac{\partial N_{ij}}{\partial N_k}(\frac{\varepsilon_{ij}}{kT} + \ln\frac{N_{ij}}{z_i N_i / 2}) + \frac{\partial N_{ij}}{\partial N_k} - \frac{N_{ij}}{z_i N_i}\frac{\partial z_i N_i}{\partial N_k}] - \sum_i \frac{\varepsilon_{ii}\frac{\partial z_i N_i}{\partial N_k}}{2kT} =$$

$$\ln\gamma_k^{ath} - \sum_i [\frac{\partial z_i N_i}{\partial N_k}(\frac{\ln\vartheta_i}{2} + \frac{1}{2}) + \frac{\sum_j N_{ij}}{z_i N_i} + \frac{\varepsilon_{ii}}{2kT}]$$

$$+\sum_i \sum_j \frac{\partial N_{ij}}{\partial N_k}(1 + \frac{\varepsilon_{ij}}{kT} + \ln\frac{N_{ij}}{z_i N_i / 2}) + \frac{\partial I}{\partial N_k} \qquad \text{(A-3-18)}$$

But according to equation C1-C4 of Knox et al (1984) we have:

$$\sum_i\sum_j[\frac{\partial N_{ij}}{\partial N_k}(1+\frac{\varepsilon_{ij}}{kT}+\ln\frac{N_{ij}}{z_iN_i/2})]=\sum_i[\frac{\partial z_iN_i/2}{\partial N_k}(1+\frac{\varepsilon_{ii}}{kT}+\ln\frac{N_{ii}}{z_iN_i/2})] \qquad \text{(A-3-19)}$$

and so A-3-18 becomes:

$$\ln\gamma_k=\ln\gamma_k^{ath}-\sum_i\frac{\partial z_iN_i}{\partial N_k}(\frac{\ln\vartheta_i}{2}+\frac{1}{2}+\frac{1}{2}+\frac{\varepsilon_{ii}}{2kT}-\frac{1}{2}-\frac{\varepsilon_{ii}}{2kT}-\frac{1}{2}\ln x_{ii})+\frac{\partial I}{\partial N_k}=$$

$$\ln\gamma_k^{ath}-\sum_i\frac{\partial z_iN_i}{\partial N_k}(\frac{\ln\vartheta_i}{2}+\frac{1}{2}-\frac{1}{2}\ln x_{ii})+\frac{\partial I}{\partial N_k}=\ln\gamma_k^{ath}-$$

$$\sum_i(\frac{\ln\vartheta_i}{2}+\frac{1}{2}-\frac{1}{2}\ln x_{ii})(\delta_{ik}z_i-z_ix_i+x_ip_{ik})+\sum_i[\frac{p_{ik}x_i}{2}-\frac{z_ix_i}{2}+\frac{z_i}{2}\delta_{ik}]\Rightarrow$$

$$\ln\gamma_k=\ln\gamma_k^{ath}-\sum_i[\frac{p_{ik}x_i}{2}-\frac{z_ix_i}{2}+\frac{z_i}{2}\delta_{ik}]\ln\frac{\vartheta_i}{x_{ii}}=\ln\gamma_k^{ath}-\frac{z_k}{2}\ln\frac{\vartheta_k}{x_{kk}}-$$

$$\sum_i\frac{(p_{ik}-z_i)x_i}{2}\ln\frac{\vartheta_i}{x_{ii}} \qquad \text{(A-3-20)}$$

Now for the athermal Gibbs model we use:

$$\frac{(\Delta G^t)^{ath}}{kT}=\sum_i N_i\ln\varphi_i+\sum_i\frac{z_iN_i}{2}\ln\frac{\vartheta_i}{\varphi_i}=\sum_i N_i\ln\frac{r_iN_i}{\sum_j r_jN_j}+\sum_i\frac{z_iN_i}{2}\ln\frac{\vartheta_i}{\varphi_i} \qquad \text{(A-3-21)}$$

and,

$$\frac{\partial(\Delta G^t/kT)^{ath}}{\partial N_k}=\sum_i[\delta_{ik}\ln\varphi_i+\frac{N_i}{\varphi_i}\frac{\partial\varphi_i}{\partial N_k}+\frac{\partial z_iN_i}{\partial N_k}\frac{\ln(\vartheta_i/\varphi_i)}{2}$$

$$+\frac{z_iN_i}{2}\frac{\varphi_i}{\vartheta_i}\frac{\frac{\partial\vartheta_i}{\partial N_k}\varphi_i-\vartheta_i\frac{\partial\varphi_i}{\partial N_k}}{\varphi_i^2}] \qquad \text{(A-3-22)}$$

But,

$$\varphi_i=\frac{r_iN_i}{\sum_j r_jN_j}\Rightarrow\frac{\partial\varphi_i}{\partial N_k}=r_i\frac{\delta_{ik}\sum_j r_jN_j-N_ir_k}{(\sum_j r_jN_j)^2}\Rightarrow\frac{\frac{\partial\varphi_i}{\partial N_k}}{\varphi_i}=\frac{\delta_{ik}\sum_j r_jN_j-N_ir_k}{(\sum_j r_jN_j)N_i}=$$

$$\frac{\delta_{ik}}{N_i} - \frac{r_k}{\sum_j r_j N_j} = \frac{\delta_{ik}}{N_i} - \frac{\varphi_k}{N_k} \qquad \text{(A-3-23)}$$

Besides,

$$\frac{\partial \vartheta_i / \partial N_k}{\vartheta_i} = \frac{\delta_{ik}}{N_i} - \frac{\vartheta_k}{N_k} \qquad \text{(A-3-24)}$$

So we have:

$$\begin{aligned}
&\ln\gamma_k^{ath} = \frac{\partial(\Delta G^t / kT)^{ath}}{\partial N_k} - \ln x_k = \ln\frac{\varphi_k}{x_k} + \sum_i N_i\Big[\frac{\delta_{ik}}{N_i} - \frac{\varphi_k}{N_k}\\
&+\Big(\frac{p_{ik}x_i}{2} - \frac{z_i x_i}{2} + \frac{z_i}{2}\delta_{ik}\Big)\ln\frac{\vartheta_i}{\varphi_i} + \frac{z_i N_i}{2}\Big(\frac{\partial\vartheta_i/\partial N_k}{\vartheta_i} - \frac{\partial\varphi_i/\partial N_k}{\varphi_i}\Big)\Big] =\\
&\ln\frac{\varphi_k}{x_k} + \sum_i\Big[\delta_{ik} - \frac{N_i\varphi_k}{N_k} + x_i\Big(\frac{p_{ik}}{2} - \frac{z_i}{2}\Big)\ln\frac{\vartheta_i}{\varphi_i} + \frac{z_i}{2}\delta_{ik}\ln\frac{\vartheta_i}{\varphi_i}\\
&+\frac{z_i N_i}{2}\Big(\frac{\varphi_k}{N_k} - \frac{\vartheta_k}{N_k}\Big)\Big] = \ln\frac{\varphi_k}{x_k} + 1 - \frac{\varphi_k}{x_k} + \sum_i x_i\Big(\frac{p_{ik}}{2} - \frac{z_i}{2}\Big)\ln\frac{\vartheta_i}{\varphi_i} + \frac{z_k}{2}\ln\frac{\vartheta_k}{\varphi_k}\\
&\Big(\frac{\varphi_k}{\vartheta_k} - 1\Big)\frac{\sum_i z_i N_i/2}{N_k}\vartheta_k
\end{aligned} \qquad \text{(A-3-25)}$$

But we have:

$$\frac{\sum_i z_i N_i/2}{N_k}\vartheta_k = \vartheta_k \frac{z_k/2}{\dfrac{z_k N_k/2}{\sum_i z_i N_i/2}} = \frac{z_k}{2} \qquad \text{(A-3-26)}$$

and so we get:

$$\begin{aligned}
&\ln\gamma_k^{ath} = \ln\frac{\varphi_k}{x_k} + 1 - \frac{\varphi_k}{x_k}\\
&+\frac{z_k}{2}\ln\frac{\vartheta_k}{\varphi_k} + \sum_i x_i\Big(\frac{p_{ik}}{2} - \frac{z_i}{2}\Big)\ln\frac{\vartheta_i}{\varphi_i} + \Big(\frac{\varphi_k}{\vartheta_k} - 1\Big)\frac{z_k}{2}
\end{aligned} \qquad \text{(A-3-27)}$$

Combining equations A-3-20 and A-3-27 we get:

$$\ln\gamma_k = \ln\frac{\varphi_k}{x_k} + 1 - \frac{\varphi_k}{x_k} + \sum_i x_i\Big(\frac{p_{ik}}{2} - \frac{z_i}{2}\Big)\ln\frac{x_{ii}}{\varphi_i} + \Big(\frac{\varphi_k}{\vartheta_k} - 1 + \ln\frac{x_{kk}}{\varphi_k}\Big)\frac{z_k}{2} \qquad \text{(A-3-28)}$$

APPENDIX A-4

Derivation of Infinite Dilution Activity Coefficients with the UNIFAC Model

i,j,l: species, k,m: groups

$$\ln\gamma_i = 1-\frac{r_i}{\sum\limits_j r_j x_j}+\ln\frac{r_i}{\sum\limits_j r_j x_j}-5q_i\left(1-\frac{\dfrac{r_i}{\sum\limits_j r_j x_j}}{\dfrac{q_i}{\sum\limits_j q_j x_j}}+\ln\frac{\dfrac{r_i}{\sum\limits_j r_j x_j}}{\dfrac{q_i}{\sum\limits_j q_j x_j}}\right)+q_i\left(1-\ln\frac{q_i}{\sum\limits_j q_j x_j}\right)$$

$$-\sum_k\left(\sum_l G_{kl}x_l\frac{\sum\limits_m G_{mi}\tau_{mk}}{\sum\limits_l s_{kl}x_l}-G_{ki}\ln\frac{\sum\limits_m G_{mi}\tau_{mk}}{\sum\limits_l s_{kl}x_l}\right) \qquad \text{(A-4-1)}$$

$$\ln\gamma_1 =$$

$$1-\frac{r_1}{r_1x_1+r_2x_2}+\ln\frac{r_1}{r_1x_1+r_2x_2}-5q_1\left(1-\frac{\dfrac{r_1}{r_1x_1+r_2x_2}}{\dfrac{q_1}{q_1x_1+q_2x_2}}+\ln\frac{\dfrac{r_1}{r_1x_1+r_2x_2}}{\dfrac{q_1}{q_1x_1+q_2x_2}}\right)$$

$$+q_1\left(1-\ln\frac{q_1}{q_1x_1+q_2x_2}\right)-\sum_k\left([G_{k1}x_1+G_{k2}x_2]\frac{\sum\limits_m G_{m1}\tau_{mk}}{s_{k1}x_1+s_{k2}x_2}\right.$$

$$\left.-G_{k1}\ln\frac{\sum\limits_m G_{m1}\tau_{mk}}{s_{k1}x_1+s_{k2}x_2}\right) \qquad \text{(A-4-2)}$$

$$\ln\gamma_2 =$$

$$1-\frac{r_2}{r_1x_1+r_2x_2}+\ln\frac{r_2}{r_1x_1+r_2x_2}-5q_2\left(1-\frac{\dfrac{r_2}{r_1x_1+r_2x_2}}{\dfrac{q_2}{q_1x_1+q_2x_2}}+\ln\frac{\dfrac{r_2}{r_1x_1+r_2x_2}}{\dfrac{q_2}{q_1x_1+q_2x_2}}\right)$$

$$+q_2\left(1-\ln\frac{q_2}{q_1x_1+q_2x_2}\right)-\sum_k\left([G_{k1}x_1+G_{k2}x_2]\frac{\sum\limits_m G_{m2}\tau_{mk}}{s_{k1}x_1+s_{k2}x_2}\right.$$

$$-G_{k2}\ln\frac{\sum\limits_m G_{m2}\tau_{mk}}{s_{k1}x_1+s_{k2}x_2}) \qquad \text{(A-4-3)}$$

$$\ln\gamma_{\substack{1\\x_1=0\\x_2=1}}^{\infty}=1-\frac{r_1}{r_2}+\ln\frac{r_1}{r_2}-5q_1(1-\frac{\frac{r_1}{r_2}}{\frac{q_1}{q_2}}+\ln\frac{\frac{r_1}{r_2}}{\frac{q_1}{q_2}})+q_1(1-\ln\frac{q_1}{q_2})$$

$$-\sum_k([G_{k2}]\frac{\sum\limits_m G_{m1}\tau_{mk}}{s_{k2}}-G_{k1}\ln\frac{\sum\limits_m G_{m1}\tau_{mk}}{s_{k2}}) \qquad \text{(A-4-4)}$$

$$\ln\gamma_{\substack{2\\x_2=0\\x_1=1}}^{\infty}=1-\frac{r_2}{r_1}+\ln\frac{r_2}{r_1}-5q_2(1-\frac{\frac{r_2}{r_1}}{\frac{q_2}{q_1}}+\ln\frac{\frac{r_2}{r_1}}{\frac{q_2}{q_1}})+q_2(1-\ln\frac{q_2}{q_1})$$

$$-\sum_k([G_{k1}]\frac{\sum\limits_m G_{m2}\tau_{mk}}{s_{k1}}-G_{k2}\ln\frac{\sum\limits_m G_{m2}\tau_{mk}}{s_{k1}}) \qquad \text{(A-4-5)}$$

where, $G_{ki}=\nu_k^{(i)}Q_k$; $\tau_{mk}=\exp(-\alpha_{mk}/T)$; $s_{ki}=\sum\limits_m G_{mi}\tau_{mk}$

I. Application to the system Methanol(1)-Water(2) (25°C).

1 CH_3 1 OH 1 H_2O

From Table D.1 from Smith and van Ness (1986) we get the k, r_k, and q_k values:

Table A-4-1 Group parameters for methanol-water

	k	R_k	Q_k	$\nu_k^{(1)}$	$\nu_k^{(2)}$
CH_3	1	0.9011	0.8480	1	0
OH	15	1.0000	1.2000	1	0
H_2O	17	0.9200	1.4000	0	1

From the values in Table A-4-1 we calculate, $r_1=1.9011$, $q_1=2.048$ and $r_2=0.92$, $q_2=1.40$

From Table D.2 from Smith and van Ness (1986) we get the α_{mk} values in K^{-1}:

Table A-4-2 α_{ij}-τ_{ij} parameters for methanol-water

	1	15	17
1	0/1	986.5/0.0366	1318/0.01203
15	156.4/0.5918	0/1	353.5/0.3055
17	300/0.3656	-229.10/2.1563	0/1

Table A-4-3 G_{ki}-s_{ki} parameters for methanol-water

k	i=1	i=2
1	0.848-1.5582	0.000-0.5118
15	1.200-1.2310	0.000-3.0188
17	0.000-0.3768	1.400-1.4000

$$\ln\gamma_1^{\infty} = 1 - \frac{1.9011}{0.92} + \ln\frac{1.9011}{0.92}$$

$$-5(2.048)\left(1 - \frac{\frac{1.9011}{0.92}}{\frac{2.048}{1.4}} + \ln\frac{\frac{1.9011}{0.92}}{\frac{2.048}{1.4}}\right) + 2.048\left(1 - \ln\frac{2.048}{1.4}\right)$$

$$+0.848\ln\frac{(1.2)(0.5918)+0.848}{0.5118} + 1.2\ln\frac{(0.848)(0.0366)+1.2}{3.0188}$$

$$-1.4\frac{(0.848)(0.01203)+(1.2)(0.3055)}{1.4} = 0.8086 \qquad \text{(A-4-6)}$$

$$\ln\gamma_2^{\infty} = 1 - \frac{0.92}{1.9011} + \ln\frac{0.92}{1.9011} - 5(1.4)\left(1 - \frac{\frac{0.92}{1.9011}}{\frac{1.4}{2.048}} + \ln\frac{\frac{0.92}{1.9011}}{\frac{1.4}{2.048}}\right)$$

$$+1.4\left(1 - \ln\frac{1.4}{2.048}\right) - 0.848\frac{(1.4)(0.3656)}{1.5582} - 1.2\frac{(1.4)(2.1563)}{1.2310}$$

$$+1.4\ln\frac{(1.4)(1)}{0.3768} = 0.4729 \tag{A-4-7}$$

II. Application to the system Acetone(1)-Methanol(2) (25°C).

1 CH_3CO 1 CH_3 1 CH_3 1OH

Table A-4-4 Group parameters for acetone-methanol

	k	R_k	Q_k	$\nu_k^{(1)}$	$\nu_k^{(2)}$
CH_3	1	0.9011	0.8480	1	1
OH	15	1.0000	1.2000	0	1
CH_3CO	19	1.6724	1.4880	1	0

From the values in Table A-4-4 we get: r_1=2.5735, q_1=2.336 and r_2=1.9011, q_2=2.048

Table A-4-5 α_{ij}-τ_{ij} parameters for acetone-methanol

	1	15	19
1	0/1	986.5/0.0366	476.4/0.2023
15	156.4/0.5918	0/1	84.0/0.7545
19	26.76/0.9142	164.50/0.5759	0/1

Table A-4-6 G_{ki}-s_{ki} parameters for acetone-methanol

k	i=1	i=2
1	0.848-2.2080	0.848-1.5582
15	0.000-0.8880	1.200-1.2310
19	1.488-1.6596	0.000-1.0770

$$\ln\gamma_1^{\infty} = 1 - \frac{2.5735}{1.9011} + \ln\frac{2.5735}{1.9011} - 5(2.336)(1 - \frac{\frac{2.5735}{1.9011}}{\frac{2.336}{2.048}} + \ln\frac{\frac{2.5735}{1.9011}}{\frac{2.336}{2.048}})$$

$$+2.336(1 - \ln\frac{2.336}{2.048}) - 0.848\frac{(0.848)(1.0) + (1.488)(0.9142)}{1.5582}$$

$$+0.848\ln\frac{(0.848)(1.0) + (1.488)(0.9142)}{1.5582} - 1.2\frac{(0.848)(0.0366) + (1.488)(0.5759)}{1.231}$$

$$+1.488\ln\frac{(0.848)(0.2023) + (1.0)(1.488)}{1.077} = 1.0309 \qquad \text{(A-4-8)}$$

$$\ln\gamma_2^{\infty} = 1 - \frac{1.9011}{2.5735} + \ln\frac{1.9011}{2.5735} - 5(2.048)(1 - \frac{\frac{1.9011}{2.5735}}{\frac{2.048}{2.336}} + \ln\frac{\frac{1.9011}{2.5735}}{\frac{2.048}{2.336}})$$

$$+2.048(1 - \ln\frac{2.048}{2.336}) - 0.848\frac{(0.848)(1) + (1.2)(0.5918)}{2.208}$$

$$+0.848\ln\frac{(0.848)(1.0) + (1.2)(0.5918)}{2.208} + 1.2\ln\frac{(0.848)(0.0366) + (1.2)(1)}{0.888}$$

$$-1.488\frac{(0.848)(0.2023) + (1.2)(0.7545)}{1.6596} = 0.9502 \qquad \text{(A-4-9)}$$

III. Application to the system (1) Acetone(1 CH_3CO 1 CH_3)-(2) Water(1 H_2O) (25°C).

Table A-4-7 Group parameters for acetone-water

	k	R_k	Q_k	$\nu_k^{(1)}$	$\nu_k^{(2)}$
CH_3	1	0.9011	0.8480	1	0
H_2O	17	0.9200	1.4000	0	1
CH_3CO	19	1.6724	1.4880	1	0

From the values in Table A-4-7 we get: r_1=2.5735, q_1=2.336 and r_2=0.92, q_2=1.40

Table A-4-8 α_{ij}-τ_{ij} parameters for acetone-water

	1	17	19
1	0/1	1318.0/0.012	476.4/0.2023
17	300.0/0.3656	0/1	-195.4/1.9259
19	26.76/0.9142	472.5/0.205	0/1

Table A-4-9 G_{ki}-s_{ki} parameters for acetone-water

k	i=1	i=2
1	0.848-2.2080	0.000-0.5118
17	0.000-0.3152	1.400-1.400
19	1.488-1.6596	0.000-2.6963

$$\ln\gamma_1^{\infty} = 1-\frac{2.5735}{0.92}+\ln\frac{2.5735}{0.92}-5(2.336)\left(1-\frac{\frac{2.5735}{0.92}}{\frac{2.336}{1.40}}+\ln\frac{\frac{2.5735}{0.92}}{\frac{2.336}{1.40}}\right)$$

$$+2.336\left(1-\ln\frac{2.336}{1.40}\right)+0.848\ln\frac{(0.848)(1.0)+(1.488)(0.9142)}{0.5118}$$

$$-1.4\frac{(0.848)(0.012)+(1.488)(0.205)}{1.4}$$

$$+1.488\ln\frac{(0.848)(0.2023)+(1.488)(1.0)}{2.6963} = 2.4399 \qquad \text{(A-4-10)}$$

$$\ln\gamma_2^{\infty} = 1-\frac{0.92}{2.5735}+\ln\frac{0.92}{2.5735}-5(1.4)\left(1-\frac{\frac{0.92}{2.5735}}{\frac{1.4}{2.336}}+\ln\frac{\frac{0.92}{2.5735}}{\frac{1.4}{2.336}}\right)$$

$$+1.4(1-\ln\frac{1.4}{2.336})-0.848\frac{(1.4)(0.3656)}{2.208}+1.4\ln\frac{(1.4)(1.0)}{0.3152}$$

$$-1.488\frac{(1.4)(1.9259)}{1.6596}=1.9962 \qquad \text{(A-4-11)}$$

APPENDIX A-5

Results with the 1FG^E/Huron-Vidal Mixing Rule

Table A-5-1 Area and volume parameters for the excess Gibbs energy model used

Component	r_i	q_i
2-propanol	2.78	2.51
acetone	2.57	2.34
benzene	3.19	2.40
chloroform	2.70	2.34
ethanol	2.11	1.97
methanol	1.43	1.43
water	0.92	7.00

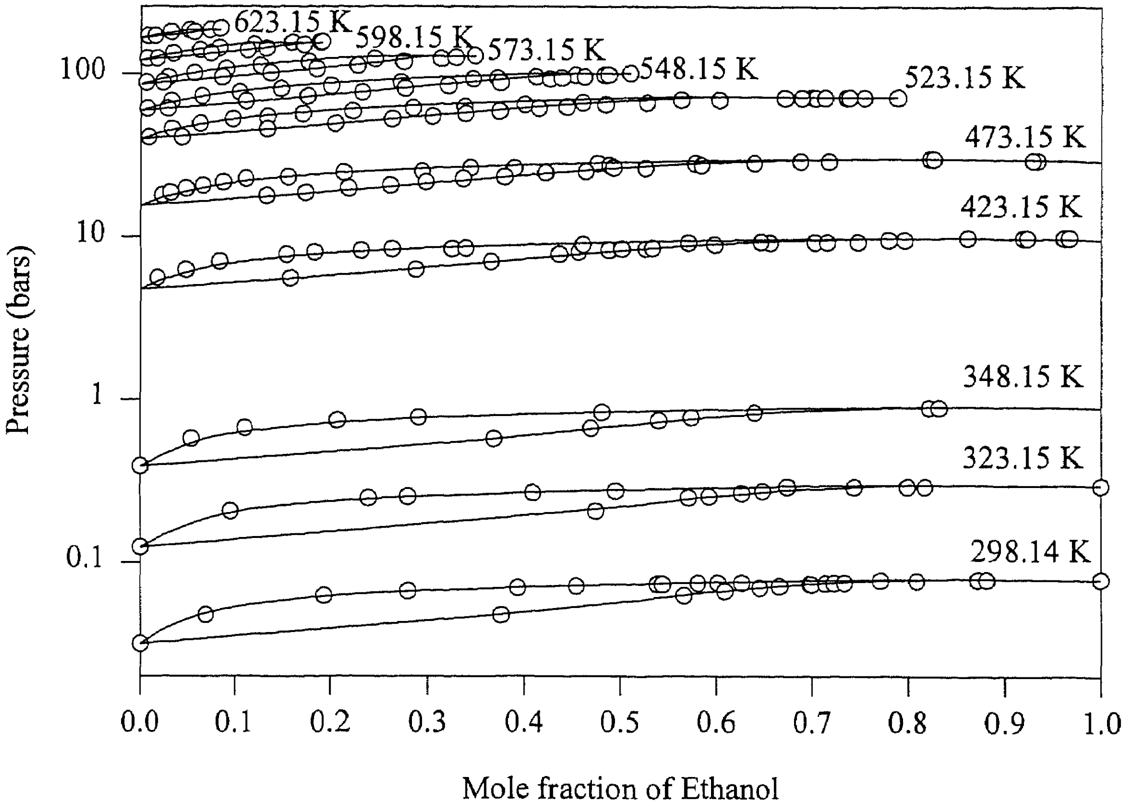

Figure A-5-1 Vapor-liquid equilibria predictions for ethanol-water

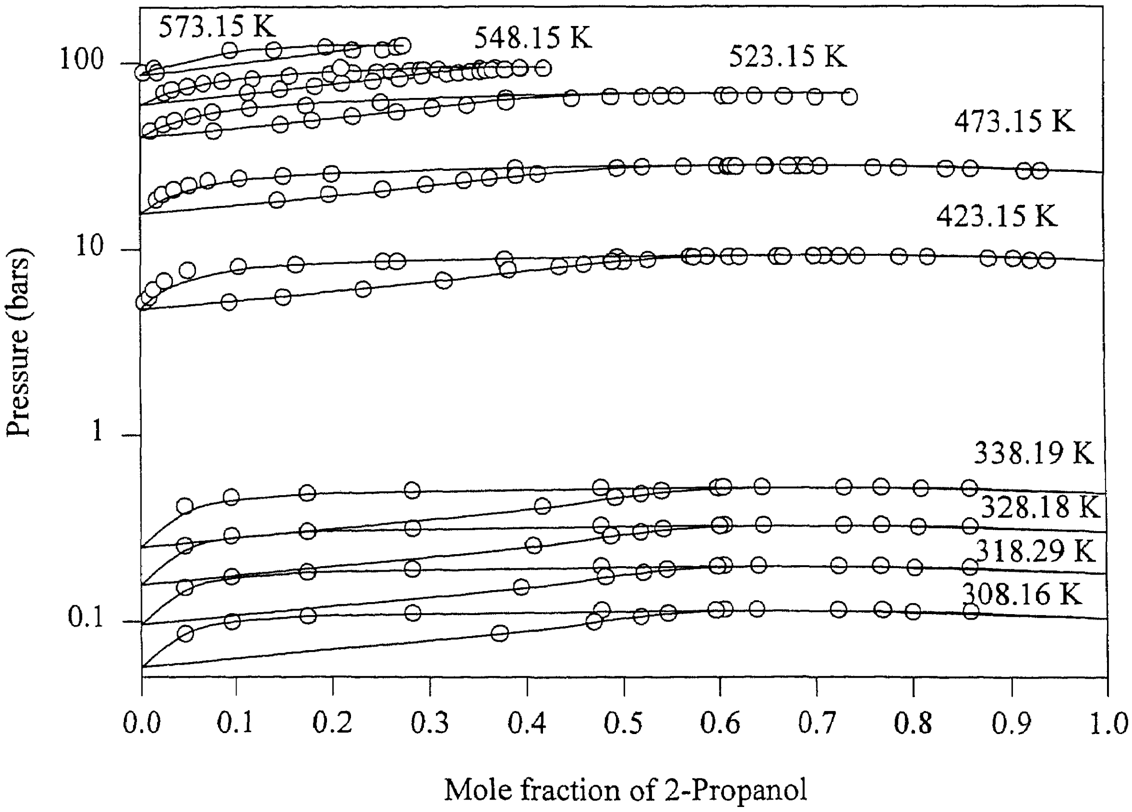

Figure A-5-2 Vapor-liquid equilibria predictions for 2propanol-water

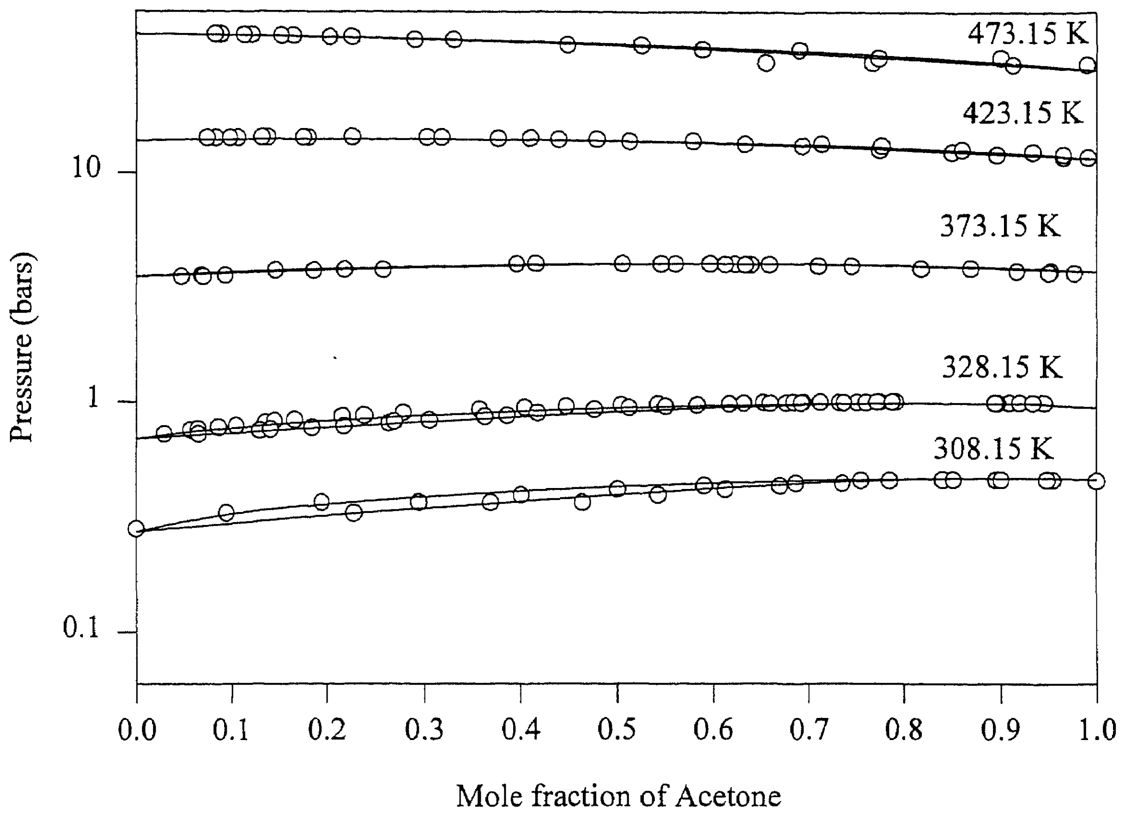

Figure A-5-3 Vapor-liquid equilibria predictions for acetone-methanol

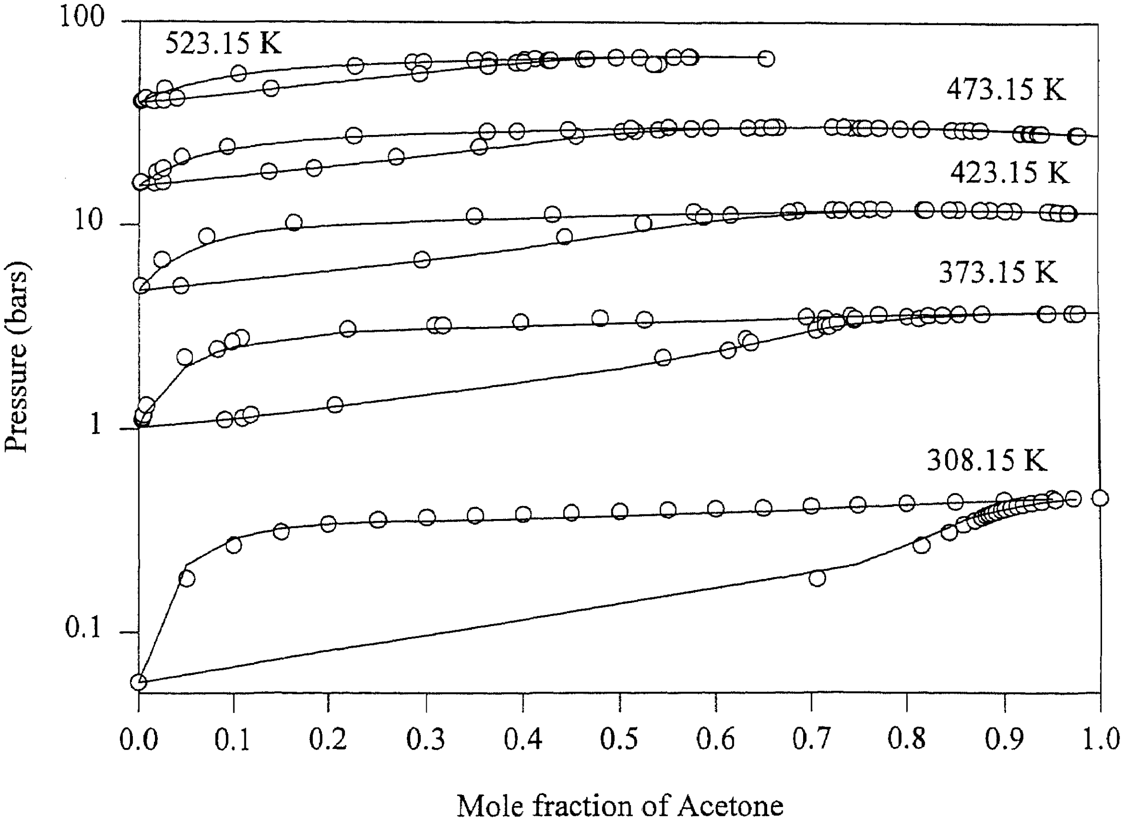

Figure A-5-4 Vapor-liquid equilibria predictions for acetone-water

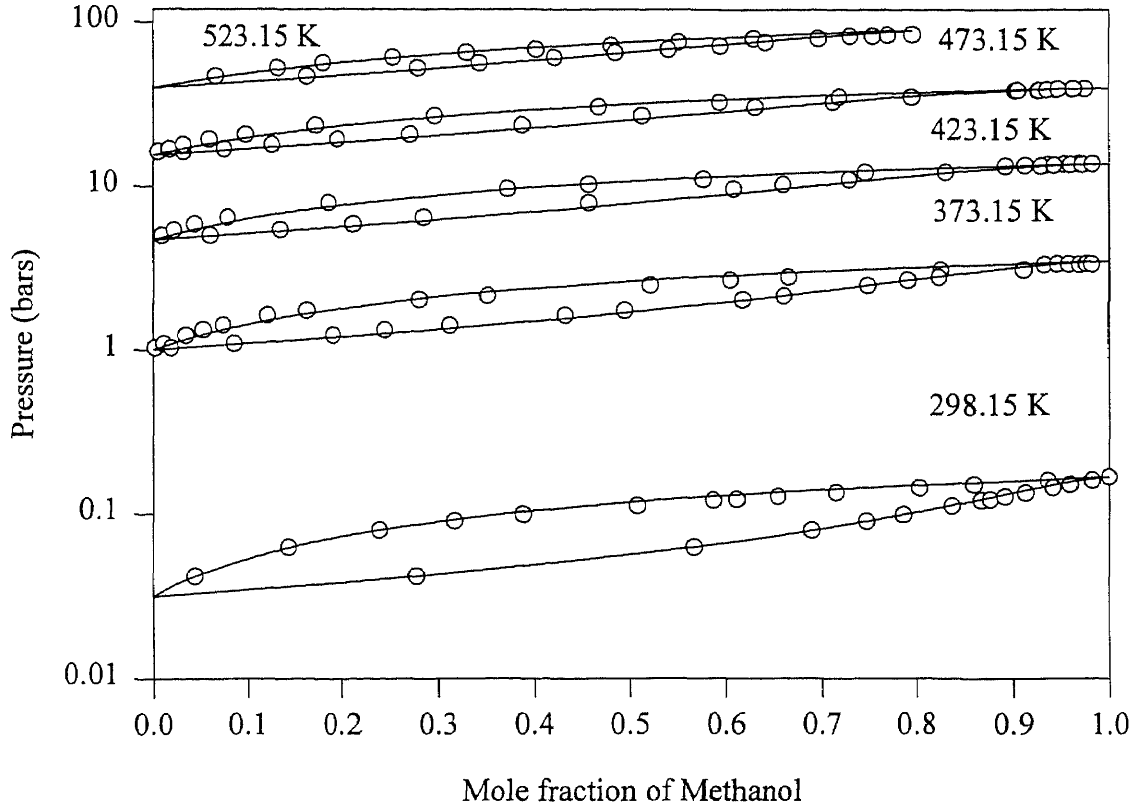

Figure A-5-5 Vapor-liquid equilibria predictions for methanol-water

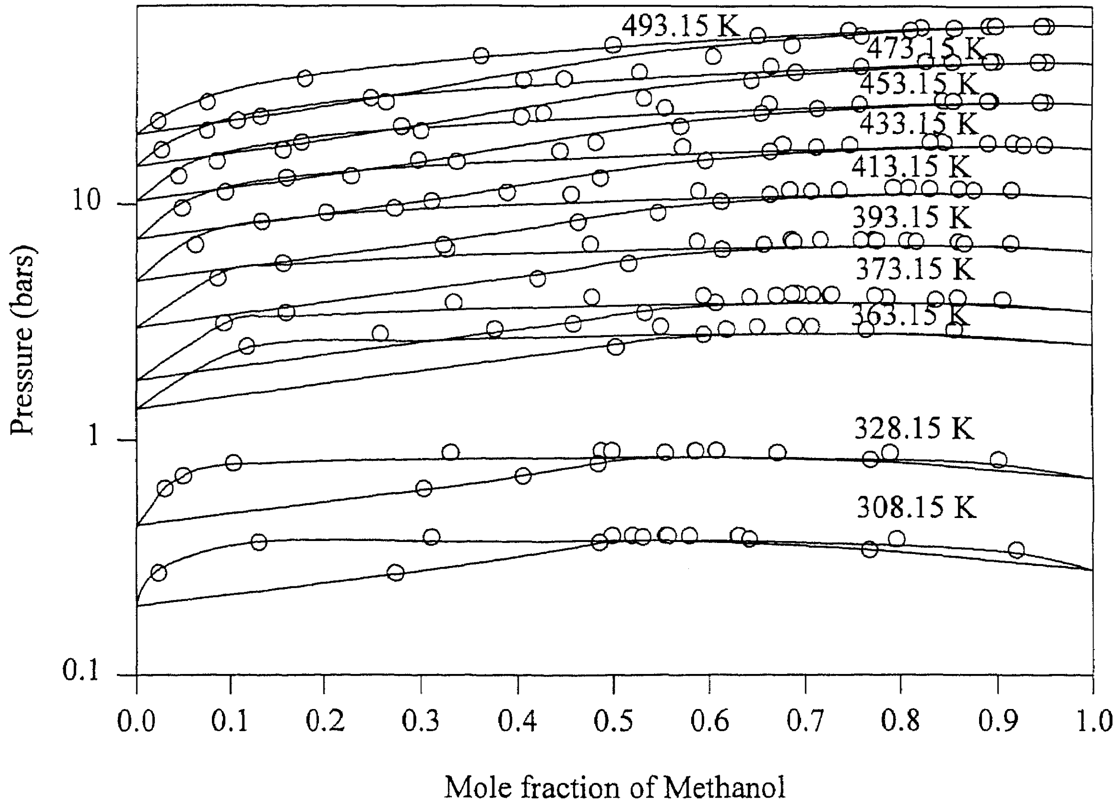

Figure A-5-6 Vapor-liquid equilibria predictions for methanol-benzene

APPENDIX B

Results for the Hydrogen Containing Systems

Table B-1 Pure component area, and volume parameters and acentric factor

	r_i	q_i	ω_i
Hydrogen	0.47	3.00	-0.218
Carbon monoxide	0.77	2.17	0.0483
Methane	1.19	1.28	0.01045
Ethane	1.80	1.70	0.09781
Propane	2.48	2.24	0.15416
n Butane	3.15	2.78	0.20096
Ethylene	1.57	4.88	0.08652
n Hexane	4.50	3.86	0.30075
n Heptane	5.17	4.40	0.35022
n Decane	7.20	6.02	0.49052
n Hexadecane	11.24	9.26	0.74397
Toluene	3.87	2.97	0.26323

Table B-2 Mixture size and energy parameters

	λ_{ij}	q_{ij}
H_2-CH_4	0.72	2.42
H_2-CO	0.88	2.44
H_2-C_7H_8	-0.11	3.25
H_2-C_2H_4	1.49	3.26
H_2-C_2H_6	3.14	1.61
H_2-C_3H_8	1.58	2.22
H_2-n C_4H_{10}	-0.49	3.48
H_2-n C_6H_{14}	-0.64	3.74
H_2-n C_7H_{16}	-0.83	3.85
H_2-n $C_{10}H_{22}$	-1.84	4.44
H_2-n $C_{16}H_{34}$	-3.07	5.34
CH_4-C_2H_6	0.27	2.08
CH_4-CO	0.51	1.52
CH_4-C_2H_4	0.40	2.75
CH_4-C_3H_8	1.33	1.38
C_2H_4-C_2H_6	0.02	3.33

Table B-3 AAD(%) in pessure and vapor phase composition for binaries

System(1-2)	T (K)	No	AADP	AADY$_1$	AADY$_2$
H_2-C_3H_8	173.15	7	12.2402	0.0308	23.9493
	198.15	4	3.5177	0.1122	24.1063
	223.15	7	1.5143	0.5087	28.5803
	248.15	5	4.5356	1.3805	25.1038
	273.15	7	5.2581	0.4717	4.5472
	298.15	5	5.5165	0.7938	4.8321
	323.15	6	5.7631	4.2489	10.1816
	Total	41	5.6585	1.0705	17.2373
H_2-nC_4H_{10}	327.65	13	1.4462	1.8971	19.9470
	344.25	12	1.9555	2.2702	15.2387
	360.95	11	2.3954	2.7938	11.6473
	377.55	12	1.7187	2.9451	7.2073
	394.25	12	1.9332	2.6831	3.0641
	Total	60	1.8740	2.5029	11.5592
H_2-nC_7H_{16}	424.15	10	9.4096	0.7065	13.5664
	471.65	11	6.3426	3.8491	16.6975
	498.85	10	8.6312	2.9043	9.0610
	Total	32	8.0101	2.4906	13.6701
H_2-nC_7H_{16}	424.15	10	7.7818	0.7097	12.475
	471.65	11	3.4007	2.0302	14.0525
	498.85	10	2.3667	6.4999	10.9524
	Total	32	4.4804	3.0425	12.5436

Table B-3 (continued)

System(1-2)	T (K)	No	AADP	AADY$_1$	AADY$_2$
H_2-nC_6H_{14}	277.59	16	4.1042	0.1674	12.000
	310.93	16	4.0047	0.3967	10.0193
	344.26	16	4.2471	0.7556	17.0416
	377.59	16	3.6919	1.3268	18.922
	410.93	16	3.6728	2.1845	18.8734
	444.26	15	5.8891	2.9843	17.2567
	Total	94	4.2338	1.2643	16.4904
H_2-n$C_{10}H_{22}$	462.45	7	2.4456	0.571	26.8659
	503.35	7	5.1985	0.7719	17.9985
	542.95	7	5.4316	2.1685	18.4863
	583.45	5	2.3905	4.0146	16.9829
	Total	26	3.9801	1.7174	20.3219
H_2-n$C_{16}H_{34}$	461.65	7	14.1379	0.0125	8.5000
	506.25	7	10.5914	0.1346	8.4440
	622.85	7	17.5534	0.8300	6.3947
	664.05	7	13.9978	1.5267	5.2100
	Total	28	14.0701	0.6260	7.1372
H_2-n$C_{16}H_{34}$	461.65	7	1.4945	0.0249	13.5476
	506.25	7	5.4675	0.0300	2.134
	622.85	7	1.044	0.5893	6.1854
	664.05	7	4.3663	2.6309	10.9675
	Total	28	3.0931	0.8188	8.2086

Table B-3 (continued)

System(1-2)	T (K)	No	AADP	AADY$_1$	AADY$_2$
H_2-C_6H_7	461.85	7	2.2516	0.386	3.03
	502.15	7	1.3159	1.4661	4.4556
	542.15	6	1.0550	3.5003	4.3096
	Total	20	1.5651	1.6983	3.9128

Table B-4 AAD(%) in pressure and vapor phase composition for H_2-CH_4-C_2H_6

System (1-2-3)	T ^oK-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
H_2-CH_4	103.15	5	5.3049	0.3709	9.7909	
	123.15	6	3.7880	1.9921	8.0145	
	143.05	6	5.1711	3.7082	8.5693	
	173.05	9	0.8609	4.2136	2.7851	
	Total	26	3.3856	2.8454	6.6740	
H_2-C_2H_6	148.15	4	6.4465	0.4622	49.9508	
	173.15	4	4.8232	0.3221	12.2980	
	198.15	4	4.5426	0.5746	7.3572	
	223.15	4	5.4486	1.4693	6.7295	
	Total	16	5.3152	0.7070	19.0838	
CH_4-C_2H_6	130.37	6	2.5840	0.0146	7.5497	
	144.26	9	3.4093	0.0306	4.8515	
	158.15	12	3.7447	0.3344	8.8930	
	172.04	11	2.4442	0.5007	7.4013	
	186.09	13	2.1988	0.8902	7.6710	
	188.04	8	0.5767	0.1079	8.6273	
	189.65	14	2.4060	1.2688	6.3423	

Table B-4 (continued)

System (1-2-3)	T ^{o}K-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
	190.87	15	2.3421	1.1320	5.7915	
	192.37	11	2.8395	1.6981	4.2827	
	193.93	7	1.1508	0.0605	2.5349	
	195.43	9	0.9686	0.2574	7.5886	
	199.93	14	2.7401	2.0367	4.6955	
	Total	129	2.3571	0.8433	6.3040	
H_2-CH_4-C_2H_6	144.26-34.47	3	8.2356	1.9799	5.6685	25.8873
	144.26-68.95	6	2.5537	0.7450	4.7570	16.4854
	199.82-34.47	4	1.2871	8.9544	4.1673	2.6360
	199.82-68.95	2	4.4749	0.9648	1.5020	3.3192
	Total	15	3.6085	3.2104	4.3480	12.6623

Table B-5 AAD(%) in prssure and vapor phase composition for H_2-CO-CH_4

System (1-2-3)	T ^{o}K-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
H_2-CO	83.30	11	5.3793	2.5676	16.7567	
	100.00	7	3.3563	3.6549	11.0139	
	Total	18	4.6653	2.9514	14.7298	
CH_4-CO	91.60	5	7.5614	9.9751	21.2047	
	97.7	4	2.3576	11.1361	15.7917	
	105.2	5	3.4918	5.2096	9.8178	
	114.5	5	2.6077	7.0295	8.2156	
	123.9	3	1.2701	11.3694	5.3506	
	Total	22	3.7066	8.6238	12.5186	

Table B-5 (continued)

System (1-2-3)	T °K-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
H_2-CO-CH_4	120-50	12	3.197	5.0123	5.0695	11.6197
	140-28.9	11	4.7798	3.4273	1.8306	1.1484
	140-50	14	3.2975	6.0191	2.1813	5.5526
	163.17-27.58	6	2.8787	16.3178	3.2732	1.6103
	163.17-41.37	8	2.4632	5.3317	1.7879	0.9681
	163.17-55.16	11	2.0995	3.2808	1.6204	1.3893
	163.17-68.95	9	2.1444	6.3347	1.6257	3.0363
	163.17-103.42	5	1.0488	3.8466	1.1139	4.4733
	173.25-41.37	6	1.923	10.0048	2.3325	0.9994
	173.25-55.16	4	4.5271	8.9111	5.3828	1.6662
	173.25-68.95	6	2.7039	8.5035	4.4647	2.9361
	173.25-103.42	3	1.1169	8.6141	2.0034	3.7715
	Total	95	2.852	6.2908	2.6498	3.6400

Table B-6 AAD(%) in pressure and vapor phase composition for H_2-C_2H_6-C_2H_4

System (1-2-3)	T °K-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
H_2-C_2H_4	158.15	6	5.1351	0.8787	30.2828	
	172.05	6	4.9025	1.3868	35.5425	
	199.85	6	3.8628	2.2096	18.8391	
	227.55	6	1.5307	5.3955	20.6347	
	241.45	5	1.5419	4.6080	6.6270	
	255.35	5	2.7342	7.3636	3.8645	
	Total	34	3.3520	3.5024	20.3015	

Table B-6 (continued)

System (1-2-3)	T °K-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
C_2H_6-C_2H_4	199.82	11	0.7026	2.0918	0.4497	
	233.15	11	3.4695	3.3114	0.8997	
	255.37	11	3.9242	4.0356	0.1880	
	263.15	10	3.8194	4.6144	3.0774	
	Total	43	2.9594	3.4851	1.1044	
H_2-C_2H_6-C_2H_4	148.15-20.26	6	6.6137	0.9699	57.8705	37.6577
	148.15-40.52	6	4.1634	0.4889	53.1920	28.0046
	148.15-60.78	4	13.4547	0.2321	43.500	12.7455
	148.15-81.04	4	10.1197	0.1149	32.9665	7.5546
	173.15-20.26	5	6.3247	0.4152	4.9550	7.2640
	173.15-40.52	5	9.1324	0.3817	4.3026	12.2614
	173.15-60.78	5	4.1696	0.2081	4.3272	9.5069
	173.15-81.04	5	2.2950	0.2966	2.4903	15.1652
	198.15-20.26	6	2.3656	1.2102	5.6291	4.6835
	198.15-40.52	6	2.4874	0.4335	2.6024	4.7759
	198.15-60.78	6	3.2661	0.3570	5.1985	8.7488
	198.15-81.04	6	3.8445	0.4197	5.8892	12.3868
	223.15-20.26	4	1.5644	4.7717	5.6593	4.1125
	223.15-40.52	4	2.3323	2.6045	7.5667	5.6631
	223.15-60.78	4	2.3976	2.0324	8.7624	4.3917
	223.15-81.04	4	2.4620	1.2001	10.0452	5.4629
	Total	80	4.6922	0.9201	16.2083	11.9781

Table B-7 AAD(%) in pressure and vapor phase composition for H_2-CH_4-C_2H_4

System (1-2-3)	T °K-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
CH_4-C_2H_4	148.09	22	1.8478	0.2574	6.2912	
	150.00	11	1.6450	0.4748	10.1949	
	159.21	16	0.9363	0.2948	4.8436	
	160.0	11	1.3637	0.5209	7.0171	
	168.65	41	1.1844	0.4580	6.5442	
	170.0	13	0.6760	0.4040	6.1752	
	180.0	11	0.7785	0.6015	3.0129	
	190.0	11	1.1278	0.4793	3.7031	
	198.15	4	4.1534	3.4593	9.4177	
	248.37	4	1.45342	4.2719	2.8372	
	Total	144	1.3171	0.6175	6.0908	
H_2-CH_4-C_2H_4	123.15-20.26	5	6.6959	3.4490	27.1306	33.7987
	123.15-40.52	4	7.7380	1.1625	16.6081	36.6801
	123.15-60.78	4	12.2096	0.6163	10.7570	28.8641
	123.15-81.04	4	4.2443	0.3098	6.9377	6.9855
	148.15-20.26	6	8.9386	16.8494	21.7707	29.3357
	148.15-40.52	6	4.4148	5.8364	18.7649	33.9130
	148.15-60.78	6	4.5792	2.8264	14.1391	18.1265
	148.15-81.04	5	1.5807	1.5224	11.5913	7.1645
	173.15-20.26	5	5.3240	19.5493	10.2000	15.6324
	173.15-40.52	4	4.1600	7.2166	6.9940	7.8835
	173.15-60.78	5	3.8022	2.4882	5.9198	6.5639
	173.15-81.04	5	5.0658	1.2944	3.9595	4.3085
	198.15-20.26	5	2.4757	6.6285	3.4751	4.3999

Table B-7 (continued)

System (1-2-3)	T °K-P(bars)	No	AADP	AADY$_1$	AADY$_2$	AADY$_3$
	198.15-40.52	6	2.4324	2.6941	4.5907	1.3748
	198.15-60.78	5	1.5663	1.3159	2.1120	3.8759
	98.15-81.04	4	0.8745	2.0202	1.6631	4.8080
	223.15-20.26	3	0.6862	4.3941	2.1444	2.7832
	223.15-40.52	4	2.2704	6.1367	0.3808	6.1827
	248.15-30.39	4	1.0873	20.027	5.3768	3.1711
	248.15-40.52	3	0.7966	12.0967	0.7082	2.7170
	Total	93	4.1885	5.9130	9.4727	13.6561

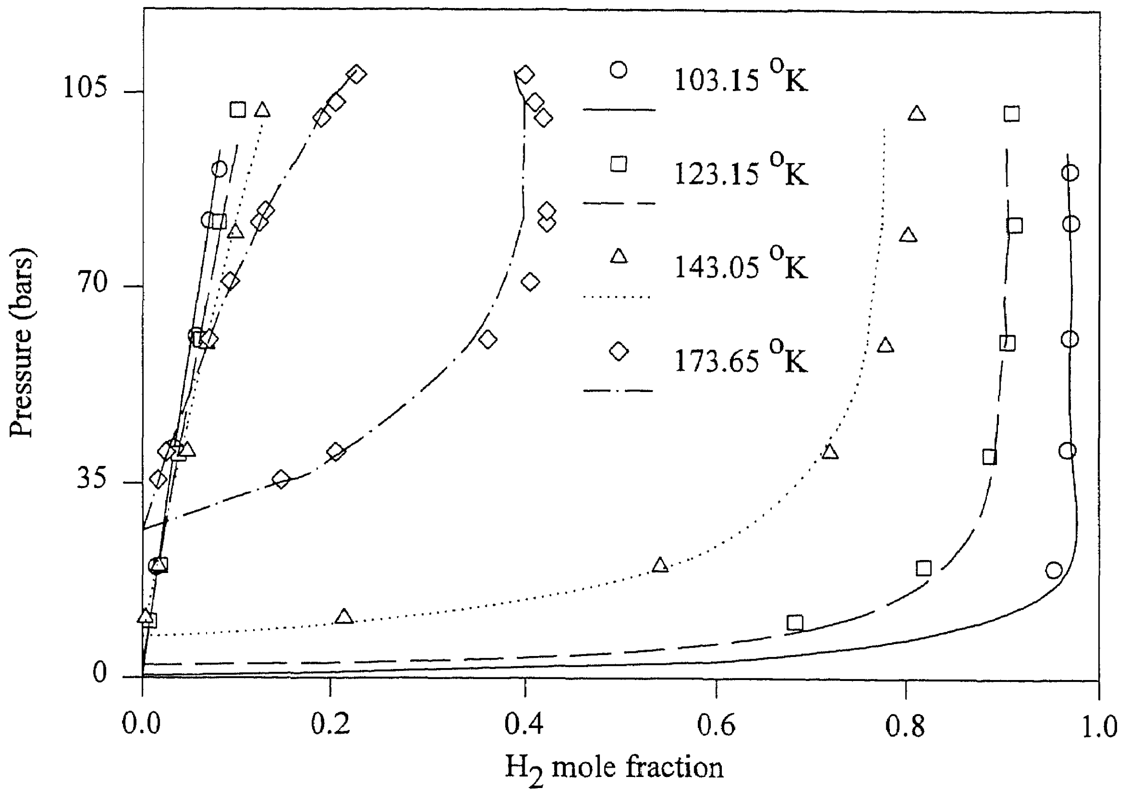

Figure B-1. Vapor-liquid equilibria for the system hydrogen-methane

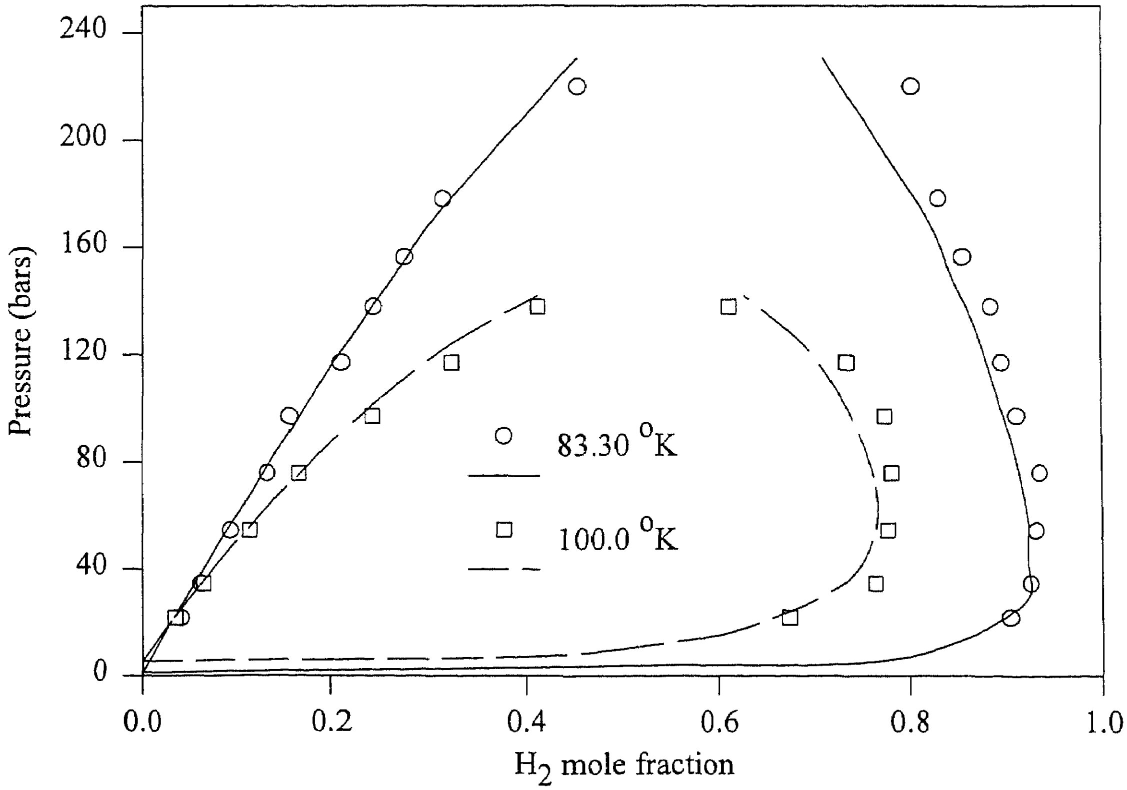

Figure B-2. Vapor-liquid equilibria for the system hydrogen-carbon monoxide

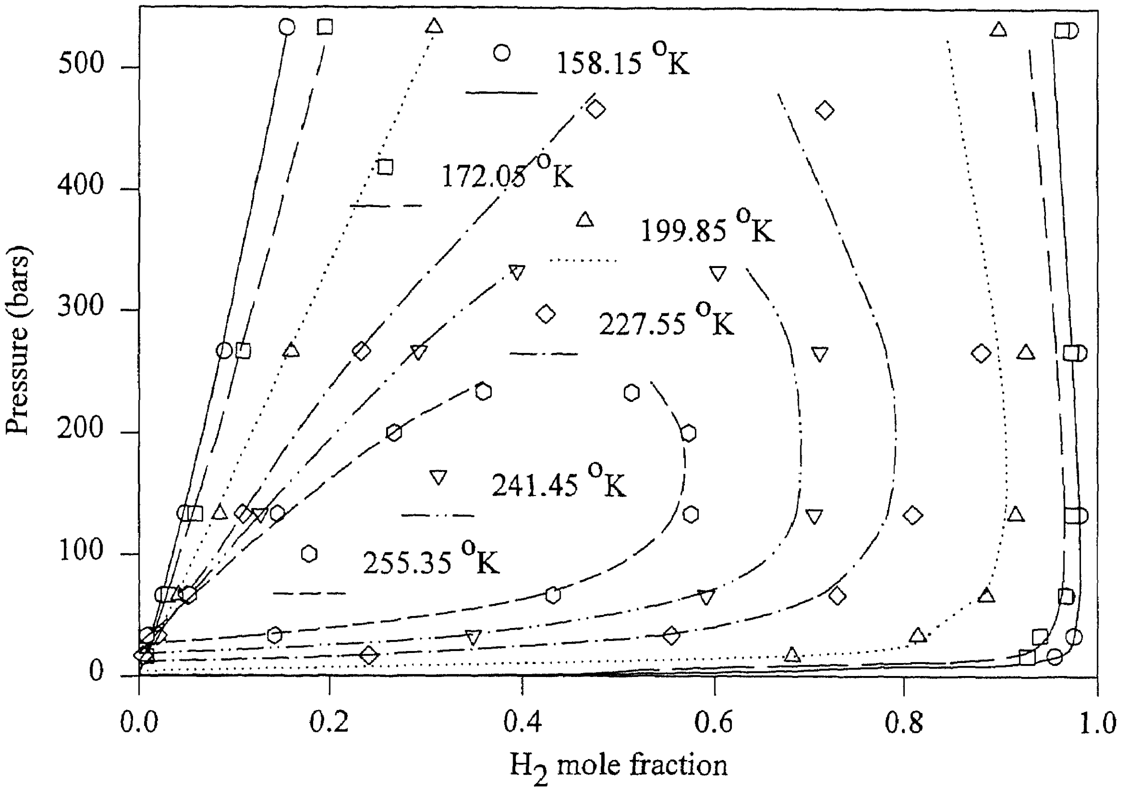

Figure B-3. Vapor-liquid equilibria for the system hydrogen-ethylene

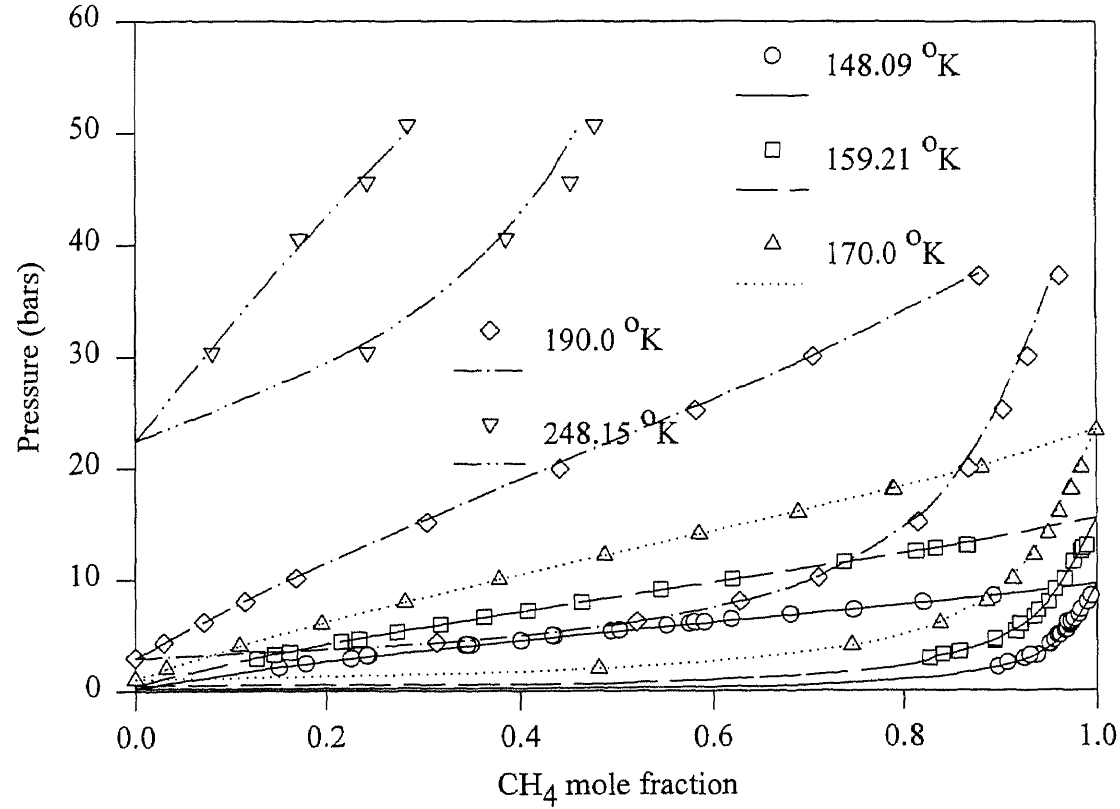

Figure B-4. Vapor-liquid equilibria for the system methane-ethylene

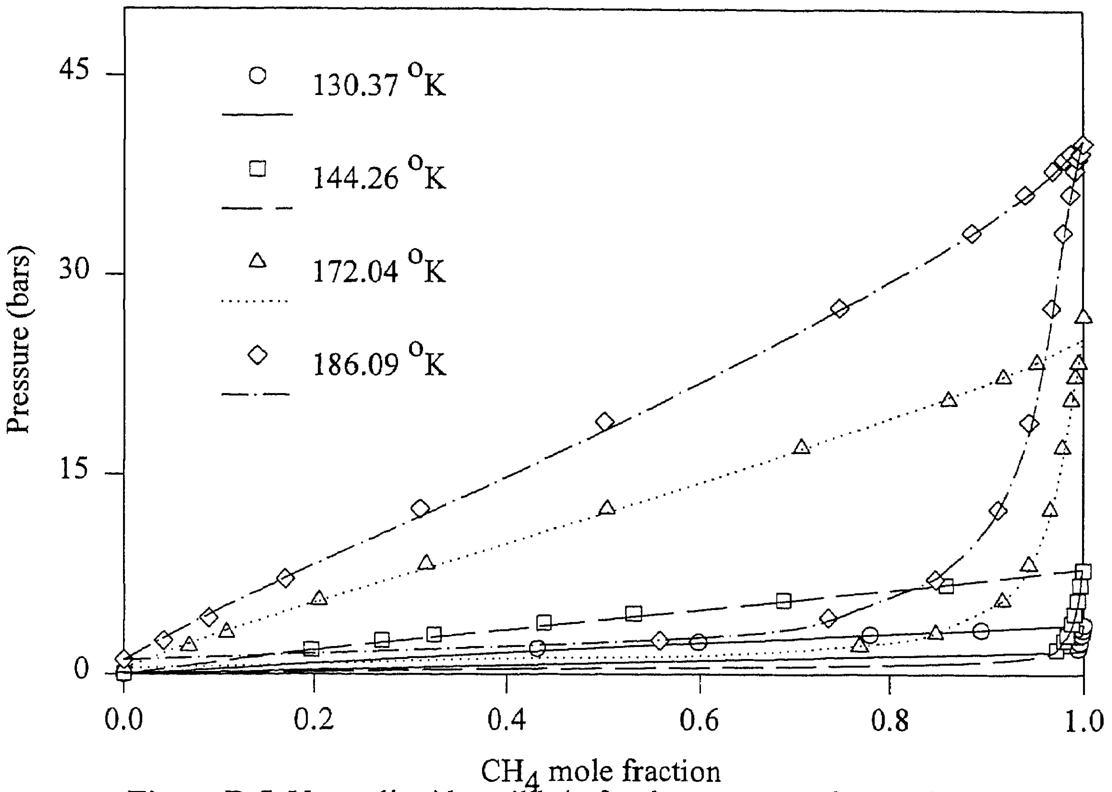

Figure B-5. Vapor-liquid equilibria for the system methane-ethane

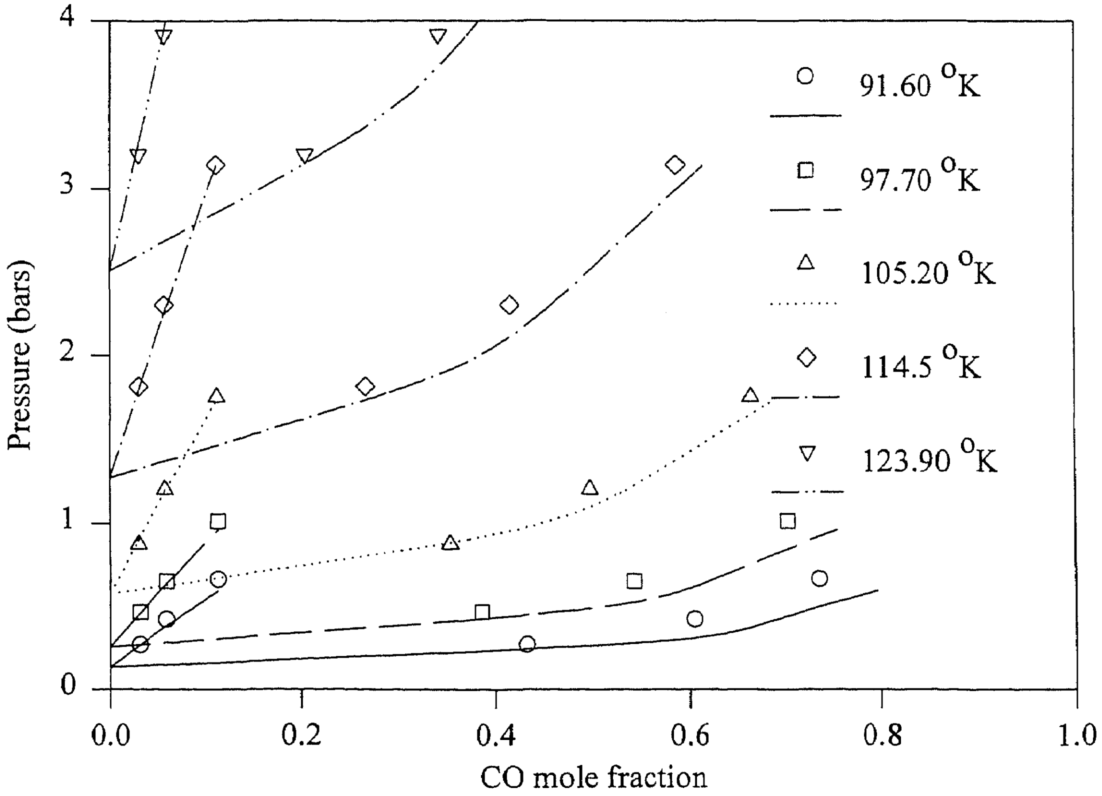

Figure B-6. Vapor-liquid equilibria for the system carbon monoxide-methane

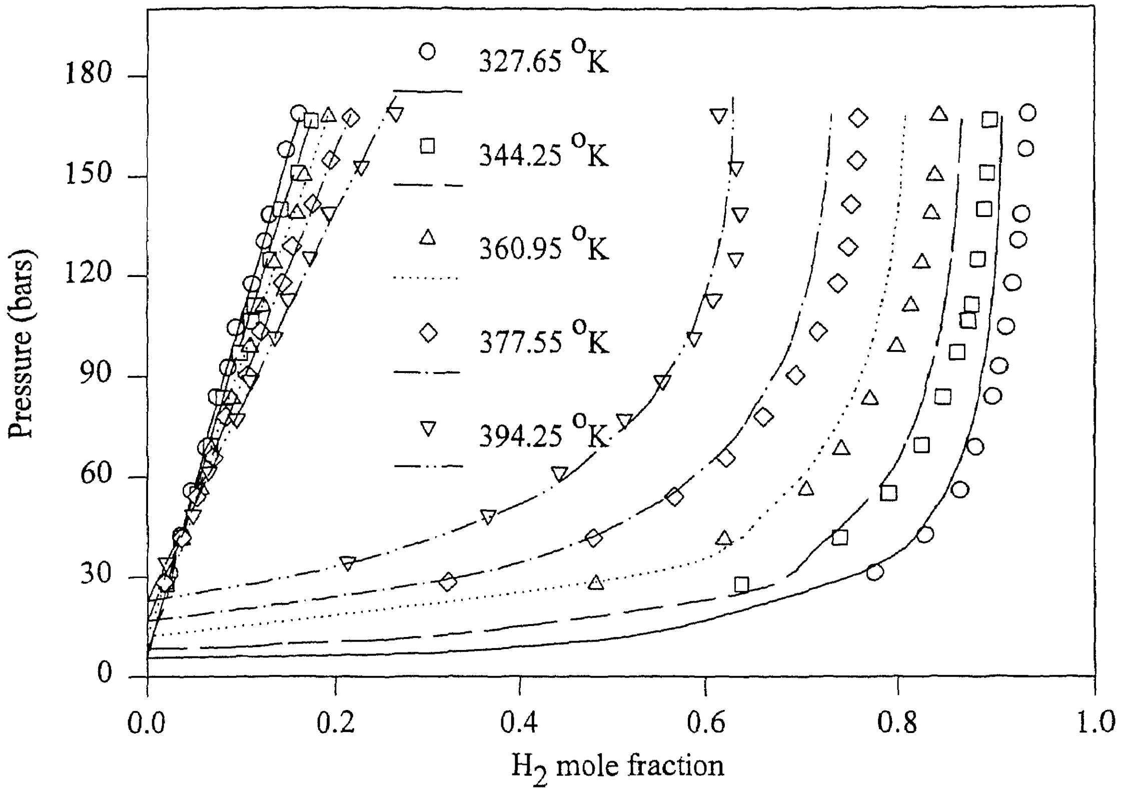

Figure B-7. Vapor-liquid equilibria for the system hydrogen-n-butane

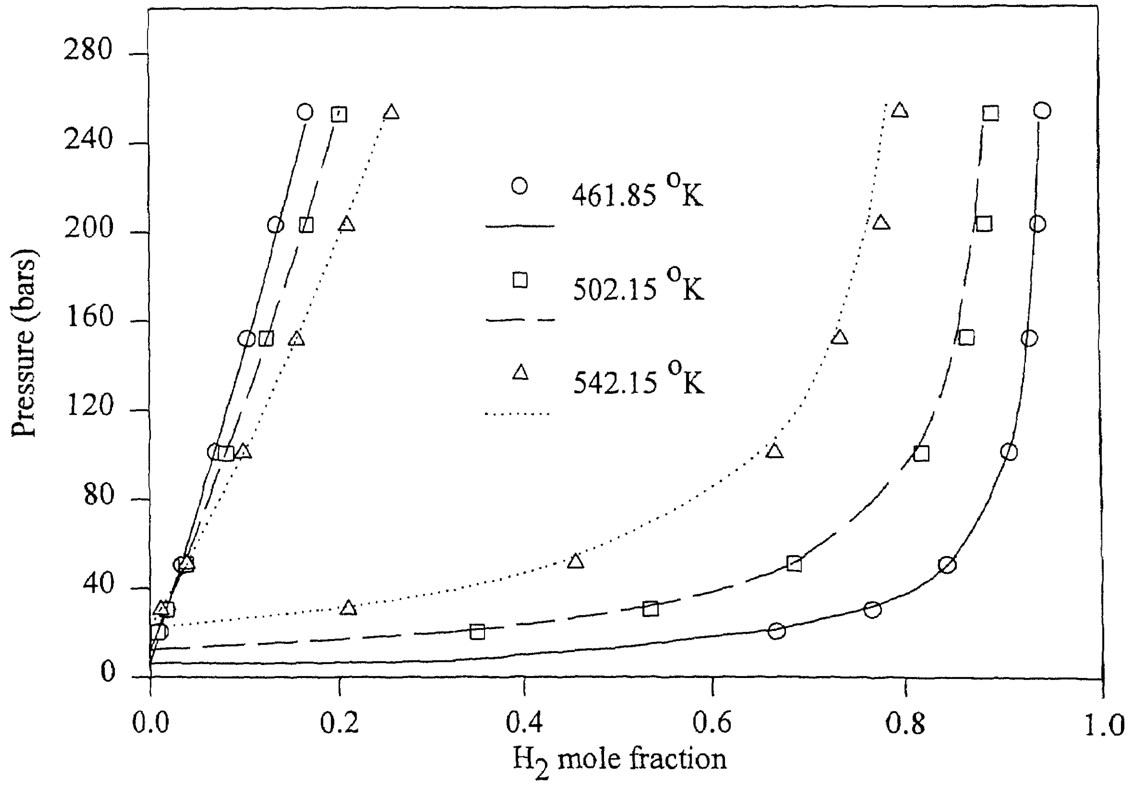

Figure B-8. Vapor-liquid equilibria for the system hydrogen-toluene

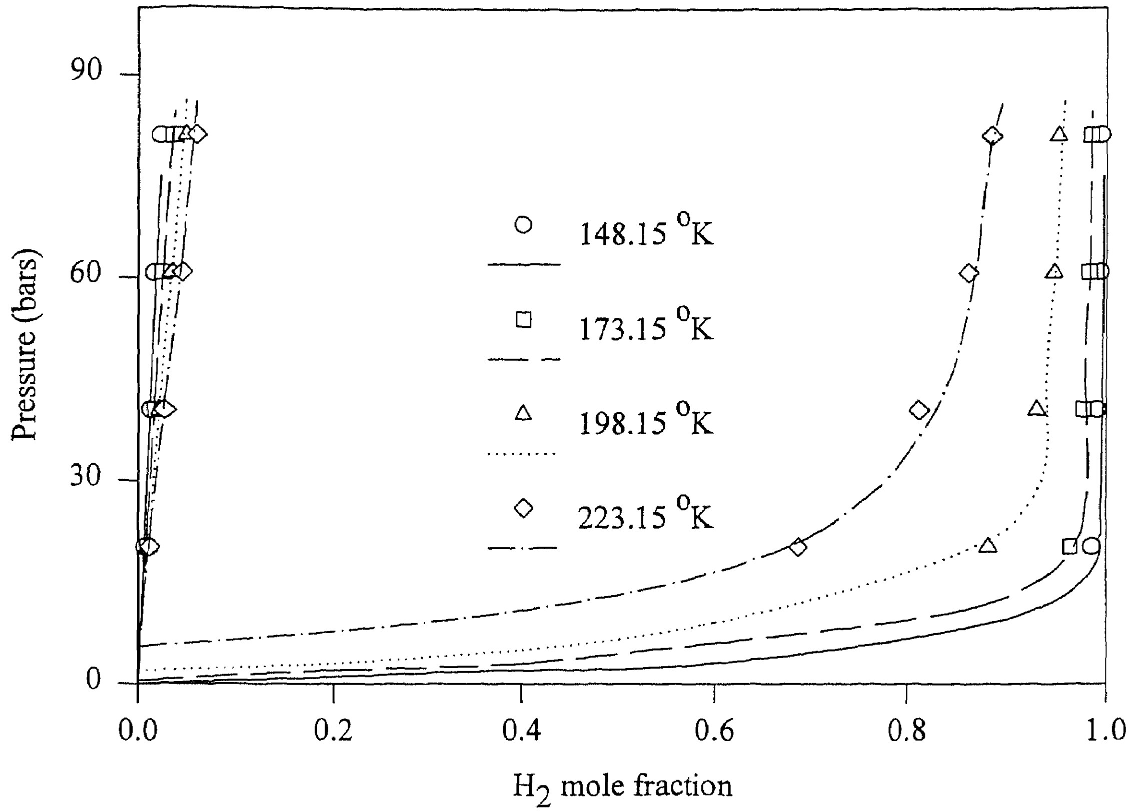

Figure B-9. Vapor-liquid equilibria for the system hydrogen-ethane

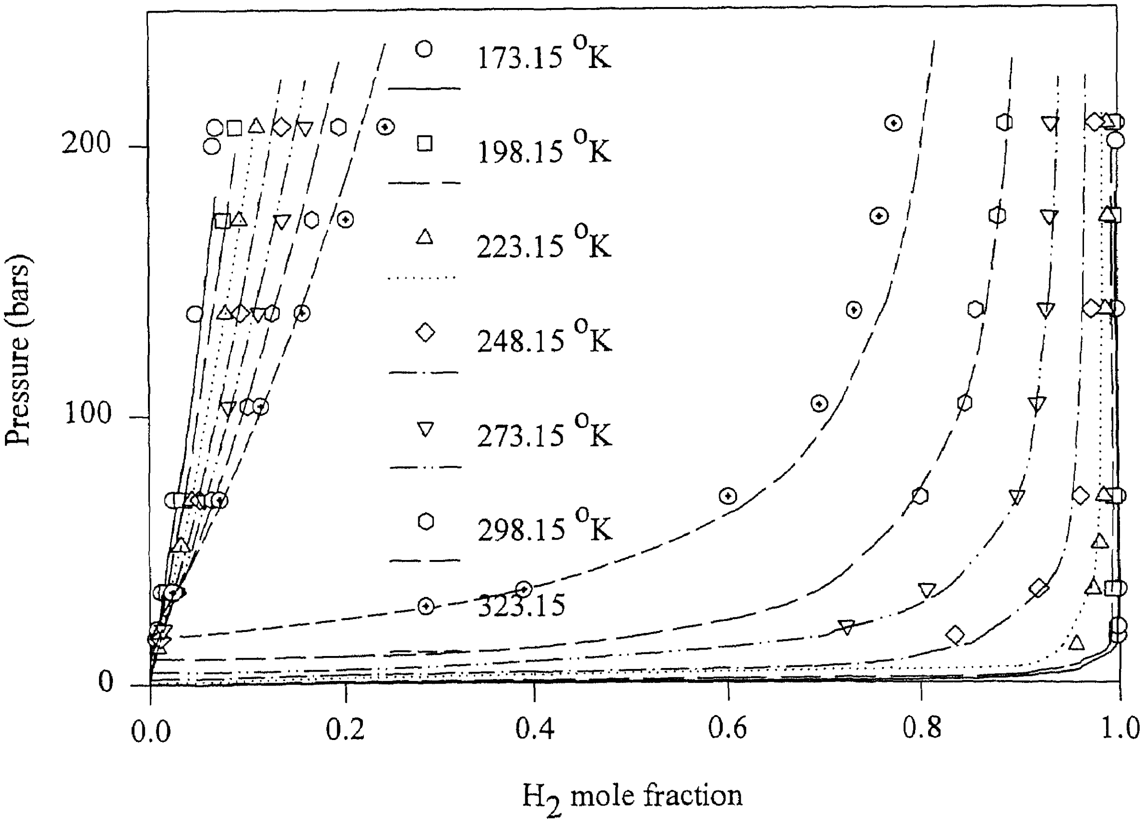

Figure B-10. Vapor-liquid equilibria for the system hydrogen-propane

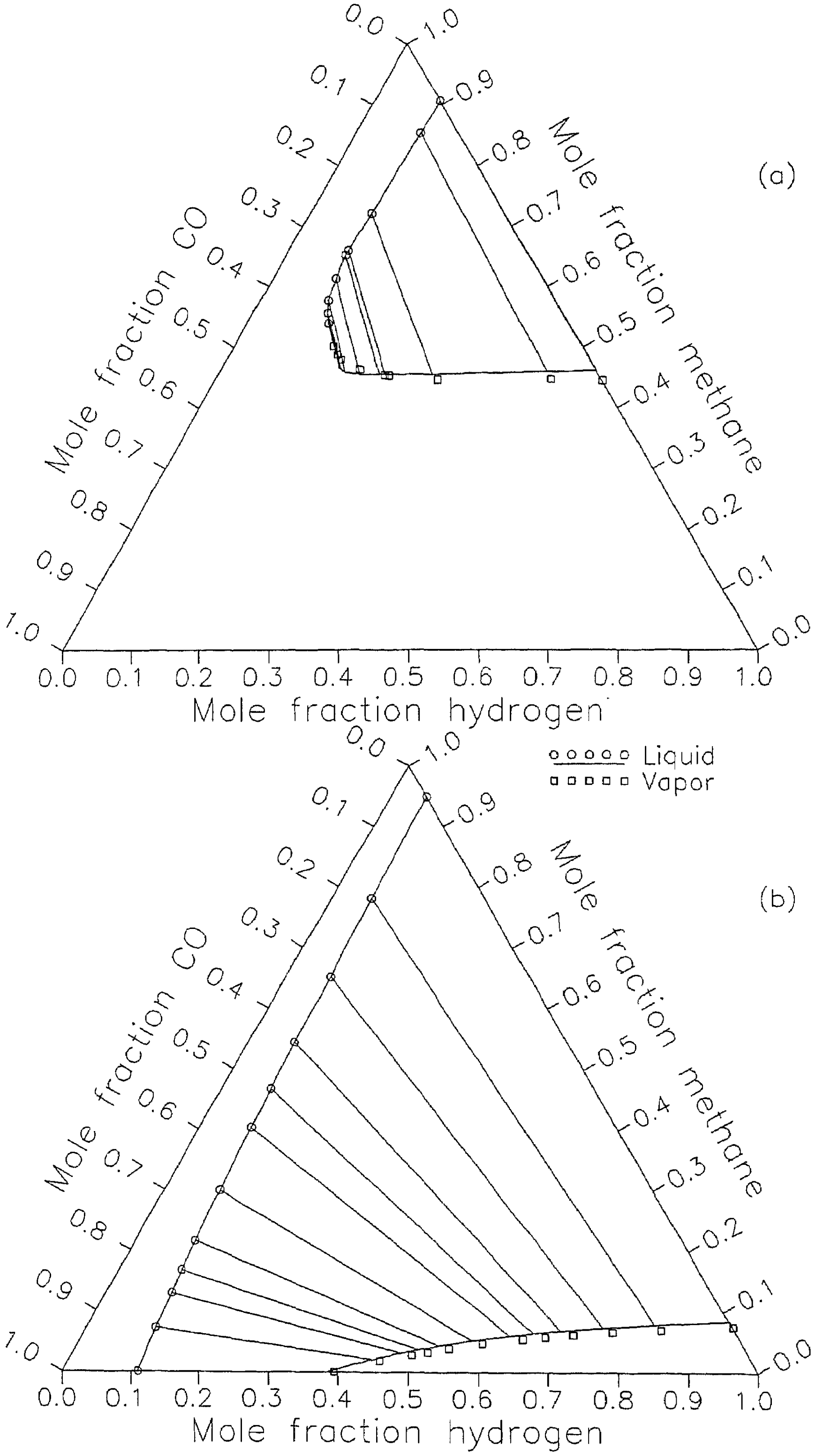

Figure B-11 Vapor-liquid equilibria for the ternary system hydrogen-carbon monoxide-methane at (a) 68.45 bars, 163.17 K, and (b) 50 bars, 120 K.

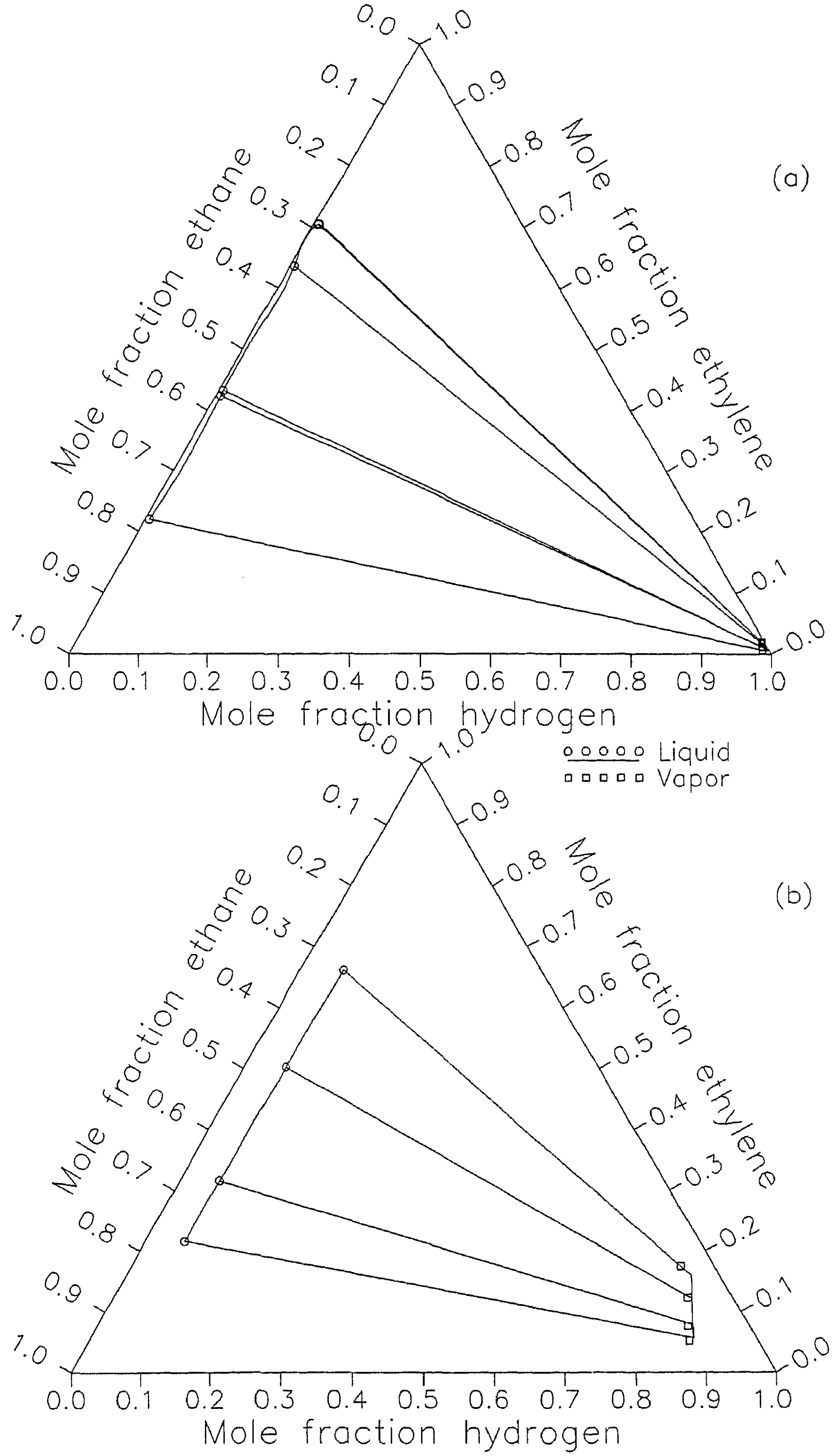

Figure B-12 Vapor-liquid equilibria for the ternary system hydrogen-ethylene-ethane at (a) 20.26 bars, 148.15 K, and (b) 81.04 bars, 223.15 K.

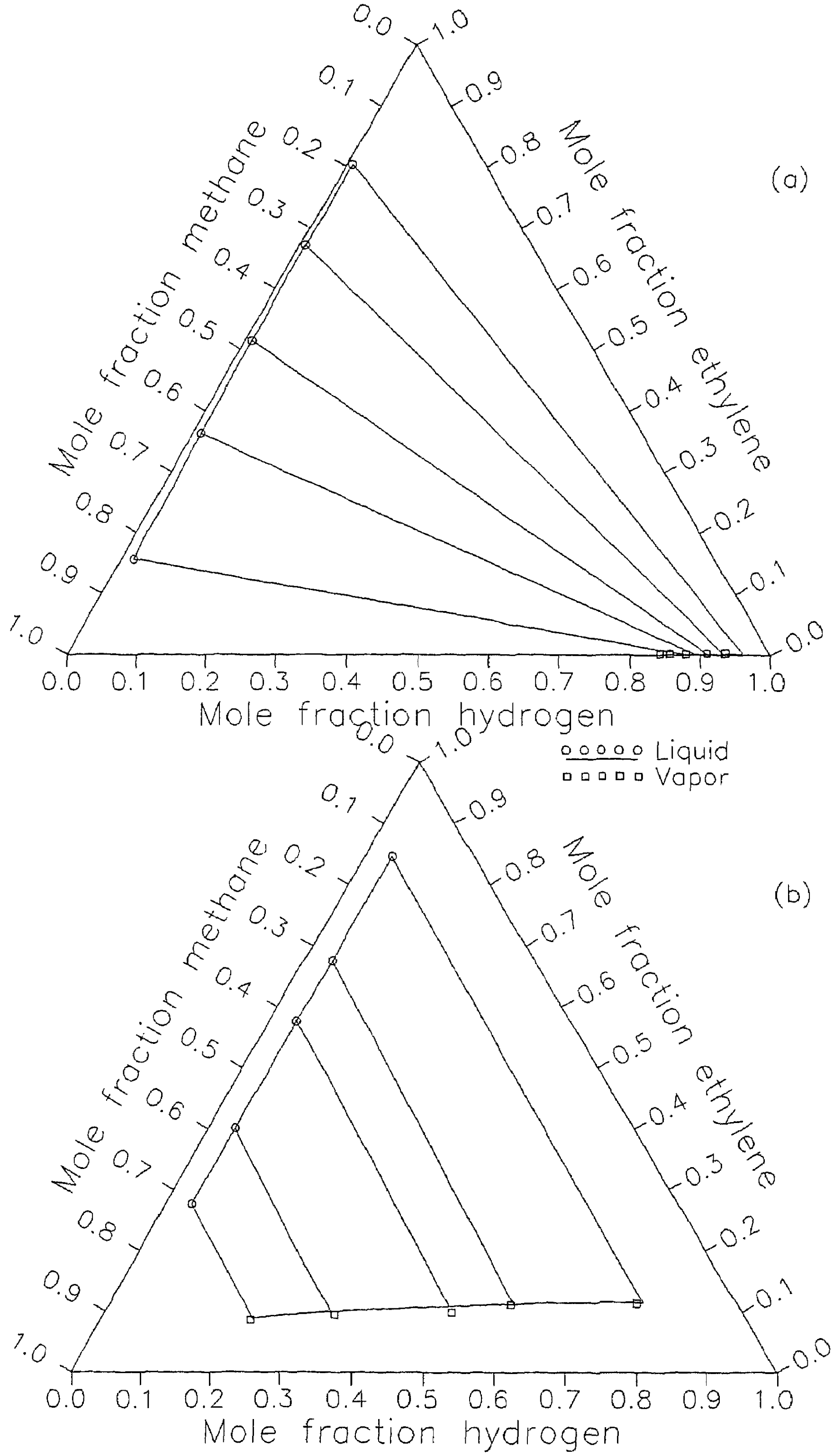

Figure B-13 Vapor-liquid equilibria for the ternary system hydrogen-ethylene-methane at (a) 20.26 bars, 123.15 K, and (b) 60.78 bars, 198.15 K.

APPENDIX C

Results for Refrigerant Systems

Table C-1 Pure component parameters

Component	Tc (K)	Pc (bars)	ω	κ_1	κ_2	κ_3	r	q
R11	471.20	44.09	0.18749	0.03708			2.89	2.60
R113	487.50	34.11	0.2515	0.05596			3.87	3.48
R123	456.86	36.65	0.2816	-0.11494	0.0912661	-1.236489	3.47	3.06
R13	301.90	38.77	0.1743	-0.07588	-1.775022	0.3753762	2.20	2.10
R134a	374.26	40.68	0.3261	-0.01030	0.179469	-0.7222333	2.48	2.38
R14	227.50	37.42	0.1798	0.02136			1.78	1.82
R152a	386.66	44.95	0.2680	0.08453	1.4804546	0.2994262	2.14	2.08
R22	369.30	49.83	0.2191	-0.07449	-1.24218	0.1812597	2.03	1.87
R23	299.06	48.41	0.2640	-0.15131	-1.843714	0.2110679	1.63	1.61
Propane	370.02	42.61	0.1514	-0.0653	-0.9023922	0.1365813	2.48	2.24
Propylene	364.85	46.05	0.1480	-0.0036	-0.0226415	-0.1959669	2.25	2.02
nButane	425.16	37.97	0.2010	0.03443	0.6767	0.461	3.15	2.78
CO_2	304.21	73.82	0.2250	0.04285			1.30	1.12

Table C-2 AAD(%) in pressure and vapor phase composition of component (1) for the 3PM model

System (1-2)	Fitting temperature (K)	Parameters α/λ/k	Δp-Δy_1
R134a-Propane	Overall	1.755/4.520/0.217	1.660-2.353
	255	0.446/3.369/0.378	0.236-2.916
	275	0.776/3.409/0.339	0.099-1.562
	298	1.497/3.912/0.254	0.394-0.994
Propylene-R134a	Overall	1.450/2.788/0.169	0.377-0.977
	251	1.389/2.295/0.240	0.129-1.556
	275	1.538/2.507/0.202	0.115-0.618
	298	1.356/2.204/0.224	0.117-0.330
R23-R13	Overall	0.383/3.642/0.068	0.927-1.817
	273	0.246/2.611/0.143	0.100-1.326
	255	0.280/2.722/0.148	0.071-0.996
	225	0.155/2.582/0.180	0.097-0.448
	199	0.258/3.054/0.172	0.317-1.425
Propylene-R22	Overall	-1.167/0.931/0.043	0.085-0.771
	258	-0.689/1.648/-0.052	0.034-0.772
	263	-0.810/1.427/-0.021	0.040-0.790
	268	-0.831/1.387/-0.015	0.053-0.839
	273	-0.359/1.781/-0.057	0.023-0.808
	278	-0.099/1.794/-0.053	0.039-0.599
	283	-0.363/1.543/-0.025	0.014-0.580

Table C-2 (continued)

System (1-2)	Fitting temperature (K)	Parameters $\alpha/\lambda/k$	Δp-Δy_1
R134a-R152a	Overall	-4.971/-0.430/-0.088	0.387-0.516
		-3.974/-0.292/-0.067	0.424-0.458
	255	-5.236/-0.514/-0.102	0.155-0.482
	275	-0.994/0.095/-0.058	0.071-0.592
	298	-2.594/0.001/-0.067	0.125-0.383

Table C-3 AAD(%) in pressure and vapor phase composition of component (1) for the 2PMa model

System (1-2)	Fitting temperature (K)	Parameters λ/k	Δp-Δy_1
R134a-Propane	Overall	3.556/0.299	1.997-2.027
	255	3.150/0.399	0.298-2.068
	275	3.048/0.373	0.292-2.323
	298	3.001/0.334	0.495-1.484
Propylene-R134a	Overall	1.391/0.316	1.200-1.520
	251	0.948/0.410	0.634-1.888
	275	0.754/0.401	0.631-1.264
	298	0.733/0.376	0.463-1.337

Table C-3 (continued)

System (1-2)	Fitting temperature (K)	Parameters λ/k	Δp-Δy_1
R23-R13	Overall	2.808/0.127	1.323-1.713
	273	1.966/0.193	0.145-0.982
	255	2.009/0.207	0.168-0.764
	225	2.245/0.212	0.144-0.493
	199	2.506/0.224	0.388-1.869
Propylene-R22	Overall	1.293/0.005	0.165-0.770
	258	2.275/-0.127	0.099-0.912
	263	2.148/-0.106	0.099-0.937
	268	2.150/-0.103	0.094-0.985
	273	2.162/-0.100	0.064-0.738
	278	1.904/-0.066	0.043-0.613
	283	1.906/-0.065	0.042-0.586
R134a-R152a	Overall	-0.441/0.044	0.300-0.419
	255	-0.464/0.037	0.093-0.705
	275	0.441/-0.104	0.071-0.591
	298	1.254/-0.205	0.128-0.342

Table C-4 AAD(%) in pressure and vapor phase composition of component (1) for the 2PMb model.

System (1-2)	Fitting temperature (K)	Parameters α/λ	ΔP-Δy_1
R134a-Propane	Overall	1.658/4.252	1.691-2.147
	255	1.274/4.940	0.762-1.528
	275	1.229/4.571	0.489-1.226
	298	1.585/4.098	0.388-1.015
Propylene-R134a	Overall	1.389/2.112	0.664-1.155
	251	1.394/2.323	0.127-1.552
	275	1.503/2.179	0.169-0.693
	298	1.344/2.068	0.125-0.366
R23-R13	Overall	0.017/1.777	2.049-1.727
	273	-0.026/1.663	0.173-0.777
	255	0.081/1.902	0.194-0.642
	225	0.478/2.186	0.143-0.423
	199	0.163/2.590	0.378-1.534
Propylene-R22	Overall	6.809/-0.311	0.294-0.940
	258	9.189/-0.448	0.200-1.078
	263	8.959/-0.446	0.184-0.928
	268	8.420/-0.429	0.169-0.852
	273	7.490/-0.365	0.198-1.079
	278	6.980/-0.336	0.198-0.689
	283	7.077/-0.384	0.173-1.096

Table C-4 (continued)

System (1-2)	Fitting temperature (K)	Parameters α/λ	ΔP-Δy_1
R134a-R152a	Overall	0.616/-2.052	1.088-1.057
	255	0.295/-1.803	0.142-0.920
	275	0.558/-1.911	0.059-0.544
	298	0.660/-2.211	0.119-0.557

Table C-5 Results (AAD%) for all refrigerant systems with the 2PMb model

System (1-2)	Parameters α/λ	ΔP-Δy_1	Source
R14-R13	-1.428/0.000	2.050-0.887	Proust and Stein (1979a)
R134a-Propane	1.658/4.252	1.691-2.147	Kleiber (1994)
Propylene-R134a	1.389/2.112	0.664-1.155	Kleiber (1994)
R23-R13	0.017/1.777	2.049-1.727	Stein and Proust (1971)
Propylene-R22	6.809/-0.311	0.294-0.940	Kleiber (1994)
R134a-R152a	0.616/-2.052	1.088-1.057	Kleiber (1994)
CO_2-R22	2.605/-1.799	1.082-1.291	Nohka et al (1973)
R14-R23	-0.919/3.135	2.986-1.817	Piacentini and Stein (1967)
R13-nButane	0.506/1.291	1.510-2.259	Weber (1989)
R13-R113	0.834/0.899	2.825-0.696	Meskel et al (1982b)
R23-R11	1.437/5.187	3.613-2.702	Chareton et al (1990)
R22-R11	3.754/-0.934	2.594-1.044	Meskel et al (1982a)
R23-R22	3.139/-1.599	1.963-5.912	Laugier et al (1994b)
R22-R123	1.245/-1.219	2.769-5.563	Nishiumi et al (1995)

Table C-6. P_{ij} values for refrigerant systems.

System (1-2)	p_{12}	p_{21}	Fitted values (α=1.464)		$\sqrt{q_1 q_2}$
			p_{12}	p_{21}	
R14-R13	2.576	1.484	1.703	2.244	1.955
R134a-Propane	2.477	2.152	2.448	2.178	2.309
Propylene-R134a	1.895	2.537	1.872	2.568	2.193
R23-R13	1.617	2.091	2.375	1.423	1.839
Propylene-R22	3.162	1.194	2.094	1.804	1.944
R134a-R152a	2.260	2.190	2.533	1.954	2.225
CO_2-R22	0.492	4.257	0.883	2.372	1.447
R14-R23	1.438	2.037	1.926	1.533	1.712
R13-nButane	2.780	2.420	1.844	3.166	2.416
R13-R113	2.284	3.200	1.661	4.398	2.703
R23-R11	1.657	3.452	1.488	3.845	2.392
R22-R11	0.754	6.444	1.605	3.029	2.205
R23-R22	1.306	3.206	1.289	3.247	2.046
R22-R123	1.169	2.576	1.502	2.004	1.735

Table C-7. AAD% in Pressure and vapor phase composition off component 1 for the cases with the α parameter 0.5 and 1.5 and the 2PMb model

Systems (1-2)	T (K)	λ parameter $\lambda_{1.5}$-$\lambda_{0.5}$	α=1.5 ΔP-Δy_1	α=0.5 ΔP-Δy_1
R14-R13	199.8	0.069-0.079	2.700-1.255	2.469-1.004
R23-R13	273	1.729-1.857	0.919-1.051	0.533-0.745
	255		1.356-2.095	0.556-0.892
	225		2.747-4.312	2.022-2.239
	200		5.296-5.818	4.533-3.612
R14-R23	145	2.901-3.170	10.968-0.261	9.146-0.226
	172		7.837-1.229	5.599-0.833
	200		3.536-3.030	2.272-2.582
	225		2.246-2.514	1.607-2.207
	255		2.921-4.473	2.338-4.366
	283		0.548-1.777	0.460-2.081
R134a-Propane	255	4.562-4.257	1.744-2.570	3.431-3.750
	275		0.507-1.186	1.482-1.862
	298		1.977-1.709	0.841-1.029
Propylene-R134a	251	2.180-2.164	0.847-2.113	1.436-1.958
	275		0.168-0.689	0.912-1.149
	298		0.591-0.617	0.602-1.348

Table C-8 AAD(%) in pressure and vapor phase composition of component (1) for the 1PM model.

System (1-2)	Fitting temperature (K)	Parameters λ	ΔP-Δy_1
CO_2-R22	Overall	-1.024	2.495-2.265
	273	-0.527	2.696-1.472
	288	-1.011	2.773-0.957
	293	-1.136	1.837-1.776
	298	-1.323	3.294-1.826
	303	-1.433	2.974-2.159
	323	-1.217	1.846-2.851
	333	-1.016	1.804-3.485
	348	-0.206	0.745-2.311
R14-R23	Overall	3.172	3.567-1.966
	145	4.306	5.472-0.561
	172	4.151	4.943-1.804
	200	3.296	2.562-2.975
	225	3.074	1.251-1.879
	255	3.193	2.380-4.406
	283	3.143	0.440-2.163
R13-nButane	Overall	1.262	1.575-2.005
	311	1.633	0.323-1.711
	350	1.180	0.600-1.266
	400	0.224	0.993-5.706

Table C-8 (continued)

System (1-2)	Fitting temperature (K)	Parameters λ	ΔP-Δy_1
R13-R113	Overall	0.806	2.423-0.737
	298	1.195	2.097-0.253
	303	1.220	2.252-0.299
	323	1.067	1.468-1.358
	348	0.734	0.555-0.715
	373	0.227	1.306-1.243
R22-R123	Overall	-1.407	3.040-6.189
	313	-1.202	3.911-4.071
	333	-0.981	1.973-2.804
	353	-1.134	2.007-2.702
	383	-1.030	1.746-4.515
	414	-1.922	2.403-14.404
R22-R11	Overall	0.366	1.738-0.846
	298	0.614	1.731-0.352
	323	0.639	0.867-0.332
	348	0.410	1.218-0.741
	362		
	368.15		
	368.65		
	373	0.218	1.561-1.344

Table C-9 AAD(%) in pressure and vapor phase composition of component (1) for the 1PM model with the parameter λ fitted at a single temperature T*.

System (1-2)	T* (K)	Parameter λ	ΔP-Δy_1
R14-R13	**199.8**	0.079	2.469-1.004
R134a-Propane	Overall	4.584	1.569-1.991
	255		1.768-2.612
	275		0.535-1.413
	298		2.218-1.957
Propylene-R134a	Overall	2.251	0.926-1.620
	251		1.189-1.602
	275		0.842-1.492
	298		0.781-1.765
R23-R13	Overall	1.750	2.459-2.325
	273		0.362-0.725
	255		1.000-1.078
	225		2.548-2.717
	199		5.157-4.223
Propylene-R22	Overall	-0.102	0.337-0.926
	258		0.463-0.928
	263		0.380-0.920
	268		0.308-0.922
	273		0.280-1.086
	278		0.270-0.547
	283		0.311-1.179

Table C-9 (continued)

System (1-2)	T* (K)	Parameter λ	ΔP-Δy_1
R134a-R152a	Overall	-1.911	0.711-0.749
	255		0.746-1.329
	275		0.081-0.473
	298		1.217-0.488
CO_2-R22	Overall	-0.527	2.328-1.674
	273		2.696-1.472
	288		2.799-1.089
	293		2.426-1.526
	298		3.555-0.884
	303		3.273-0.607
	323		1.911-1.387
	333		1.530-2.872
	348		1.144-3.228
R14-R23	Overall	3.143	3.435-1.936
	145		9.391-0.236
	172		5.636-0.881
	200		2.239-2.497
	225		1.534-2.119
	255		2.302-4.319
	283		0.440-2.163
R13-nButane	Overall	1.633	1.490-2.842
	311		0.323-1.711
	350		2.425-1.850
	400		2.627-6.898

Table C-9 (continued)

System (1-2)	T* (K)	Parameter λ	ΔP-Δy_1
R13-R113	Overall	1.195	3.108-1.117
	298		2.097-0.253
	303		2.199-0.286
	323		2.279-1.360
	348		3.398-1.398
	373		7.575-2.650
R22-R123	Overall	-1.202	2.624-5.976
	313		3.911-4.071
	333		2.503-3.185
	353		2.070-2.771
	383		2.118-4.450
	414		2.865-14.727
R22-R11	Overall	0.614	1.436-0.650
	298		1.731-0.352
	323		0.889-0.353
	348		1.373-0.606
	362		0.790-0.549
	368.15		1.342-1.242
	368.65		2.612-1.482
	373		1.722-1.170

Table C-10 AAD(%) in pressure and vapor phase composition of component (1) for vdW with the parameter k fitted at a single temperature T*.

System (1-2)	T* (K)	Parameter k	ΔP-Δy_1
R14-R23	Overall	0.143	11.925-4.122
	145		35.422-1.915
	172		16.485-3.218
	200		8.720-6.754
	225		4.773-4.616
	255		3.773-5.618
	283		0.413-1.919
R13-R113	Overall	0.026	4.042-0.605
	298		1.596-0.039
	303		1.766-0.039
	323		2.166-1.154
	348		6.109-0.716
	373		12.723-1.601

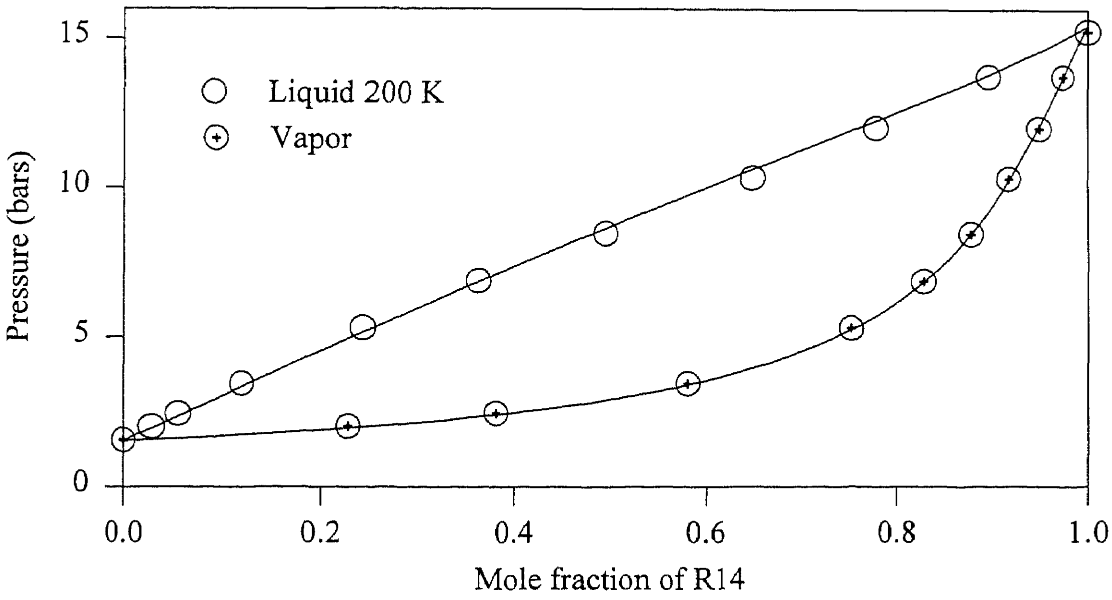

Figure C-1 Phase equilibria predictions for the system R14-R13

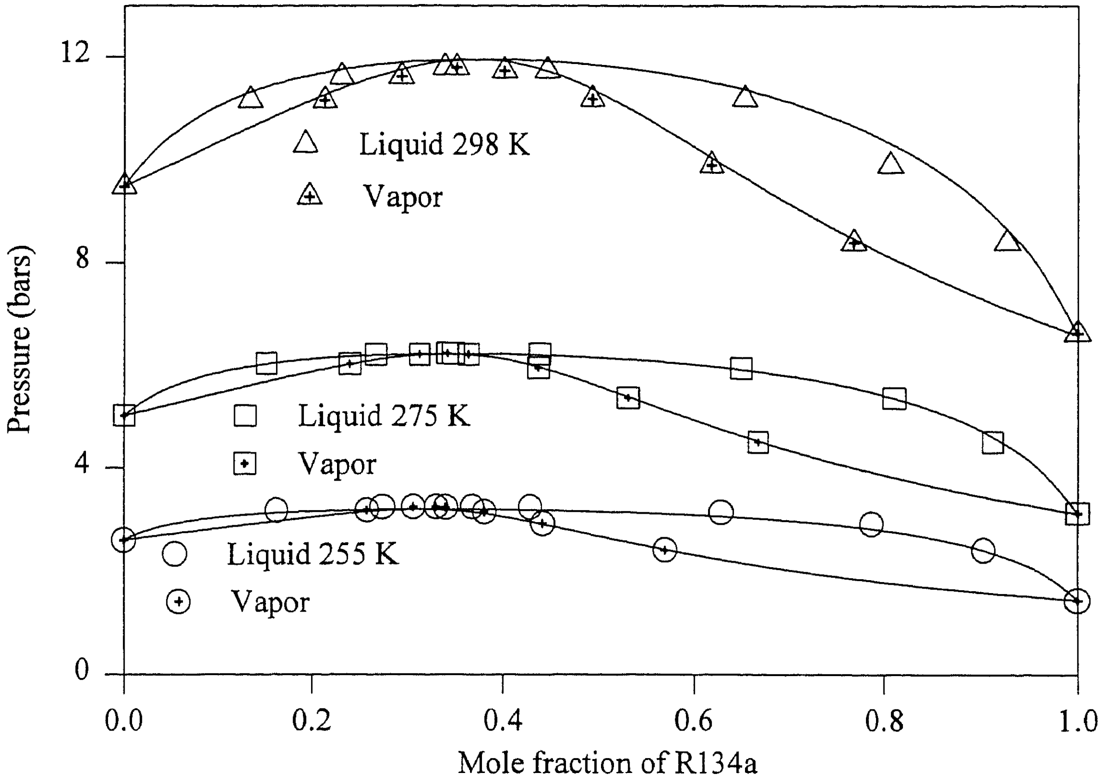

Figure C-2 Phase equilibria predictions for the system R134a-Propane

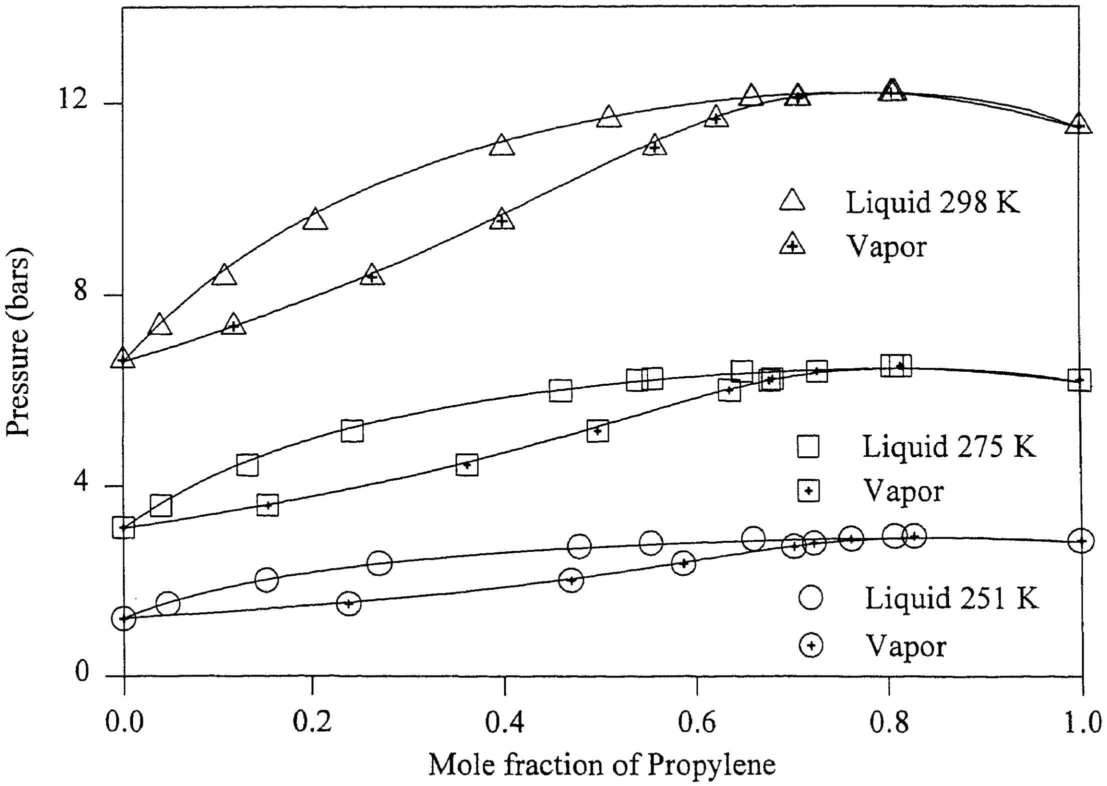

Figure C-3 Phase equilibria predictions for the system Propylene-R134a

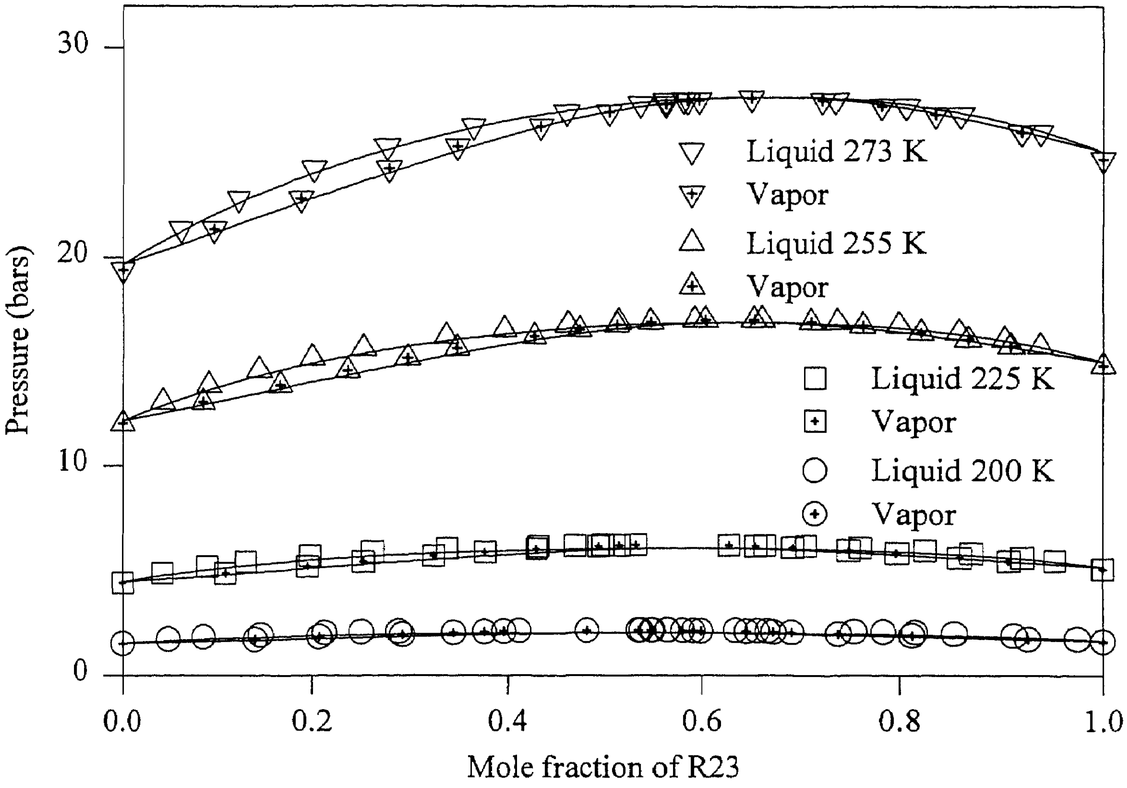

Figure C-4 Phase equilibria predictions for the system R23-R13

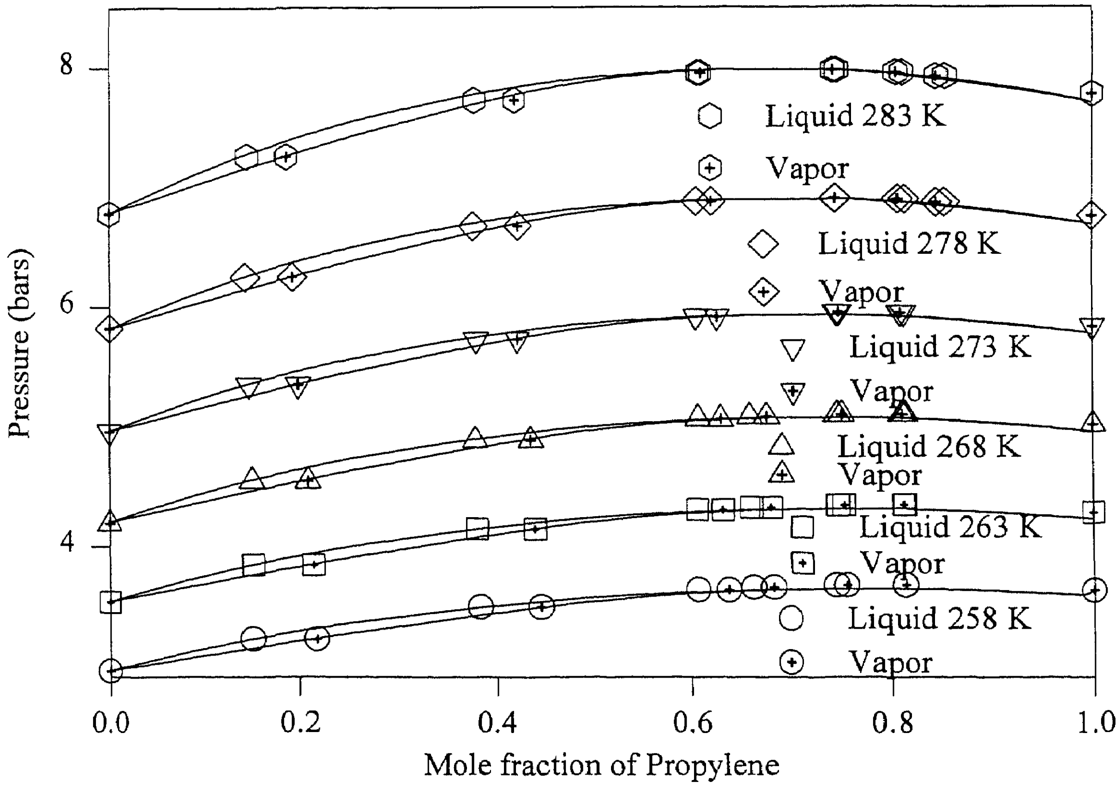

Figure C-5 Phase equilibria predictions for the system Propylene-R22

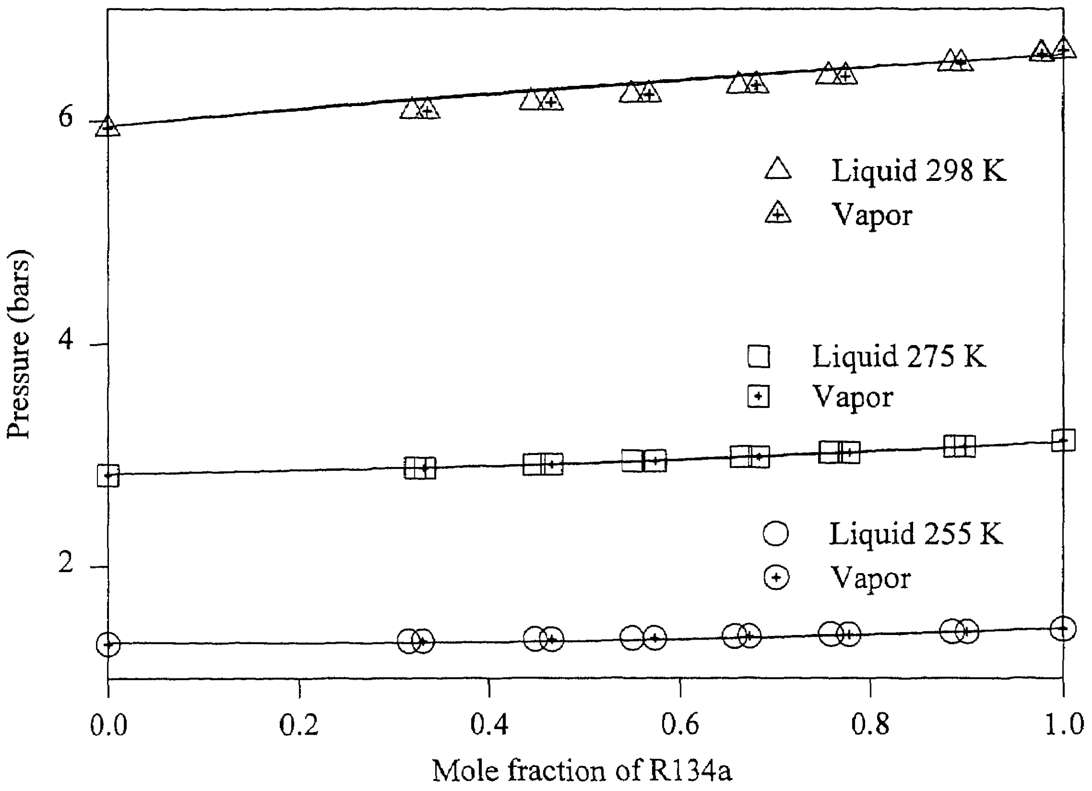

Figure C-6 Phase equilibria predictions for the system R134a-R152a

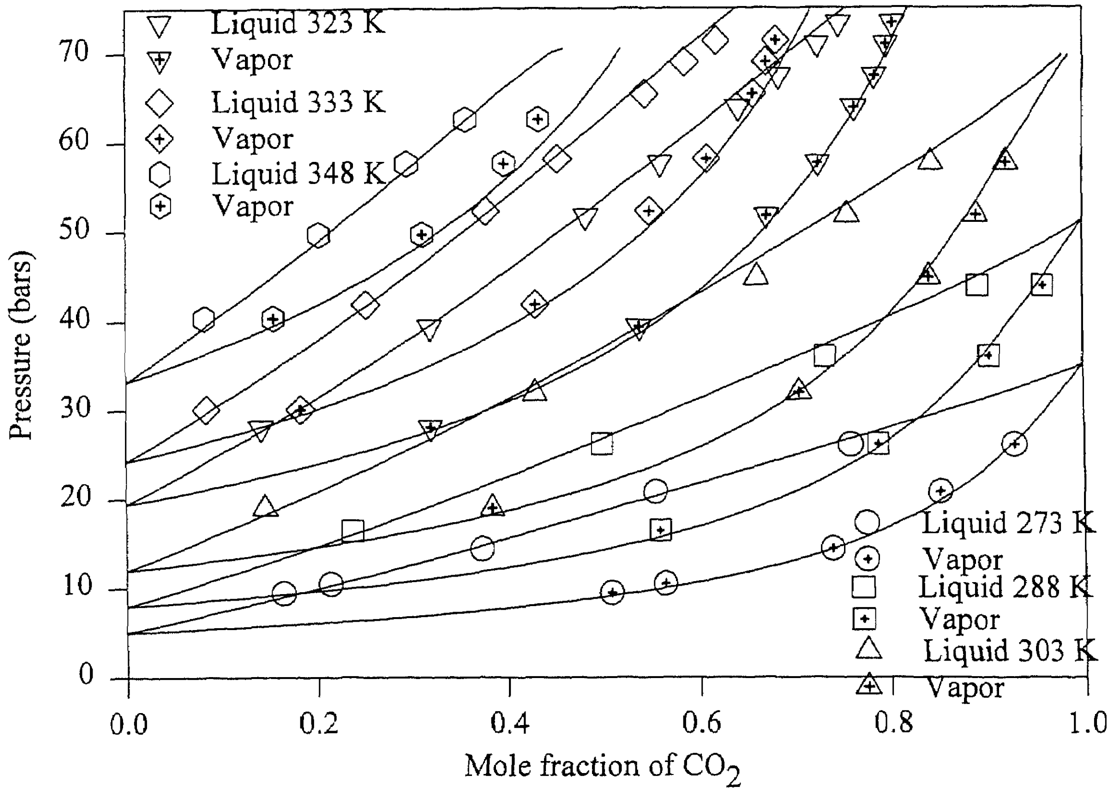

Figure C-7 Phase equilibria predictions of the system CO_2-R22

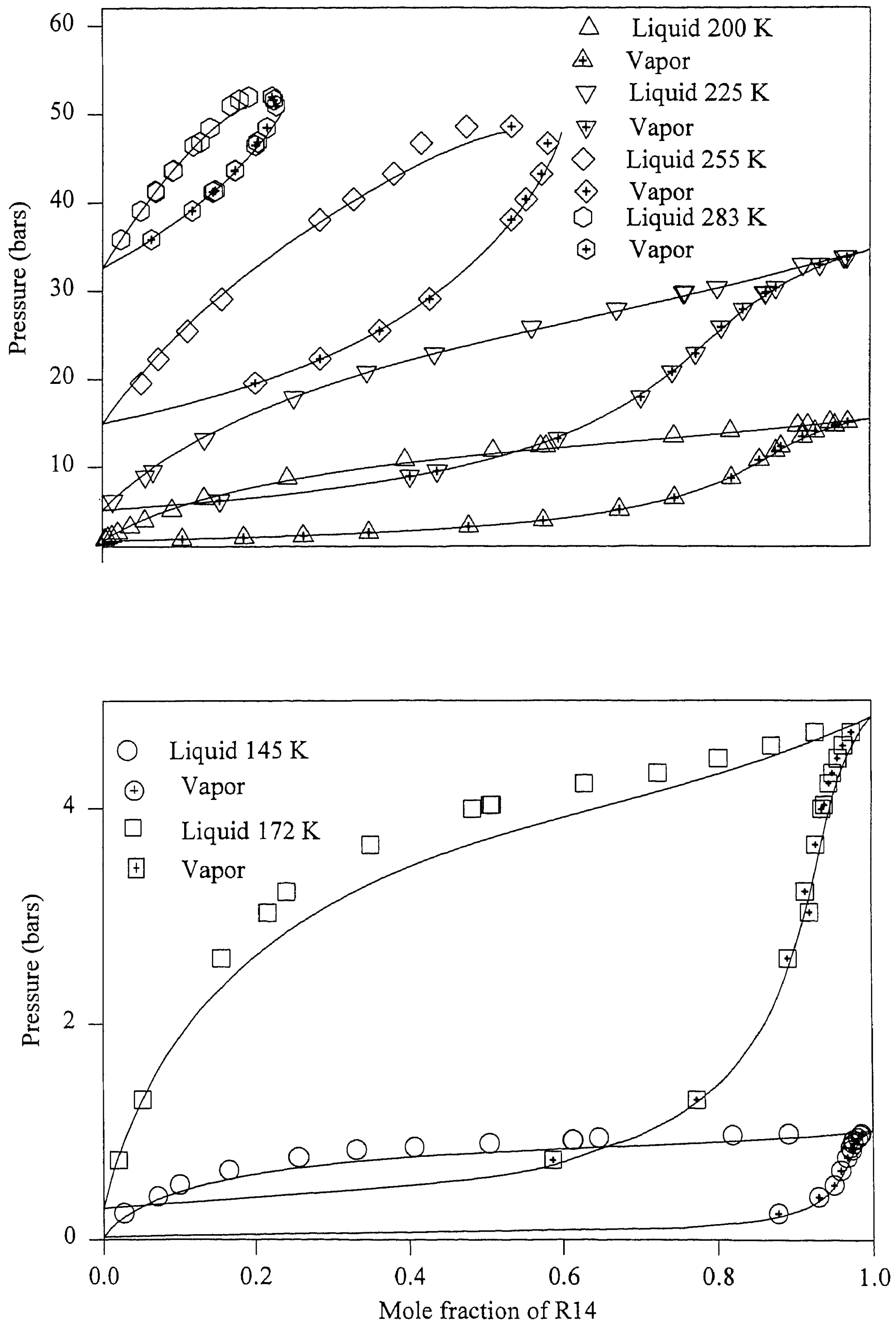

Figure C-8 Phase equilibria predictions for the system R14-R23

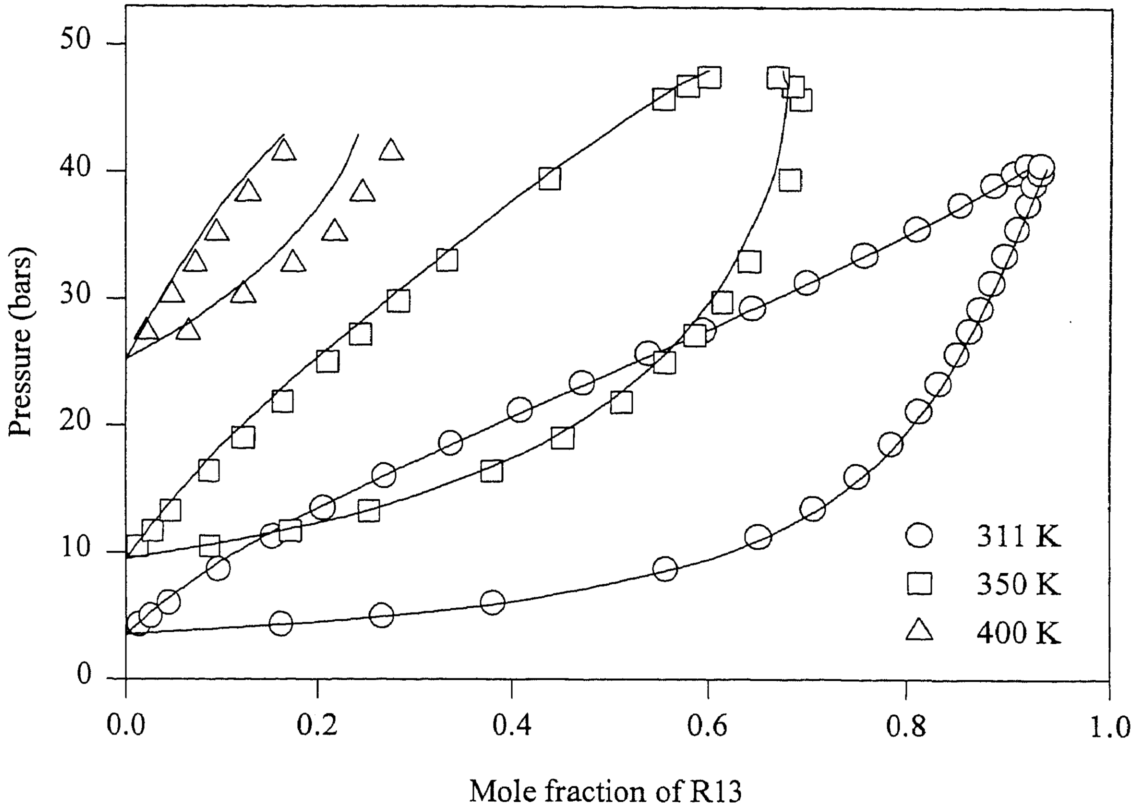

Figure C-9 Phase equilibria predictions for the system R13-n-Butane

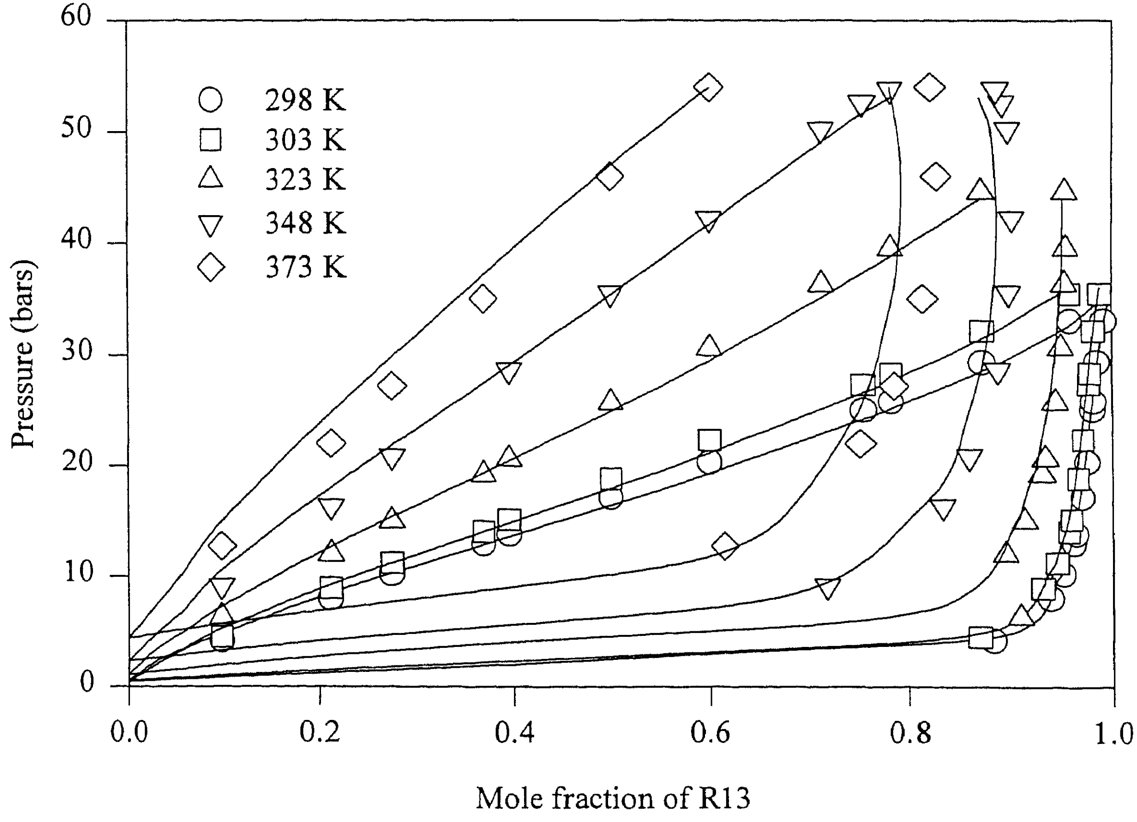

Figure C-10 Phase equilibrium predictions for the system R13-R113

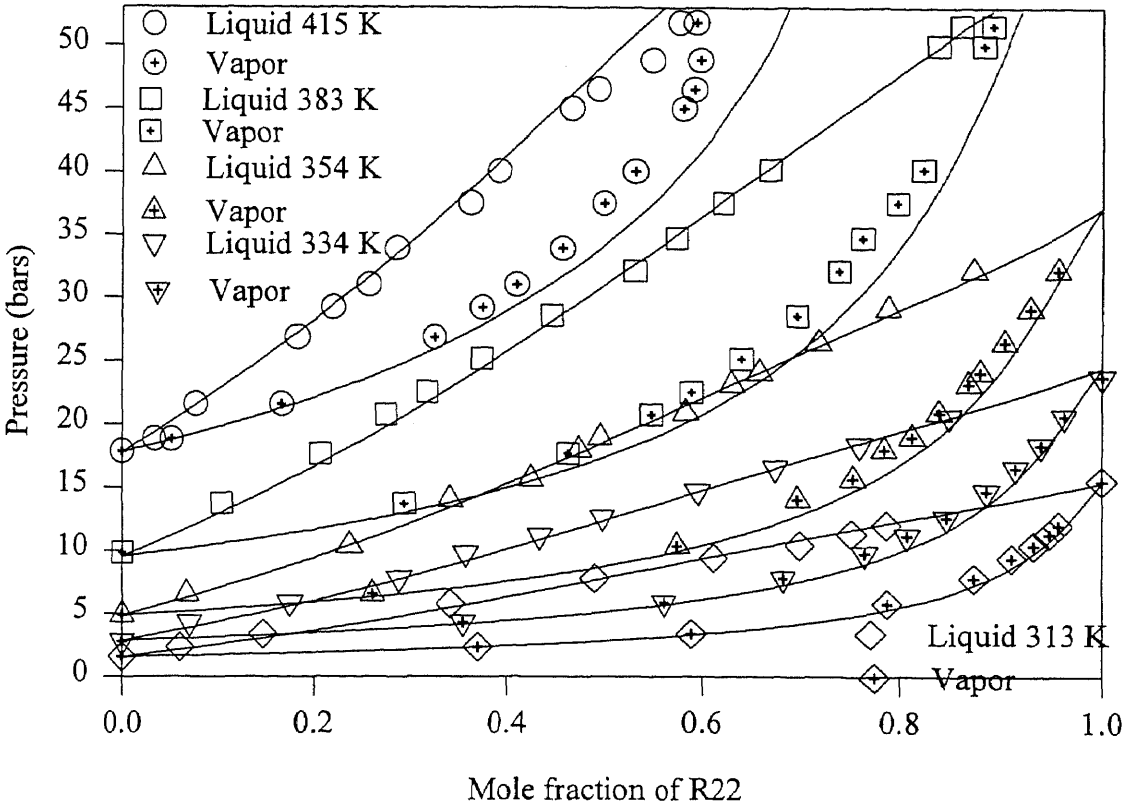

Figure C-11 Phase equilibria predictions for the system R22-R123

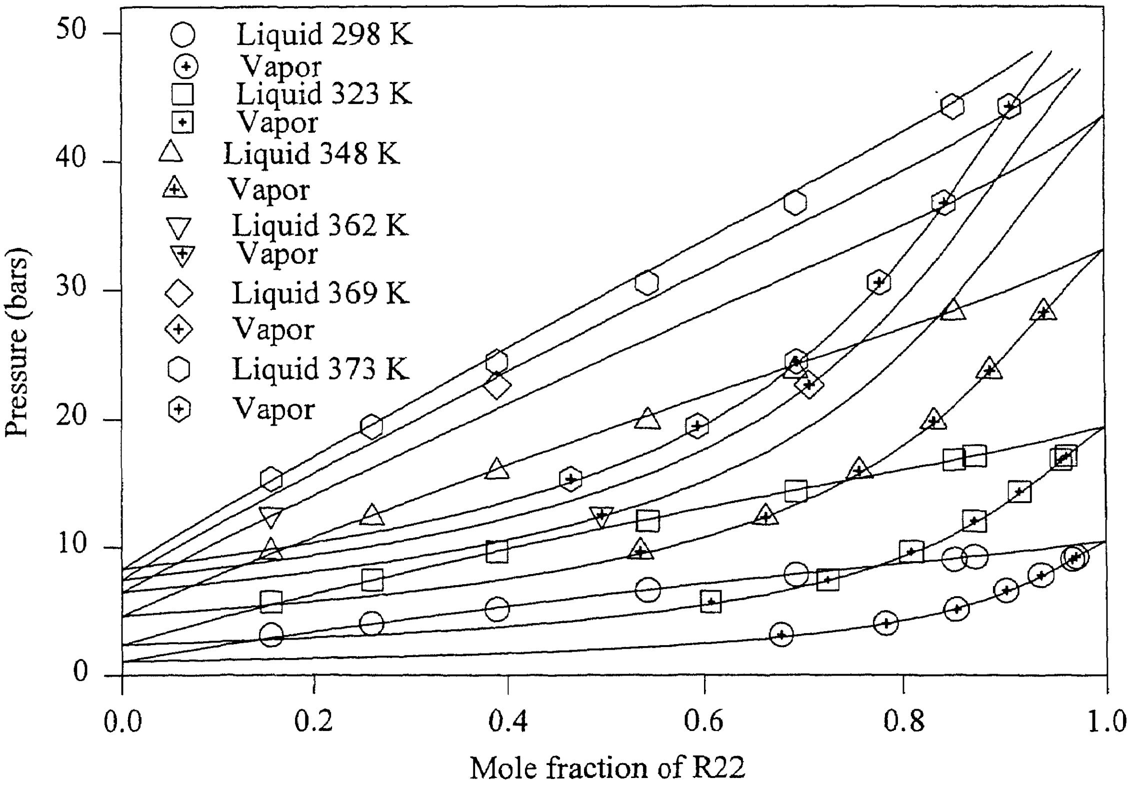

Figure C-12 Phase equilibria predictions for the system R22-R11

APPENDIX D

COMPUTER CODES

D-1 Infinite Dilution Activity Coefficient Calculation with the UNIFAC Model

D-2 Computer Code for Vapor-Liquid Equilibria Calculation

D-3 Sample Program for R134a-Propane

APPENDIX D-1

Infinite Dilution Activity Coefficient Calculation with the UNIFAC Model

```
      PROGRAM INF
C CALCULATE INFINITE DILUTION ACTIVITY COEFFICIENTS WITH UNIFAC
C EACH GROUP GETS AN ID (K) FROM TABLE D.1. SPECIES ARE DENOTED
C WITH INDEX I. RK AND QK ARE THE VOLUME AND SURFACE GROUP PARA-
C METERS. R AND Q REFER TO SPECIES. G, S AND TAU HAVE DOUBLE INDEX
C WITH G(M,I) OR G(K,I), S(K,I) AND TAU(M,K) WHERE M REFERS TO
C GROUPS. A(M,K) IS THE ENERGY INTERACTION PARAMETER BETWEEN GROUPS
C N(K,I) DENOTES THE NUMBER OF GROUPS K IN SPECIES I. NI IS INDEX
C EQUAL TO 1 WHEN THE GROUP EXISTS FOR THE MIXTURE. APPENDIX D
C SMITH AND VAN NESS
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (NG=51,RR=83.1439)
      DIMENSION RK(NG),QK(NG),R(2),Q(2),G(NG,2),S(NG,2),
   @     TAU(NG,NG),A(NG,NG),NC(NG,2),NI(NG,2),GAMMA(2),
   @     TC(2),PC(2),BB(2)

C                 DECLARE VARIABLES
      INTEGER   ITMAX, N
      REAL      ERRREL
      PARAMETER  (N=2)
C
      INTEGER   K, NOUT
      REAL      FNORM, X(N), XGUESS(N)
      EXTERNAL  FCN, LSJAC, NEQNJ, UMACH
C                 SET VALUES OF INITIAL GUESS
C                 XGUESS = ( 4.0  4.0  4.0  )
C
      COMMON/GA/GAMMA
      COMMON/PA/BB
       DATA XGUESS/4.,-4./
C
   ERRREL = 0.0001
   ITMAX  = 100
C
C CRITICAL PARAMETERS
C     TC(1)=508.1
C     TC(1)=512.58
      TC(2)=647.286
C     TC(2)=536.55
      TC(1)=513.92
C     PC(1)=46.96
C     PC(1)=80.9579
      PC(2)=220.8975
C     PC(2)=54.72
      PC(1)=61.48
C CALCULATE B1,B2 FROM PRSV
      DO 14 I=1,2
      BB(I)=0.077796*RR*TC(I)/PC(I)
 14   CONTINUE
```

```
C GIVE DATA FROM TABLE D1 AND D2.
      RK(1)=0.9011
      RK(2)=0.6744
      RK(15)=1.
      RK(16)=1.4311
      RK(17)=0.92
      RK(19)=1.6724
      RK(51)=2.87

      QK(1)=0.848
      QK(2)=0.540
      QK(15)=1.2
      QK(16)=1.432
      QK(17)=1.4
      QK(19)=1.488
      QK(51)=2.41

      TAU(1,1)=1.
      A(1,2)=0.
      A(1,15)=986.5
      A(1,16)=697.2
      A(1,17)=1318.
      A(1,19)=476.4
      A(1,51)=24.90

      A(2,1)=0.
      TAU(2,2)=1.
      A(2,15)=986.5
      A(2,16)=697.2
      A(2,17)=1318.
      A(2,19)=476.4
      A(2,51)=24.90

      A(15,1)=156.4
      A(15,2)=156.4
      TAU(15,15)=1.
      A(15,16)=-137.1
      A(15,17)=353.5
      A(15,19)=84.
      A(15,51)=-98.12

      A(16,1)=16.51
      A(16,2)=16.51
      A(16,15)=249.1
      TAU(16,16)=1.
      A(16,17)=-181.
      A(16,19)=23.39
      A(16,51)=-139.4

      A(17,1)=300.
      A(17,2)=300.
      A(17,15)=-229.1
      A(17,16)=289.6
      TAU(17,17)=1.
```

```
        A(17,19)=-195.4
        A(17,51)=353.7

        A(19,1)=26.76
        A(19,2)=26.76
        A(19,15)=164.5
        A(19,16)=108.7
        A(19,17)=472.5
        TAU(19,19)=1.
        A(19,51)=-354.6

        A(51,1)=36.7
        A(51,2)=36.7
        A(51,15)=742.1
        A(51,16)=649.1
        A(51,17)=826.7
        A(51,19)=552.1
        TAU(51,51)=1.
C DEFINE SPECIES
        NC(1,1)=1
        NC(2,1)=1
        NC(15,1)=1
C       NC(1,2)=1
C       NC(16,2)=1
        NC(17,2)=1
C       NC(15,1)=1
        NI(1,1)=1
        NI(2,1)=1
        NI(15,1)=1
        NI(17,1)=1
        NI(1,2)=1
        NI(2,2)=1
        NI(15,2)=1
        NI(17,2)=1
        T=298.15
C CALCULATE R AND Q FOR EACH SPECIES
        DO 1 I=1,2
        CC=0.
        DD=0.
        DO 2 K=1,NG
        C=NC(K,I)*RK(K)
        D=NC(K,I)*QK(K)
        CC=CC+C
        DD=DD+D
2       CONTINUE
        R(I)=CC
        Q(I)=DD
1       CONTINUE
C CALCULATE G (D.18)
        DO 3 I=1,2
        DO 4 M=1,NG
        G(M,I)=NC(M,I)*QK(M)
4       CONTINUE
3       CONTINUE
```

```
C CALCULATE TAU D.22
      DO 5 K=1,NG
      DO 6 M=1,NG
      IF (A(K,M).NE.0) THEN
      TAU(K,M)=EXP(-A(K,M)/T)
      ENDIF
 6    CONTINUE
 5    CONTINUE
C CALCULATE S(K,I) D.20
      DO 7 I=1,2
      DO 8 K=1,NG
      FF=0.
      DO 9 M=1,NG
      AF=G(M,I)*TAU(M,K)*NI(K,I)
      FF=FF+AF
 9    CONTINUE
      S(K,I)=FF
 8    CONTINUE
 7    CONTINUE

      DO 12 I=1,2
      BLL=0.
      IF (I.EQ.1) THEN
      J=2.
      ELSE
      J=1
      ENDIF
      DO 10 K=1,NG
      IF (NI(K,I).EQ.1) THEN
      HH=0.
      DO 11 M=1,NG
      H=G(M,I)*TAU(M,K)
      HH=HH+H
 11   CONTINUE
      AL=HH/S(K,J)
      BL=G(K,J)*AL-G(K,I)*LOG(AL)
      BLL=BLL+BL
      ENDIF
 10   CONTINUE
      GAMMA(I)=1.-R(I)/R(J)+LOG(R(I)/R(J))-5.*Q(I)*(1.-R(I)*Q(J)/R(J)
   @ /Q(I)+LOG(R(I)*Q(J)/R(J)/Q(I)))+Q(I)*(1.-LOG(Q(I)/Q(J)))-BLL
 12   CONTINUE
      WRITE(*,*) GAMMA
C     GAMMA(1)=2.4399
C     GAMMA(2)=1.9962
C     GAMMA(1)=1.0309
C     GAMMA(2)=.9502
C     GAMMA(1)=1.1071
C     GAMMA(2)=.7123
C                FIND THE SOLUTION
      CALL NEQNJ (FCN, LSJAC, ERRREL, N, ITMAX, XGUESS, X, FNORM)
      WRITE(*,*) X
      END
C                USER-SUPPLIED SUBROUTINE
```

```
      SUBROUTINE FCN (X, F, N)
      INTEGER   N
      REAL      X(N), F(N)
      REAL*8 GAMMA(2),BB(2)
      COMMON/GA/GAMMA
      COMMON/PA/BB
C
      REAL      EXP, SIN
      INTRINSIC  EXP, SIN
C
      F(1) = GAMMA(1)-X(1)*BB(1)/BB(2)*EXP(-.1*X(1))-X(2)
      F(2) = GAMMA(2)-X(2)*BB(2)/BB(1)*EXP(-.1*X(2))-X(1)
      RETURN
      END
C                   USER-SUPPLIED SUBROUTINE TO
C                   COMPUTE JACOBIAN
      SUBROUTINE LSJAC (N, X, FJAC)
      INTEGER   N
      REAL      X(N), FJAC(N,N)
C
      REAL      COS, EXP
      REAL*8 BB(2)
      INTRINSIC  COS, EXP
      COMMON/PA/BB
C
      FJAC(1,1) = -BB(1)/BB(2)*EXP(-.1*X(1))+
     @      X(1)*0.1*BB(1)/BB(2)*EXP(-.1*X(1))
      FJAC(1,2) = -1.
      FJAC(2,1) = -1.
      FJAC(2,2) = -BB(2)/BB(1)*EXP(-.1*X(2))+
     @      X(2)*0.1*BB(2)/BB(1)*EXP(-.1*X(2))
      RETURN
      END
```

APPENDIX D-2

Computer Code for Vapor-Liquid Equilibria Calculation

```
          PROGRAM G702
C PRESSURE IN BARS AND MOLAR VOLUME IN CC/MOLE,AE IS IN UNITS BARS*CC/MOLE
C CUBIC: 1 FOR PRSV-WONG-SANDLER, 3 FOR SRK
C       4 & 5 FOR PANAGIOTOPOULOS PRSV
C       11 FOR MHV1 (TOCHIGI)
C ACT: 1 FOR NRTL, 2 FOR VANLAAR 3 FOR UNIQUAC 5 FOR WILSON 6 FOR T-S-WILSON
C ROT: 1 BUBBLE P, 2 BUBBLE T, 3 DEW P, 4 DEW T
C IN THE INIT.TXT FILE THE NUMBERS ARE: CUBIC,ACT,MXACO,T,P,ROT
C DY=SUM(ABS(DY))/ND, PSD=SUM(DP**2.), TOCH=SUM(ABS(DP)/PEX),
C DPH-V=SQRT((SUM(DP**2.))/ND), DYH-V=SQRT((SUM(DY**2.))/ND)
C
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (R = 83.1439, Z=10,KKK=8)
      PARAMETER(NDATA=1000,LINIT=9)
      DIMENSION
     @      X(KKK,NDATA),X1(KKK),Y(KKK,NDATA),
     @      BINARY(KKK,KKK),CROSS(KKK,KKK),
     @      XEX(KKK,NDATA),PEX(KKK,NDATA),YEX(KKK,NDATA),
     @      TEX(KKK,NDATA),DY(KKK,NDATA),DX(KKK,NDATA),
     @      DP(KKK,NDATA),PSP(NDATA),YSP(NDATA),Y5(NDATA),Y6(NDATA)
     @      ,XSP(NDATA),DTEM(KKK,NDATA)

      CHARACTER*16 SYM(KKK)
      CHARACTER*13 FNAME1,FNAME2,FNAME3,FNAME4


          COMMON/XY/X,Y
          COMMON/EQU/ROT
          COMMON/KK/KK
          COMMON/ICO/ICOUNT


          OPEN (LINIT,FILE='INIT.TXT',STATUS='OLD')

          READ(LINIT,'(A13)') FNAME1
          READ(LINIT,'(A13)') FNAME2
          READ(LINIT,'(A13)') FNAME3
          READ(LINIT,'(A13)') FNAME4

      CALL MXINP (SYM,T,P,BINARY)

          IF ((ROT.EQ.1).OR.(ROT.EQ.2).OR.(ROT.EQ.3).OR.(ROT.EQ.4)) THEN
          OPEN(10,FILE=FNAME1,STATUS='UNKNOWN')
          OPEN(11,FILE=FNAME2,STATUS='OLD')
          OPEN(19,FILE=FNAME3,STATUS='NEW')
          OPEN(20,FILE=FNAME4,STATUS='NEW')
          ENDIF

          IF (KK.EQ.2) THEN
```

```
            IF (ROT.EQ.1.) THEN
            WRITE (19,*) '  XEX    PCALC   PEXP    YCALC   YEXP
    @       DY      DP'
            ENDIF
            IF (ROT.EQ.2.) THEN
            WRITE (19,*) '  XEX    TCALC   TEXP    YCALC   YEXP
    @       DY      DTEM'
            ENDIF
            IF (ROT.EQ.3.) THEN
            WRITE (19,*) '  YEX    PCALC   PEXP    XCALC   XEXP
    @       DX      DP'
            ENDIF
            IF (ROT.EQ.4.) THEN
            WRITE (19,*) '  YEX    TCALC   TEXP    XCALC   XEXP
    @       DX      DTEM'
            ENDIF
            ENDIF
            IF (KK.EQ.3) THEN
            IF (ROT.EQ.1.) THEN
            WRITE (19,*) '  XEX1    PCALC    PEXP1    YCALC1    YEXP1
    @       DY1     DP1'
            WRITE (20,*) '  XEX2    PCALC    PEXP2    YCALC2    YEXP2
    @       DY2     DP2'
            ENDIF
            IF (ROT.EQ.2.) THEN
            WRITE (19,*) '  XEX1  TCALC1    TEXP1    YCALC1    YEXP1
    @       DY1     DTEM1'
            WRITE (20,*) '  XEX2  TCALC2    TEXP2    YCALC2    YEXP2
    @       DY2     DTEM2'
            ENDIF
            IF (ROT.EQ.3.) THEN
            WRITE (19,*) '  YEX1    PCALC    PEXP1    XCALC1    XEXP1
    @       DX1     DP1'
            WRITE (20,*) '  YEX2    PCALC    PEXP2    XCALC2    XEXP2
    @       DX2     DP2'
            ENDIF
            IF (ROT.EQ.4.) THEN
            WRITE (19,*) '  YEX1    TCALC    TEXP1    XCALC1    XEXP1
    @       DX1     TP1'
            WRITE (20,*) '  YEX2    TCALC    TEXP2    XCALC2    XEXP2
    @       DX2     TP2'
            ENDIF
            ENDIF
            KDATA=1
4           READ(10,1002,END=3) PEX(1,KDATA),XEX(1,KDATA),YEX(1,KDATA)
            IF (KK.EQ.3) THEN
            READ(11,1002,END=3) PEX(2,KDATA),XEX(2,KDATA),YEX(2,KDATA)
            ENDIF
            KDATA=KDATA+1
            GOTO 4
1002        FORMAT(3F10.4)
3           KDATA=KDATA-1
            IF ((ROT.EQ.2.).OR.(ROT.EQ.4)) THEN
            TEX(1,1)=PEX(1,1)
```

```
IF (KK.EQ.3) THEN
TEX(2,1)=PEX(2,1)
ENDIF
ENDIF

IF ((ROT.EQ.1.).OR.(ROT.EQ.2.)) THEN
IF (KK.EQ.2) THEN
X(1,1)=XEX(1,1)
X(2,1)=1.-XEX(1,1)
Y(1,0)=X(1,1)
Y(2,0)=X(2,1)
ELSE
IF (KK.EQ.3) THEN
X(1,1)=XEX(1,1)
X(2,1)=XEX(2,1)
X(3,1)=1.-XEX(1,1)-XEX(2,1)
Y(1,0)=X(1,1)
Y(2,0)=X(2,1)
Y(3,0)=X(3,1)
ELSE
ENDIF
ENDIF
ELSE
ENDIF

IF ((ROT.EQ.3.).OR.(ROT.EQ.4.)) THEN
IF (KK.EQ.2) THEN
Y(1,1)=YEX(1,1)
Y(2,1)=1.-YEX(1,1)
X(1,0)=Y(1,1)
X(2,0)=Y(2,1)
ELSE
IF (KK.EQ.3) THEN
Y(1,1)=YEX(1,1)
Y(2,1)=YEX(2,1)
Y(3,1)=1.-YEX(1,1)-YEX(2,1)
X(1,0)=Y(1,1)
X(2,0)=Y(2,1)
X(3,0)=Y(3,1)
ELSE
ENDIF
ENDIF
ELSE
ENDIF

ICOUNT=1.
CALL MXEOSPAR (T,X1,BINARY)
IF (ROT.EQ.1.) THEN
CALL MXBUBBLE(T,P,BINARY,CROSS,VL,VG)
ENDIF
IF (ROT.EQ.2.) THEN
CALL MXBUBBLET(T,P,BINARY,CROSS,VL,VG)
ENDIF
IF (ROT.EQ.3.) THEN
```

```
      CALL MXDEW(T,P,BINARY,CROSS,VL,VG)
      ENDIF
      IF (ROT.EQ.4.) THEN
      CALL MXDEWT(T,P,BINARY,CROSS,VL,VG)
      ENDIF

      IF ((ROT.EQ.1.).OR.(ROT.EQ.2.)) THEN
      DY(1,1)=Y(1,1)-YEX(1,1)
      IF (KK.EQ.3) THEN
      DY(2,1)=Y(2,1)-YEX(2,1)
      ENDIF
      IF (ROT.EQ.1.) THEN
      DP(1,1)=P-PEX(1,1)*0.0689473
      WRITE (19,1004) X(1,1),P,PEX(1,1)*0.0689473,Y(1,1),
@     YEX(1,1),DY(1,1),DP(1,1)
      IF (KK.EQ.3) THEN
      DP(2,1)=P-PEX(2,1)*0.0689473
      WRITE (20,1004) X(2,1),P,PEX(2,1)*0.0689473,Y(2,1),
@     YEX(2,1),DY(2,1),DP(2,1)
      ENDIF
      ELSE
      IF (ROT.EQ.2.) THEN
      DTEM(1,1)=T-TEX(1,1)-273.15
      WRITE (19,1004) X(1,1),T,TEX(1,1)+273.15,Y(1,1),
@     YEX(1,1),DY(1,1),DTEM(1,1)
      IF (KK.EQ.3) THEN
      DTEM(2,1)=T-TEX(2,1)-273.15
      WRITE (20,1004) X(2,1),T,TEX(2,1)+273.15,Y(2,1),
@     YEX(2,1),DY(2,1),DTEM(2,1)
      ENDIF
      ENDIF
      ENDIF
      ENDIF

      IF ((ROT.EQ.3.).OR.(ROT.EQ.4.)) THEN
      DX(1,1)=X(1,1)-XEX(1,1)
      IF (KK.EQ.3) THEN
      DX(2,1)=X(2,1)-XEX(2,1)
      ENDIF
      IF (ROT.EQ.3.) THEN
      DP(1,1)=P-PEX(1,1)*0.0689473
      WRITE (19,1004) Y(1,1),P,PEX(1,1)*0.0689473,X(1,1),
@     XEX(1,1),DX(1,1),DP(1,1)
      IF (KK.EQ.3) THEN
      DP(2,1)=P-PEX(2,1)*0.0689473
      WRITE (20,1004) Y(2,1),P,PEX(2,1)*0.0689473,X(2,1),
@     XEX(2,1),DX(2,1),DP(2,1)
      ENDIF
      ELSE
      IF (ROT.EQ.4.) THEN
      DTEM(1,1)=T-TEX(1,1)-273.15
      WRITE (19,1004) Y(1,1),T,TEX(1,1)+273.15,X(1,1),
@     XEX(1,1),DX(1,1),DTEM(1,1)
      IF (KK.EQ.3) THEN
```

```
            DTEM(2,1)=T-TEX(2,1)-273.15
            WRITE (20,1004) Y(2,1),T,TEX(2,1)+273.15,X(2,1),
    @       XEX(2,1),DX(2,1),DTEM(2,1)
            ENDIF
            ENDIF
            ENDIF
            ENDIF

            DO 1110  ICOUNT=2,KDATA
C           DO 1110  ICOUNT=2,500
            IF ((ROT.EQ.2.).OR.(ROT.EQ.4)) THEN
            TEX(1,ICOUNT)=PEX(1,ICOUNT)
            IF (KK.EQ.3) THEN
            TEX(2,ICOUNT)=PEX(2,ICOUNT)
            ENDIF
            ENDIF

            IF ((ROT.EQ.1.).OR.(ROT.EQ.2.)) THEN
            X(1,ICOUNT)=XEX(1,ICOUNT)
            X(2,ICOUNT)=1.-X(1,ICOUNT)
            IF (KK.EQ.3) THEN
            X(2,ICOUNT)=XEX(2,ICOUNT)
            X(3,ICOUNT)=1.-X(1,ICOUNT)-X(2,ICOUNT)
            ENDIF
            ENDIF

C           DO 124 I=2,500
C           X(1,I)=I/500.
C           X(2,I)=1.-X(1,I)
C 124       CONTINUE

            IF ((ROT.EQ.3.).OR.(ROT.EQ.4.)) THEN
            Y(1,ICOUNT)=YEX(1,ICOUNT)
            Y(2,ICOUNT)=1.-Y(1,ICOUNT)
            IF (KK.EQ.3) THEN
            Y(2,ICOUNT)=YEX(2,ICOUNT)
            Y(3,ICOUNT)=1.-Y(1,ICOUNT)-Y(2,ICOUNT)
            ENDIF
            ENDIF

            IF (ROT.EQ.1.) THEN
            CALL MXBUBBLEP(T,P,BINARY,CROSS,VL,VG)
            ENDIF
            IF (ROT.EQ.2.) THEN
            CALL MXBUBBLET(T,P,BINARY,CROSS,VL,VG)
            ENDIF
            IF (ROT.EQ.3.) THEN
            CALL MXDEWP(T,P,BINARY,CROSS,VL,VG)
            ENDIF
            IF (ROT.EQ.4.) THEN
            CALL MXDEWT(T,P,BINARY,CROSS,VL,VG)
            ENDIF

            IF ((ROT.EQ.1.).OR.(ROT.EQ.2.)) THEN
```

```
      DY(1,ICOUNT)=Y(1,ICOUNT)-YEX(1,ICOUNT)
      IF (KK.EQ.3) THEN
      DY(2,ICOUNT)=Y(2,ICOUNT)-YEX(2,ICOUNT)
      ENDIF
      IF (ROT.EQ.1.) THEN
      DP(1,ICOUNT)=P-PEX(1,ICOUNT)*0.0689473
      WRITE (19,1004) X(1,ICOUNT),P,PEX(1,ICOUNT)*0.0689473,
@     Y(1,ICOUNT),YEX(1,ICOUNT),DY(1,ICOUNT),DP(1,ICOUNT)
      IF (KK.EQ.3) THEN
      DP(2,ICOUNT)=P-PEX(2,ICOUNT)*0.0689473
      WRITE (20,1004) X(2,ICOUNT),P,PEX(2,ICOUNT)*0.0689473,
@     Y(2,ICOUNT),YEX(2,ICOUNT),DY(2,ICOUNT),DP(2,ICOUNT)
      ENDIF
      ELSE
      IF (ROT.EQ.2.) THEN
      DTEM(1,ICOUNT)=T-TEX(1,ICOUNT)-273.15
      WRITE (19,1004) X(1,ICOUNT),T,TEX(1,ICOUNT)+273.15,Y(1,ICOUNT),
@     YEX(1,ICOUNT),DY(1,ICOUNT),DTEM(1,ICOUNT)
      IF (KK.EQ.3) THEN
      DTEM(2,ICOUNT)=T-TEX(2,ICOUNT)-273.15
      WRITE (20,1004) X(2,ICOUNT),T,TEX(2,ICOUNT)+273.15,Y(2,ICOUNT),
@     YEX(2,ICOUNT),DY(2,ICOUNT),DTEM(2,ICOUNT)
      ENDIF
      ENDIF
      ENDIF
      ENDIF
      ENDIF

      IF ((ROT.EQ.3.).OR.(ROT.EQ.4.)) THEN
      DX(1,ICOUNT)=X(1,ICOUNT)-XEX(1,ICOUNT)
      IF (KK.EQ.3) THEN
      DX(2,ICOUNT)=X(2,ICOUNT)-XEX(2,ICOUNT)
      ENDIF
      IF (ROT.EQ.3.) THEN
      DP(1,ICOUNT)=P-PEX(1,ICOUNT)*0.0689473
      WRITE (19,1004) Y(1,ICOUNT),P,PEX(1,ICOUNT)*0.0689473,
@     X(1,ICOUNT),XEX(1,ICOUNT),DX(1,ICOUNT),DP(1,ICOUNT)
      IF (KK.EQ.3) THEN
      DP(2,ICOUNT)=P-PEX(2,ICOUNT)*0.0689473
      WRITE (20,1004) Y(2,ICOUNT),P,PEX(2,ICOUNT)*0.0689473,
@     X(2,ICOUNT),XEX(2,ICOUNT),DX(2,ICOUNT),DP(2,ICOUNT)
      ENDIF
      ELSE
      IF (ROT.EQ.4.) THEN
      DTEM(1,ICOUNT)=T-TEX(1,ICOUNT)-273.15
      WRITE (19,1004) Y(1,ICOUNT),T,TEX(1,ICOUNT)+273.15,X(1,ICOUNT),
@     XEX(1,ICOUNT),DX(1,ICOUNT),DTEM(1,ICOUNT)
      IF (KK.EQ.3) THEN
      DTEM(2,ICOUNT)=T-TEX(2,ICOUNT)-273.15
      WRITE (20,1004) Y(2,ICOUNT),T,TEX(2,ICOUNT)+273.15,X(2,ICOUNT),
@     XEX(2,ICOUNT),DX(2,ICOUNT),DTEM(2,ICOUNT)
      ENDIF
      ENDIF
      ENDIF
      ENDIF
```

```
1004     FORMAT(7(F8.5,1X))
1110     CONTINUE

         IF ((ROT.EQ.1.).OR.(ROT.EQ.2.)) THEN
         DS=0.
         PS=0.
         DO 1021 I=1,KDATA
         DS=DS+ABS(DY(1,I))
         DYS=DYS+ABS(DY(1,I))**2.
         IF (KK.EQ.3) THEN
         DS2=DS2+ABS(DY(2,I))
         DY2S=DY2S+ABS(DY(2,I))**2.
         ENDIF
         IF (ROT.EQ.1.) THEN
         PS=PS+ABS(DP(1,I))**2.
         PS2=PS2+ABS(DP(1,I))/PEX(1,I)/0.0689473
         IF (KK.EQ.3) THEN
         PS3=PS3+ABS(DP(2,I))**2.
         PS4=PS4+ABS(DP(2,I))/PEX(2,I)/0.0689473
         ENDIF
         ELSE
         IF (ROT.EQ.2.) THEN
         TS=TS+ABS(DTEM(1,I))**2.
         TS2=TS2+ABS(DTEM(1,I))/TEX(1,I)/0.0689473
         IF (KK.EQ.3) THEN
         TS3=TS3+ABS(DTEM(2,I))**2.
         TS4=TS4+ABS(DTEM(2,I))/TEX(2,I)/0.0689473
         ENDIF
         ENDIF
         ENDIF
1021     CONTINUE
         DS=DS/(KDATA)
         DYS3=SQRT(DYS/KDATA)
         IF (KK.EQ.3) THEN
         DYS4=SQRT(DY2S/KDATA)
         ENDIF
         IF (ROT.EQ.1.) THEN
         PS1=PS
         PS5=SQRT(PS/KDATA)
         WRITE(*,*) 'DY1=',DS,'PSDECH=',PS1,'TOCHIGI=',PS2,
  @      'DP1 H-V=',PS5,'DY1 H-V=',DYS3
         IF (KK.EQ.3) THEN
         PS7=PS3
         PS8=SQRT(PS3/KDATA)
         WRITE(*,*) 'DY1=',DS2,'PSDECH=',PS7,'TOCHIGI=',PS4,
  @      'DP1 H-V=',PS8,'DY1 H-V=',DYS4
         ENDIF
         ELSE
         IF (ROT.EQ.2.) THEN
         TS1=TS
         TS5=SQRT(TS/KDATA)
         WRITE(*,*) 'DY1=',DS,'TSDECH=',TS1,'TOCHIGI=',TS2,
  @      'DT H-V=',TS5,'DY1 H-V=',DYS3
```

```
        IF (KK.EQ.3) THEN
        TS7=TS3
        TS8=SQRT(TS3/KDATA)
        WRITE(*,*) 'DY1=',DS2,'TSDECH=',TS7,'TOCHIGI=',TS4,
  @     'DT H-V=',TS8,'DY1 H-V=',DYS4
        ENDIF
        ENDIF
        ENDIF
        ENDIF

        IF ((ROT.EQ.3.).OR.(ROT.EQ.4.)) THEN
        DS=0.
        PS=0.
        DO 9021 I=1,KDATA
        DS=DS+ABS(DX(1,I))
        DYS=DYS+ABS(DX(1,I))**2.
        IF (KK.EQ.3) THEN
        DS2=DS2+ABS(DX(2,I))
        DY2S=DY2S+ABS(DX(2,I))**2.
        ENDIF
        IF (ROT.EQ.3.) THEN
        PS=PS+ABS(DP(1,I))**2.
        PS2=PS2+ABS(DP(1,I))/PEX(1,I)/0.0689473
        IF (KK.EQ.3) THEN
        PS3=PS3+ABS(DP(2,I))**2.
        PS4=PS4+ABS(DP(2,I))/PEX(2,I)/0.0689473
        ENDIF
        ELSE
        IF (ROT.EQ.4.) THEN
        TS=TS+ABS(DTEM(1,I))**2.
        TS2=TS2+ABS(DTEM(1,I))/TEX(1,I)/0.0689473
        IF (KK.EQ.3) THEN
        TS3=TS3+ABS(DTEM(2,I))**2.
        TS4=TS4+ABS(DTEM(2,I))/TEX(2,I)/0.0689473
        ENDIF
        ENDIF
        ENDIF
9021    CONTINUE
        DS=DS/(KDATA)
        DYS3=SQRT(DYS/KDATA)
        IF (KK.EQ.3) THEN
        DYS4=SQRT(DY2S/KDATA)
        ENDIF
        IF (ROT.EQ.3.) THEN
        PS1=PS
        PS5=SQRT(PS/KDATA)
        WRITE(*,*) 'DX1=',DS,'PSDECH=',PS1,'TOCHIGI=',PS2,
  @     'DP1 H-V=',PS5,'DX1 H-V=',DYS3
        IF (KK.EQ.3) THEN
        PS7=PS3
        PS8=SQRT(PS3/KDATA)
        WRITE(*,*) 'DX1=',DS2,'PSDECH=',PS7,'TOCHIGI=',PS4,
  @     'DP1 H-V=',PS8,'DX1 H-V=',DYS4
        ENDIF
```

```
       ELSE
       IF (ROT.EQ.4.) THEN
       TS1=TS
       TS5=SQRT(TS/KDATA)
       WRITE(*,*) 'DX1=',DS,'TSDECH=',TS1,'TOCHIGI=',TS2,
 @     'DT H-V=',TS5,'DX1 H-V=',DYS3
       IF (KK.EQ.3) THEN
       TS7=TS3
       TS8=SQRT(TS3/KDATA)
       WRITE(*,*) 'DX1=',DS2,'TSDECH=',TS7,'TOCHIGI=',TS4,
 @     'DT H-V=',TS8,'DX1 H-V=',DYS4
       ENDIF
       ENDIF
       ENDIF
       ENDIF

       END

  SUBROUTINE MXINP (SYM,T,P,BINARY)
  IMPLICIT DOUBLE PRECISION (A-H,O-Z)
  PARAMETER (LSPEC = 6, LCRIT = 7, LNRTL = 8, LINIT=9)
  PARAMETER (R = 83.1439, Z=10,KKK=8)
  DIMENSION  TC(KKK),PC(KKK),AKK(KKK),OMEGA(KKK),GG(KKK),GQ(KKK),
 @     PAR1(KKK,KKK),PAR2(KKK,KKK),
 @       BINARY(KKK,KKK),RUN(KKK),QUN(KKK)
  CHARACTER*16 SYM(KKK), LINE, PREV_LINE, LINE2

       COMMON/PRA/PAR1,PAR2
       COMMON/CA/CUBIC,ACT
       COMMON/RN/RUN,QUN,VSTARL
       COMMON/CR/TC,PC,AKK,OMEGA,GQ,GG
       COMMON/MXACO/MXAC
       COMMON/EQU/ROT
       COMMON/KK/KK

       OPEN (LSPEC,FILE='SPECIES.TXT',STATUS='OLD')
       READ (LINIT,*) KK
       DO 20 I = 1,KK
       TC(I)=0.
       PC(I)=0.
         DO 10 J = 1,KKK
         BINARY(I,J)=0.
         PAR2(I,J)=0.
           IF (I.EQ.J) THEN
           PAR1(I,J) = 1
           ELSE
           PAR1(I,J)=0.
           ENDIF
10     CONTINUE
20     CONTINUE
       READ (LINIT,*) CUBIC
       READ (LINIT,*) ACT
       READ (LINIT,*) MXAC
       READ (LSPEC,'(I3)') ISPEC
```

```
         DO 50 I = 1,ISPEC
         READ (LSPEC,'(A16)') LINE
           PREV_LINE = LINE
 50      CONTINUE
 60      CONTINUE
         DO 90 I = 1,KK
         READ (LINIT,'(A16)') SYM(I)
90       CONTINUE
         READ (LINIT,*) T
         READ (LINIT,*) P
         READ (LINIT,*) ROT
C READ CRITICAL PROPERTY DATA
         OPEN (LCRIT,FILE='CRITICAL.TXT',STATUS='OLD')
         DO 130 I = 1,KK
         REWIND (LCRIT)
           DO 110 J = 1,ISPEC
         READ (LCRIT,88)
   @     LINE, TC(I),PC(I),AKK(I),OMEGA(I),RUN(I),QUN(I),GG(I),GQ(I)
 88      FORMAT(A13,F8.3,3F8.5,F5.3,F4.3,2F9.7)
           PC(I) = PC(I)
             IF (LINE .EQ. SYM(I)) GOTO 120
 110     CONTINUE
 120     CONTINUE
 130     CONTINUE
C GET BINARY PARAMETERS FOR ACTIVITY MODEL
         U = 0.0
         V = 0.0
         W = 0.0
         IF (ACT.EQ.1.) THEN
         OPEN (LNRTL,FILE='NRTL.TXT',STATUS='OLD')
         ELSE
           IF (ACT.EQ.2.) THEN
           OPEN (LNRTL,FILE='VANLAAR.TXT',STATUS='OLD')
           ELSE
             IF (ACT.EQ.3.) THEN
             OPEN (LNRTL,FILE='UNIQUAC.TXT',STATUS='OLD')
         ELSE
         IF ((ACT.EQ.5.).OR.(ACT.EQ.6.)) THEN
                OPEN (LNRTL,FILE='WILSON.TXT',STATUS='OLD')
                        ELSE
                        ENDIF
             ENDIF
           ENDIF
         ENDIF
         DO 150 I = 1,KK
         REWIND (LNRTL)
           DO 140 J = 1,KK
           REWIND (LNRTL)
             IF (J.NE.I) THEN
                        DO 135 K = 1,ISPEC**2
               READ (LNRTL,81,END=170) LINE,LINE2,U,V,W,TEM
81       FORMAT(A16,A16,F9.4,F9.4,F9.4,F9.4)
         IF ((LINE .EQ. SYM(I)).AND.(LINE2 .EQ. SYM(J))) THEN
         IF (TEM.EQ.T) THEN
```

```
            PAR1(I,J) = U
            PAR2(I,J) = V
            BINARY(I,J) = W
 82         FORMAT(A16,A16,F10.4,F10.4,F10.4,F10.4)
            GOTO 140
            ELSE
            ENDIF
            ELSE
            ENDIF
 135       CONTINUE
            ENDIF
 140        CONTINUE
 150          CONTINUE
            GOTO 170
 160        CONTINUE
            STOP
 170        CONTINUE
            T = T+273.15
            RETURN
            END

      SUBROUTINE MXEOSPAR(T,X1,BINARY)
C      SUBROUTINE TO DETERMINE AI'S AND BI'S BASED ON THE EOS USED
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (R = 83.1439, Z=10, KKK=8)
       DIMENSION  A(KKK),B(KKK),TC(KKK),PC(KKK),BEOS(KKK,KKK),
   @        AKK(KKK),OMEGA(KKK),AEOS(KKK,KKK),BINARY(KKK,KKK),
   @        X1(KKK),GG(KKK),GQ(KKK)

            COMMON/CA/CUBIC,ACT
            COMMON/AB/AEOS,BEOS
            COMMON/CR/TC,PC,AKK,OMEGA,GQ,GG
            COMMON/KK/KK

C     PURE COMPONENT A'S AND B'S FOR PENG-ROBINSON
C     NOTE THAT IT IS TEMPERATURE DEPENDENT
      IF ((CUBIC.EQ.1.).OR.(CUBIC.EQ.11.)) THEN
              DO 10 I = 1, KK
                 A(I) = 0.457235*((R*TC(I))**2)/PC(I)
                 B(I) = 0.077796*(R*TC(I))/PC(I)
C                BETA = 0.37464+1.54226*OMEGA(I)-0.26992*OMEGA(I)**2
                 BETA = 0.378893+1.4897153*OMEGA(I)-0.17131848*
   @        OMEGA(I)**2+0.0196554*OMEGA(I)**3
                 TR = T/TC(I)
C                ALPHA = (1 + BETA*(1 - SQRT(TR)))**2
                 ALPHA = BETA+(AKK(I)+GG(I)*(GQ(I)-TR)*(1-SQRT(TR)))*
   @          (1+SQRT(TR))*(0.7-TR)
                 AKI=(1+ALPHA*(1-SQRT(TR)))
                 A(I) = A(I)*AKI**2
  10        CONTINUE
            DO 65 I=1,KK
            DO 66 J=1,KK
            AEOS(I,J)=(A(I)+A(J))/2.*(1-BINARY(I,J))
            BEOS(I,J)=(B(I)+B(J))/2.*(1-BINARY(I,J))
```

```
 66          CONTINUE
 65          CONTINUE
             ENDIF
C    PURE COMPONENT A'S AND B'S FOR SOAVE-REDLICH-KWONG EOS
             IF (CUBIC.EQ.3.) THEN
              DO 300 I = 1,KK
                A(I) = 0.42748*(R**2)*(TC(I)**2)/PC(I)
                B(I) = 0.08664*R*TC(I)/PC(I)
                BETA = 0.48+1.574*OMEGA(I)-0.176*OMEGA(I)**2
                TR = T/TC(I)
                ALPHA = (1 + BETA*(1 - SQRT(TR)))**2
                A(I) = A(I)*ALPHA
 300         CONTINUE
             DO 615 I=1,KK
             DO 616 J=1,KK
             AEOS(I,J)=(A(I)+A(J))/2.*(1-BINARY(I,J))
             BEOS(I,J)=(B(I)+B(J))/2.*(1-BINARY(I,J))
 616         CONTINUE
 615         CONTINUE
             ENDIF
C    PURE COMPONENT A'S AND B'S FOR PENG-ROBINSON, WITH
C    PANAGIOTOPOULOS MIXING RULE
             IF (CUBIC.EQ.4.) THEN
              DO 100 I = 1, KK
                A(I) = 0.457235*((R*TC(I))**2)/PC(I)
                B(I) = 0.077796*(R*TC(I))/PC(I)
                BETA = 0.378893+1.4897153*OMEGA(I)-0.17131848*
   @         OMEGA(I)**2+0.0196554*OMEGA(I)**3
                TR = T/TC(I)
                ALPHA = BETA+AKK(I)*(1+SQRT(TR))*(0.7-TR)
                AKI=(1+ALPHA*(1-SQRT(TR)))
                A(I) = A(I)*AKI**2
 100         CONTINUE
             DO 650 I=1,KK
             DO 660 J=1,KK
             AEOS(I,J)=SQRT(A(I)*A(J))*(1-BINARY(I,J)+(BINARY(I,J)
   @                          -BINARY(J,I))*X1(I))
             IF (I.EQ.J) THEN
             BEOS(I,J)=(B(I)+B(J))/2.
             ENDIF
 660         CONTINUE
 650         CONTINUE
             ENDIF
C    PURE COMPONENT A'S AND B'S FOR PENG-ROBINSON, WITH
C    PANAGIOTOPOULOS QUADARTIC MIXING RULE
             IF (CUBIC.EQ.5.) THEN
              DO 1100 I = 1, KK
                A(I) = 0.457235*((R*TC(I))**2)/PC(I)
                B(I) = 0.077796*(R*TC(I))/PC(I)
                BETA = 0.378893+1.4897153*OMEGA(I)-0.17131848*
   @         OMEGA(I)**2+0.0196554*OMEGA(I)**3
                TR = T/TC(I)
                ALPHA = BETA+AKK(I)*(1+SQRT(TR))*(0.7-TR)
                AKI=(1+ALPHA*(1-SQRT(TR)))
```

```
             A(I) = A(I)*AKI**2
1100      CONTINUE
          SNRR=0.
          DO 6150 I=1,KK
          DO 6161 J=1,KK
          IF (I.LT.J) THEN
          AEOS(I,J)=SQRT(A(I)*A(J))*(1-BINARY(I,J))
          AEOS(J,I)=AEOS(I,J)
          ENDIF
6161      CONTINUE
          AEOS(I,I)=A(I)
          BEOS(I,I)=B(I)
6150      CONTINUE
          ENDIF

          RETURN
          END

          SUBROUTINE MXACT(T,X1,GAMMA,AE)
          IMPLICIT DOUBLE PRECISION (A-H,O-Z)
          PARAMETER (R = 83.1439, Z=10, KKK=8)
          DIMENSION X1(KKK),PAR1(KKK,KKK),PAR2(KKK,KKK),
  @                   RUN(KKK),QUN(KKK),G(KKK,KKK),TH(KKK),
  @                   PH(KKK),DL(KKK),DT(KKK,KKK),GR(KKK),
  @                   GC(KKK),GAMMA(KKK),XIJ(KKK,KKK),VSTARL(KKK),
  @                  XX(KKK,KKK),PHUN(KKK),THUN(KKK),QUNN(KKK,KKK),
  @                 ZQUN(KKK)
          COMMON/CA/CUBIC,ACT
          COMMON/PRA/PAR1,PAR2
          COMMON/RN/RUN,QUN,VSTARL
          COMMON/ACTIV/G,TH,PH,DL,DT,GR,GC
          COMMON/MXACO/MXAC
          COMMON/KK/KK

          IF (MXAC.EQ.0) THEN
          RETURN
          ENDIF

C CALCULATE AE, GAMMA(I) FOR NRTL EQUATION
          IF (ACT.EQ.1.) THEN
          DO 48 I=1,KK
            DO 44 J=1,KK
            DT(I,J)=PAR2(I,J)/1.987/T
            G(I,J)=EXP(-PAR1(I,J)*DT(I,J))
44          CONTINUE
48        CONTINUE
          AIS=0.0
          AIST=0.0
          DO 45 I=1,KK
          UU=0.0
          UUT=0.0
          UST=0.0
          USTT=0.0
          DD=0.0
```

```
             DDT=0.0
             DO 46 J=1,KK
               DS=0.0
               DSA=0.0
               US=0.0
               USA=0.0
                 DO 47 L=1,KK
                 US=X1(L)*DT(L,J)*G(L,J)
                 DS=X1(L)*G(L,J)
                 USA=USA+US
                 DSA=DSA+DS
47               CONTINUE
               UST=X1(J)*G(I,J)*(DT(I,J)-USA/DSA)/DSA
               USTT=USTT+UST
               DD=X1(J)*DT(J,I)*G(J,I)
               DDT=DDT+DD
               UU=X1(J)*G(J,I)
               UUT=UUT+UU
46             CONTINUE
             GAMMA(I)=DDT/UUT+USTT
             AIS=X1(I)*DDT/UUT
             AIST=AIST+AIS
45           CONTINUE
C THE UNITS OF AE IN BARS*CC/MOLE, TO GET CAL/MOLE MULTIPLY BY (1.987/83.145)
             AE=R*T*AIST
             RETURN
C CALCULATE AE, GAMMA(I) FOR VAN LAAR EQUATION
             ELSE
             IF (ACT.EQ.2.) THEN
             DO 49 I=1,KK
             VLL=0.
             VLLD=0.
             VL=0.
             VLD=0.
             DO 410 K=1,KK
               IF (I-K) 411,410,412
411            VL=PAR1(I,K)*(X1(K)*PAR1(K,I)/(X1(I)*PAR1(I,K)
  @              +X1(K)*PAR1(K,I)))**2
               VLL=VLL+VL
               GOTO 410
412              VLD=PAR1(I,K)*(X1(K)*PAR1(K,I)/(X1(I)*PAR1(I,K)
  @              +X1(K)*PAR1(K,I)))**2
                 VLLD=VLLD+VLD
410            CONTINUE
             GAMMA(I)=VLL+VLLD
49           CONTINUE
             GGVL=0.
             GVL=0.
             DO 414 I=1,KK-1
               DO 415 J=I+1,KK
               GVL=X1(I)*X1(J)*PAR1(J,I)*PAR1(I,J)/(X1(I)*PAR1(I,J)+X1(J)
  @               *PAR1(J,I))
                  GGVL=GGVL+GVL
415            CONTINUE
```

```
 414         CONTINUE
C THE UNITS OF AE IN KPA*CC, TO GET CAL/MOLE MULTIPLY BY (1.987/8314.5)
             AE=R*T*GGVL
             RETURN
C CALCULATE AE, GAMMA(I) FOR UNIQUAC EQUATION
C FIND SHAPE-SIZE PARAMETERS
             ELSE
             IF (ACT.EQ.3.) THEN
             TT=0.
             RR=0.
             RRT=0.
             TTT=0.
               DO 416 I=1,KK
               RR=RUN(I)*X1(I)
               TT=QUN(I)*X1(I)
               RRT=RRT+RR
               TTT=TTT+TT
 416           CONTINUE
                 DO 417 I=1,KK
                 TH(I)=QUN(I)*X1(I)/TTT
                 PH(I)=RUN(I)*X1(I)/RRT
                 DL(I)=Z*(RUN(I)-QUN(I))/2.-(RUN(I)-1.)
 417             CONTINUE
             XLT=0.
             XL=0.
                   DO 4 J=1,KK
                           XL=X1(J)*DL(J)
                           XLT=XLT+XL
 4                 CONTINUE
                     DO 418 I=1,KK
                             DO 419 J=1,KK
                             DT(J,I)=EXP(-PAR2(J,I)/1.987/T)
 419                         CONTINUE
 418                 CONTINUE
C
C CALCULATE GAMMA(I)
                       DO 420 I=1,KK
                       CC=0.
                             CCT=0.
                             CCTT=0.
                             CC1=0.0
                             CC1T=0.
                               DO 422 J=1,KK
                                       CC=TH(J)*DT(I,J)
                                       CC1=TH(J)*DT(J,I)
                                       CC1T=CC1T+CC1
                                       BB=0.
                                       BBT=0.
                                         DO 421 K=1,KK
                                         BB=TH(K)*DT(K,J)
                                         BBT=BBT+BB
 421                                     CONTINUE
                                       CCT=CC/BBT
                                       CCTT=CCTT+CCT
```

```
 422                          CONTINUE
               GR(I)=QUN(I)*(1.-LOG(CC1T)-CCTT)
                  GC(I)=LOG(PH(I)/X1(I))+Z*QUN(I)*LOG(TH(I)/PH(I))/2.
  @                         +DL(I)-PH(I)*XLT/X1(I)
                        GAMMA(I)=GR(I)+GC(I)
 420        CONTINUE
C CALCULATE AE
            AAT=0.
            AAP=0.
            AAB=0.
            AATT=0.
            AAPT=0.
            AABT=0.
            DO 423 I=1,KK
            THT=0.
            THTT=0.
             DO 424 J=1,KK
             THT=TH(J)*DT(J,I)
             THTT=THTT+THT
 424         CONTINUE
            AAT=QUN(I)*X1(I)*LOG(THTT)
            AAP=Z*QUN(I)*X1(I)*LOG(TH(I)/PH(I))/2.
            AAB=X1(I)*LOG(PH(I)/X1(I))
            AATT=AATT+AAT
            AAPT=AAPT+AAP
            AABT=AABT+AAB
 423        CONTINUE
            GUN=AABT+AAPT-AATT
            AE=R*T*GUN
            ENDIF
            ENDIF
            ENDIF

C KNOX'S MODEL
            IF (ACT.EQ.4.) THEN
            DO 443 I=1,KK
            DO 444 J=I+1,KK
            QUNN(I,J)=PAR2(I,J)
            QUNN(J,I)=PAR2(J,I)
444         CONTINUE
            QUNN(I,I)=QUN(I)
            PAR1(I,I)=0.
            PAR2(I,I)=0.
443         CONTINUE

            DO 445 I=1,KK
            QQA=0.
            DO 446 J=1,KK
            QQ=X1(J)*QUNN(I,J)
            QQA=QQA+QQ
 446        CONTINUE
            ZQUN(I)=QQA
 445        CONTINUE
```

```
      ASUM=0.
      ALUS=0.
      DO 346 I=1,KK
      ASU=RUN(I)*X1(I)
      ASUM=ASUM+ASU
      ALU=ZQUN(I)*X1(I)
      ALUS=ALUS+ALU
 346  CONTINUE
      RSS=0.
      DO 345 I=1,KK
      PHUN(I)=X1(I)*RUN(I)/ASUM
      THUN(I)=ZQUN(I)*X1(I)/ALUS
      RS=X1(I)*LOG(PHUN(I)/X1(I))
      RSS=RSS+RS
 345  CONTINUE
      CALL XSOLVE(T,THUN,XX)
      DO 399 I=1,KK
      QSS=0.
      DO 400 J=1,KK
      IF (I.NE.J) THEN
      QS=XX(I,J)
      QSS=QSS+QS
      ENDIF
 400  CONTINUE
      XX(I,I)=1.-QSS
 399  CONTINUE
C     IF (KK.EQ.2) THEN
C     TT=ZQUN(2)*X1(2)/ZQUN(1)/X1(1)
C     XX(1,2)=2.*TT/(1.+TT+SQRT(TT**2.+1.+2.*TT*(2./
C    @     EXP(-1.E4*/R/T)-1.)))
C
C     XX(2,1)=XX(1,2)/TT
C     XX(1,1)=1.-XX(1,2)
C     XX(2,2)=1.-XX(2,1)
C     ENDIF

      FSS=0.
      DO 37 I=1,KK
      FS=ZQUN(I)*X1(I)*LOG(XX(I,I)/PHUN(I))/2.
      FSS=FSS+FS
      GAMMA(I)=1.-PHUN(I)/X1(I)+LOG(PHUN(I)/X1(I))+ZQUN(I)*
   @     (PHUN(I)/THUN(I)-1.+LOG(XX(I,I)/PHUN(I)))/2.
 37   CONTINUE
      AE=R*T*(RSS+FSS)
      ENDIF

C WILSON'S EQUATION

      IF ((ACT.EQ.5.).OR.(ACT.EQ.6.)) THEN
      DO 695 I=1,KK
      DO 696 J=1,KK
      DT(I,J)=VSTARL(J)/VSTARL(I)*EXP(-PAR1(I,J)/1.987/T)
      IF (I.EQ.J) THEN
```

```
          DT(I,J)=1.
          ENDIF
 696      CONTINUE
 695      CONTINUE
C         DT(1,2)=0.95*EXP(-PAR1(I,J)/1.987/T)
C         DT(2,1)=1.07*EXP(-PAR1(I,J)/1.987/T)
          AIST=0.0
          AIS1T=0.
          DO 425 I=1,KK
          USTT=0.0
          DDT=0.0
          RTLL=0.
          SSRT=0.
          DO 426 J=1,KK
           USA=0.0
          ANNT=0.
          DO 427 L=1,KK
          US=X1(L)*DT(J,L)
          USA=USA+US
          ANN=X1(L)*VSTARL(L)/VSTARL(J)
          ANNT=ANNT+ANN
 427      CONTINUE
          UST=X1(J)*DT(J,I)/USA
          USTT=USTT+UST
          DD=X1(J)*DT(I,J)
          DDT=DDT+DD
          RTL=X1(J)*VSTARL(J)/VSTARL(I)
          RTLL=RTLL+RTL
          SSR=X1(J)*VSTARL(I)/VSTARL(J)/ANNT
          SSRT=SSRT+SSR
 426      CONTINUE
          GAMMA(I)=-LOG(DDT)+1.-USTT
          IF (ACT.EQ.6.) THEN
          GAMMA(I)=-LOG(DDT)-USTT+LOG(RTLL)+SSRT
          ENDIF
          AIS=X1(I)*LOG(DDT)
          AIS1=X1(I)*LOG(RTLL)
          AIS1T=AIS1T+AIS1
          AIST=AIST+AIS
 425      CONTINUE
C THE UNITS OF AE IN BARS*CC/MOLE, TO GET CAL/MOLE MULTIPLY BY (1.987/83.145)
          AE=-R*T*AIST
          IF (ACT.EQ.6.) THEN
          AE=-R*T*(AIST-AIS1T)
          ENDIF
          RETURN

          ENDIF
          RETURN
          END

          SUBROUTINE MXMIX(T,BINARY,CROSS,X1,AE)
          IMPLICIT DOUBLE PRECISION (A-H,O-Z)
          PARAMETER (R = 83.1439, Z=10, KKK=8)
```

```
      DIMENSION CROSS(KKK,KKK),X1(KKK),BINARY(KKK,KKK),
     @          AEOS(KKK,KKK),BEOS(KKK,KKK)

      EXTERNAL TOCHI

      REAL*8 FUN
      COMMON/CA/CUBIC,ACT
      COMMON/AMBM/AM,BM
      COMMON/AB/AEOS,BEOS
      COMMON/SUMM/QMX,DMX
      COMMON/S5/SS5
      COMMON/FUNC/SUNT,FUNN,AAE,Q1,XRTT1,XRTT
      COMMON/KK/KK

      IF (CUBIC.EQ.4.) THEN
      SSS=0.
      SSSU=0.
      DO 25 I=1,KK
      DO 26 J=1,KK
      SSU=AEOS(I,J)*X1(I)*X1(J)
      SSSU=SSSU+SSU
 26   CONTINUE
      SS=X1(I)*BEOS(I,I)
      SSS=SSS+SS
 25   CONTINUE
      AM=SSSU
      BM=SSS
      ENDIF

      IF (CUBIC.EQ.5.) THEN
      SSRU=0.
      DO 925 I=1,KK
      DO 926 J=1,KK
      SSU=AEOS(I,J)*X1(I)*X1(J)
      SSRU=SSRU+SSU
 926  CONTINUE
 925  CONTINUE
      SDR=0.
      SNTH=0.
      DO 927 I=1,KK
      DO 928 J=1,KK
      IF (I.LT.J)  THEN
      SD=X1(I)*X1(J)*(X1(I)-X1(J))*BINARY(J,I)
      SDR=SDR+SD
      ENDIF
      IF (I.GT.J)  THEN
      SD=X1(I)*X1(J)*(X1(I)-X1(J))*BINARY(I,J)
      SDR=SDR+SD
      ENDIF
 928  CONTINUE
      SNT=BEOS(I,I)*X1(I)
      SNTH=SNTH+SNT
 927  CONTINUE
```

```
        BM=SNTH
        SS5=SDR
        AM=SSRU
        ENDIF

        IF (CUBIC.EQ.11.) THEN
        SUNT=0.
        XRTT=0.
        XRTT1=0.
        Q1=-.53
        DO 1237 I=1,KK
        SUN=X1(I)*AEOS(I,I)/BEOS(I,I)
        SUNT=SUNT+SUN
        XRT1=X1(I)*LOG(BEOS(I,I))
        XRTT1=XRTT1+XRT1
        XRT=X1(I)*(BEOS(I,I)-AEOS(I,I)/R/T)
        XRTT=XRTT+XRT
1237    CONTINUE
        FUNN=R*T
        AAE=AE
        DO 1239 I=1,20
        BM=ZBRENT(TOCHI,5.,80.,0.0001)
1239    CONTINUE
        AM=BM*(SUNT+1./Q1*(AE+R*T*(LOG(BM)-XRTT1)))
        ENDIF

        DO 51 I=1,KK
                DO 52 J=1,KK
        IF (I.NE.J) THEN
        CROSS(I,J)=((BEOS(I,I)-AEOS(I,I)/R/T)+(BEOS(J,J)-AEOS(J,J)
  @         /R/T))/2.*(1-BINARY(I,J))
        ELSE
        CROSS(I,J)=((BEOS(I,I)-AEOS(I,I)/R/T)+(BEOS(J,J)-AEOS(J,J)
  @                /R/T))/2.
        ENDIF
52              CONTINUE
51      CONTINUE

        IF ((CUBIC.EQ.1.).OR.(CUBIC.EQ.3.)) THEN
        STRAIGHTT=0.
        QMX=0.
        SMMM=0.
        UMMM=0.
        DO 53 I=1,KK
        SUMT=0.
        SMM=0.
                DO 54 J=1,KK
        SUM=X1(I)*X1(J)*CROSS(I,J)
        SUMT=SUMT+SUM
54              CONTINUE
        QMX=QMX+SUMT
        STRAIGHT=X1(I)*AEOS(I,I)/BEOS(I,I)/R/T
        STRAIGHTT=STRAIGHTT+STRAIGHT
53      CONTINUE
```

```
      IF ((CUBIC.EQ.1.)) THEN
      C=1./SQRT(2.)*LOG(SQRT(2.)-1.)
      DMX=STRAIGHTT+AE/C/R/T
      BM=QMX/(1-DMX)
      AM=BM*DMX*R*T
      ELSE
      IF (CUBIC.EQ.3.) THEN
      C=-LOG(2.)
      DMX=STRAIGHTT+AE/C/R/T
      BM=QMX/(1-DMX)
      AM=BM*DMX*R*T
      ELSE
      ENDIF
      ENDIF
      ENDIF
      RETURN
      END

      FUNCTION TOCHI(ABM)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      COMMON/FUNC/SUNT,FUNN,AAE,Q1,XRTT1,XRTT
      TOCHI=ABM*(1.-SUNT/FUNN-AAE/Q1/FUNN+XRTT1/Q1)-ABM*LOG(ABM)/Q1
@     -XRTT
      RETURN
      END

      SUBROUTINE MXVOL(T,P,VL,VG)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (R = 83.1439, Z=10, KKK=8)
      REAL*8 RTR(3),RTI(3),A(4),RTRR(4),RTII(4),A5(5)
      REAL*8 VL,VG

      COMMON/AMBM/AM,BM
      COMMON/CA/CUBIC,ACT
      COMMON/S5/SS5
      COMMON/KK/KK

      VL=1.E37
      VG=0.0
      IF ((CUBIC.EQ.1.).OR.(CUBIC.EQ.4.).OR.
@       (CUBIC.EQ.11.)) THEN
      A(4)=1
      A(3)=BM-R*T/P
      A(2)=(AM-2*R*T*BM)/P-3*BM**2
      A(1)=BM**3+(R*T*BM**2-AM*BM)/P
      ELSE
      IF (CUBIC.EQ.5.) THEN
      A5(5)=1
      A5(4)=BM-R*T/P
      A5(3)=(AM-2.*R*T*BM)/P-3*BM**2.
      A5(2)=BM**3.+(R*T*BM**2.-AM*BM+BM*SS5/R/T)/P
      A5(1)=-BM**2.*SS5/R/T/P
      ELSE
                           IF (CUBIC.EQ.3.) THEN
```

```
                        A(4)=1
                        A(3)=-R*T/P
                        A(2)=(AM-R*T*BM)/P-BM**2
                        A(1)=-(AM*BM)/P
                        ELSE
                        ENDIF
      ENDIF
      ENDIF
      M=3
      DD=1.E-7
      DDD=1.E-7
      IF (CUBIC.EQ.5.) THEN
      M=4
      CALL ZRHQR(A5,M,RTRR,RTII)
      DO 631 I=1,4
      IF (ABS(RTII(I)).LT.DD) THEN
      IF (RTRR(I).GT.DDD) THEN
      VL=MIN(VL,RTRR(I))
      VG=MAX(VG,RTRR(I))
      ENDIF
      ENDIF
631   CONTINUE
      RETURN
      ENDIF
      CALL ZRHQR(A,M,RTR,RTI)
      DO 63 I=1,3
      IF (ABS(RTI(I)).LT.DD) THEN
      IF (RTR(I).GT.DDD) THEN
      VL=MIN(VL,RTR(I))
      VG=MAX(VG,RTR(I))
      ENDIF
      ENDIF
63    CONTINUE
      RETURN
      END

      SUBROUTINE MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (R = 83.1439, Z=10, KKK=8)
      DIMENSION GAMMA(KKK),X1(KKK),A(KKK),B(KKK),CROSS(KKK,KKK),
     @          PHI(KKK),AEOS(KKK,KKK),BEOS(KKK,KKK),
     @    BINARY(KKK,KKK),VSTARL(KKK),GQ(KKK),GG(KKK),
     @          TC(KKK),PC(KKK),AKK(KKK),OMEGA(KKK)


      COMMON/AMBM/AM,BM
      COMMON/AB/AEOS,BEOS
      COMMON/CA/CUBIC,ACT
      COMMON/SUMM/QMX,DMX
      COMMON/CR/TC,PC,AKK,OMEGA,GQ,GG
      COMMON/KK/KK

      IF (CUBIC.EQ.1.) THEN
      C=1./SQRT(2.)*LOG(SQRT(2.)-1.)
```

```
        DO 711 I=1,KK
                 QQQ=0.
                 QQSS=0.
                 DO 721 J=1,KK
                 QQ=X1(J)*CROSS(I,J)
                 QQQ=QQQ+QQ
721              CONTINUE
        DN=AEOS(I,I)/BEOS(I,I)/R/T+GAMMA(I)/C
        DNBM=2.*QQQ/(1.-DMX)-QMX*(1.-DN)/(1.-DMX)**2.
        DNAM=R*T*(DMX*DNBM+BM*DN)
        PHI(I)=-LOG(P*(V-BM)/R/T)+DNBM/BM*(P*V/R/T-1.)
 @           +AM/2./SQRT(2.)/BM/R/T*(DNAM/AM-DNBM/BM)
 @           *LOG((V+BM*(1.-SQRT(2.)))/(V+BM*(1.+SQRT(2.))))
711     CONTINUE
        ENDIF
        IF (CUBIC.EQ.3.) THEN
        C=-LOG(2.)
        DO 751 I=1,KK
                 QQQ=0.0
                 DO 761 J=1,KK
                 QQ=X1(J)*CROSS(I,J)
                 QQQ=QQQ+QQ
761              CONTINUE
        DN=AEOS(I,I)/BEOS(I,I)/R/T+GAMMA(I)/C
        DNBM=2.*QQQ/(1.-DMX)-QMX*(1.-DN)/(1.-DMX)**2.
        DNAM=R*T*(DMX*DNBM+BM*DN)
        PHI(I)=-LOG(P*(V-BM)/R/T)+DNBM/(V-BM)-DNAM/R/T/BM*LOG((V+BM)
 @      /V)+AM*DNBM*LOG((V+BM)/V)/BM**2./R/T-AM*DNBM/(V+BM)/R/T/BM
751     CONTINUE
        ENDIF
        IF (CUBIC.EQ.4.) THEN
        DO 435 K=1,KK
        SNN=0.
        STNN=0.
        STT=0.
        DO 436 I=1,KK
        ST=X1(I)*(AEOS(I,K)+AEOS(K,I))
        STT=STT+ST
        IF (I.NE.K) THEN
        STN=X1(I)*(BINARY(K,I)-BINARY(I,K))*SQRT(AEOS(K,K)*AEOS(I,I))
        STNN=STNN+STN
        ENDIF
        DO 437 J=1,KK
        IF (I.NE.J) THEN
        SN=X1(I)**2.*X1(J)*(BINARY(I,J)-BINARY(J,I))*SQRT(AEOS(I,I)
 @               *AEOS(J,J))
        SNN=SNN+SN
        ENDIF
437     CONTINUE
436     CONTINUE
        PHI(K)=BEOS(K,K)*(P*V/R/T-1.)/BM-LOG(P*(V-BM)/R/T)+((STT-SNN+
 @               X1(K)*STNN)/AM-BEOS(K,K)/BM)
 @           *AM/2./SQRT(2.)/BM/R/T*LOG((V+BM*(1.-SQRT(2.)))/
 @      (V+BM*(1.+SQRT(2.))))
```

```
435       CONTINUE
          ENDIF

          IF (CUBIC.EQ.5.) THEN
          DO 4435 K=1,KK
          SKK=0.
          SIKK=0.
          STKK=0.
          SOKK=0.
          DO 4436 I=1,KK
          DO 4423 J=1,KK
          IF (I.LT.J) THEN
          SK=BINARY(J,I)*X1(I)*X1(J)*(X1(I)-X1(J))*SQRT(AEOS(I,I)
  @       *AEOS(J,J))
          SKK=SKK+SK
          ENDIF
4423      CONTINUE
          IF (I.LT.K) THEN
          STK=BINARY(K,I)*X1(I)**2.
          SIK=-BINARY(K,I)*X1(I)*X1(K)
          SOK=X1(I)*(1.-BINARY(I,K))*SQRT(AEOS(I,I)*AEOS(J,J))
          STKK=STKK+STK
          SIKK=SIKK+SIK
          SOKK=SOKK+SOK
          ENDIF
          IF (I.GT.K) THEN
          STK=-BINARY(I,K)*X1(I)**2.
          SIK=X1(I)*X1(K)*BINARY(I,K)
          SOK=X1(I)*(1.-BINARY(K,I))*SQRT(AEOS(I,I)*AEOS(J,J))
          STKK=STKK+STK
          SIKK=SIKK+SIK
          SOKK=SOKK+SOK
          ENDIF
          IF (I.EQ.K) THEN
          SOK=X1(I)*AEOS(I,I)
          SOKK=SOKK+SOK
          ENDIF
4436      CONTINUE
          PHI(K)=BEOS(K,K)*(P*V/R/T-1.)/BM-LOG(P*(V-BM)/R/T)+
  @       (-AM*BEOS(K,K)+2.*BM*SOKK-(2.*BEOS(K,K)/BM*SKK-2.*SIKK-STKK))
  @       /2./SQRT(2.)/BM**2./R/T*LOG((V+BM*(1.-SQRT(2.)))/
  @       (V+BM*(1.+SQRT(2.))))+(2.*BEOS(K,K)/BM*SKK-2.*SIKK-STKK)/2.
  @       /BM**2./R/T*LOG(V**2./(V**2.+2.*BM*V-BM**2.))
4435      CONTINUE
          ENDIF


          IF (CUBIC.EQ.11.) THEN
          DO 71731 I=1,KK
          Q1=-0.53
          C1=-1./R/T
          C2=1.
          C3=AM/R/T-BEOS(I,I)+AEOS(I,I)/R/T
          D1=1./R/T/BM
```

```
        D2=-1./BM*(AM/R/T/BM+1./Q1)
        D3=-AEOS(I,I)/R/T/BEOS(I,I)-1./Q1*(GAMMA(I)
  @     +LOG(BM/BEOS(I,I))-1.)
        DNBM=(D1*C3-C1*D3)/(D2*C1-D1*C2)
        DNAM=(C2*D3-C3*D2)/(D2*C1-D1*C2)
        PHI(I)=-LOG(P*(V-BM)/R/T)+DNBM/BM*(P*V/R/T-1.)
  @         +AM/2./SQRT(2.)/BM/R/T*(DNAM/AM-DNBM/BM)
  @         *LOG((V+BM*(1-SQRT(2.)))/(V+BM*(1+SQRT(2.))))
71731   CONTINUE
        ENDIF

        RETURN
        END

        SUBROUTINE MXBUBBLE(T,P,BINARY,CROSS,VL,VG)
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        PARAMETER (MAXIT=200,ERR=1.E-3,ERRR=1.E-5)
        PARAMETER (R = 83.1439, Z=10, KKK=8)
        PARAMETER (CON=1.4,CON2=CON*CON,BIG=1.E30,NTAB=10,SAFE=2.)
        PARAMETER(NDATA=1000)
        DIMENSION X(KKK,NDATA),Y(KKK,NDATA),X1(KKK),
  @     PAR1(KKK,KKK),PAR2(KKK,KKK),
  @              BINARY(KKK,KKK),CROSS(KKK,KKK),
  @     PHIV(KKK),PHIL(KKK),PHI(KKK),DK(KKK),SIT(MAXIT),
  @              GAMMA(KKK),GAMMAV(KKK),GAMMAL(KKK)


        COMMON/CA/CUBIC,ACT
        COMMON/PHUG/PHIV,PHIL
        COMMON/XY/X,Y
        COMMON/ALV/AEL,AEV
        COMMON/GLV/GAMMAV,GAMMAL
        COMMON/RN/RUN,QUN,VSTARL
        COMMON/KK/KK
        COMMON/ICO/ICOUNT

        DO 1 I=1,KK
        PHI(I)=0.
        PHIL(I)=0.
        PHIV(I)=0.
        X1(I)=0.
1       CONTINUE
        SIT(1)=1.E37
        NSD=0.
26      CONTINUE
        DO 3000 I=2,MAXIT
        SIT(I)=0.
3000    CONTINUE
        DO 24 ITER=2,MAXIT
        DO 27 I=1,KK
        X1(I)=X(I,ICOUNT)
27      CONTINUE
        CALL MXACT(T,X1,GAMMA,AE)
        DO 3131 I=1,KK
```

```
          GAMMAL(I)=GAMMA(I)
3131      CONTINUE
          AEL=AE
          CALL MXMIX(T,BINARY,CROSS,X1,AE)
          CALL MXVOL(T,P,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 29 I=1,KK
          PHIL(I)=PHI(I)
29        CONTINUE
          NSD=NSD+ICOUNT
          IF (NSD.EQ.ICOUNT) THEN
          DO 210 I=1,KK
          X1(I)=Y(I,ICOUNT-1)
210       CONTINUE
          ELSE
          DO 213 I=1,KK
          X1(I)=Y(I,ICOUNT)
213       CONTINUE
          ENDIF
          CALL MXACT(T,X1,GAMMA,AE)
          DO 3133 I=1,KK
          GAMMAV(I)=GAMMA(I)
3133      CONTINUE
          AEV=AE
          CALL MXMIX(T,BINARY,CROSS,X1,AE)
          CALL MXVOL(T,P,VL,VG)
          V=VG
          CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 211 I=1,KK
          PHIV(I)=PHI(I)
211       CONTINUE
          DO 212 I=1,KK
          DK(I)=EXP(PHIL(I))/EXP(PHIV(I))
212       CONTINUE
          DO 22 I=1,KK
          SI=DK(I)*X(I,ICOUNT)
          SIT(ITER)=SIT(ITER)+SI
22        CONTINUE
          IF (ABS(SIT(ITER)-SIT(ITER-1)).LT.ERR) THEN
          GOTO 25
          ENDIF
          DO 23 I=1,KK
          Y(I,ICOUNT)=DK(I)*X(I,ICOUNT)/SIT(ITER)
23        CONTINUE
24        CONTINUE
          PAUSE 'TOO MANY ITERATIONS IN MXBUBBLE'
25        IF ((ABS(LOG(SIT(ITER)))-0.).LT. ERRR) THEN
          RETURN
          ELSE
          P=P*SIT(ITER)
          GOTO 26
          ENDIF
          RETURN
```

```
        END

        SUBROUTINE MXDEW(T,P,BINARY,CROSS,VL,VG)
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        PARAMETER (MAXIT=200,ERR=1.E-3,ERRR=1.E-5)
        PARAMETER (R = 83.1439, Z=10, KKK=8)
        PARAMETER (CON=1.4,CON2=CON*CON,BIG=1.E30,NTAB=10,SAFE=2.)
        PARAMETER(NDATA=1000)
        DIMENSION X(KKK,NDATA),Y(KKK,NDATA),X1(KKK),
  @    PAR1(KKK,KKK),PAR2(KKK,KKK),
  @                 BINARY(KKK,KKK),CROSS(KKK,KKK),
  @                 GAMMA(KKK),PHIL(KKK),
  @    PHIV(KKK),PHI(KKK),DK(KKK),SIT(MAXIT),
  @                 GAMMAV(KKK),GAMMAL(KKK),VSTARL(KKK)


        COMMON/CA/CUBIC,ACT
        COMMON/PHUG/PHIV,PHIL
        COMMON/XY/X,Y
        COMMON/ALV/AEL,AEV
        COMMON/GLV/GAMMAV,GAMMAL
        COMMON/RN/RUN,QUN,VSTARL
        COMMON/KK/KK
        COMMON/ICO/ICOUNT

        DO 1 I=1,KK
        PHI(I)=0.
        PHIL(I)=0.
        PHIV(I)=0.
        X1(I)=0.
1       CONTINUE
        SIT(1)=1.E37
        NSD=0.
26      CONTINUE
        DO 3000 I=2,MAXIT
        SIT(I)=0.
3000    CONTINUE
        DO 24 ITER=2,MAXIT
        DO 27 I=1,KK
        X1(I)=Y(I,ICOUNT)
27      CONTINUE
        CALL MXACT(T,X1,GAMMA,AE)
        DO 3131 I=1,KK
        GAMMAV(I)=GAMMA(I)
3131    CONTINUE
        AEV=AE
        CALL MXMIX(T,BINARY,CROSS,X1,AE)
        CALL MXVOL(T,P,VL,VG)
        V=VG
        CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 29 I=1,KK
        PHIV(I)=PHI(I)
29      CONTINUE
        NSD=NSD+ICOUNT
```

```
        IF (NSD.EQ.ICOUNT) THEN
        DO 210 I=1,KK
        X1(I)=X(I,ICOUNT-1)
210     CONTINUE
        ELSE
        DO 213 I=1,KK
        X1(I)=X(I,ICOUNT)
213     CONTINUE
        ENDIF
        CALL MXACT(T,X1,GAMMA,AE)
        DO 3133 I=1,KK
        GAMMAL(I)=GAMMA(I)
3133    CONTINUE
        AEV=AE
        CALL MXMIX(T,BINARY,CROSS,X1,AE)
        CALL MXVOL(T,P,VL,VG)
        V=VL
        CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 211 I=1,KK
        PHIL(I)=PHI(I)
211     CONTINUE
        DO 212 I=1,KK
        DK(I)=EXP(PHIL(I))/EXP(PHIV(I))
212     CONTINUE
        DO 22 I=1,KK
        SI=Y(I,ICOUNT)/DK(I)
        SIT(ITER)=SIT(ITER)+SI
22      CONTINUE
        IF (ABS(SIT(ITER)-SIT(ITER-1)).LT.ERR) THEN
        GOTO 25
        ENDIF
        DO 23 I=1,KK
        X(I,ICOUNT)=Y(I,ICOUNT)/DK(I)/SIT(ITER)
23      CONTINUE
24      CONTINUE
        PAUSE 'TOO MANY ITERATIONS IN MXBUBBLE'
25      IF ((ABS(LOG(SIT(ITER)))-0.).LT. ERRR) THEN
        RETURN
        ELSE
        P=P/SIT(ITER)
        GOTO 26
        ENDIF
        RETURN
        END

        SUBROUTINE  MXBUBBLEP(T,P,BINARY,CROSS,VL,VG)
        IMPLICIT DOUBLE PRECISION (A-H,O-Z)
        PARAMETER (MAXIT=200,ERR=1.E-3,ERRR=1.E-5)
        PARAMETER (R = 83.1439, Z=10, KKK=8)
        PARAMETER (CON=1.4,CON2=CON*CON,BIG=1.E30,NTAB=10,SAFE=2.)
        PARAMETER (NDATA=1000)
        DIMENSION X(KKK,NDATA),Y(KKK,NDATA),X1(KKK),
   @    PAR1(KKK,KKK),PAR2(KKK,KKK),
   @                BINARY(KKK,KKK),CROSS(KKK,KKK),
```

```
     @                    GAMMA(KKK),PHIL(KKK),
     @                    PHIV(KKK),PHI(KKK),DK(KKK),SIT(MAXIT),
     @                    GAMMAV(KKK),GAMMAL(KKK),DPHIDP(KKK),
     @                    DPHIDPV(KKK),DPHIDPL(KKK),DKDP(KKK),
     @                    ADERL(NTAB,NTAB),ADERV(NTAB,NTAB),PHIL_H(KKK),
     @                    PHIL_MH(KKK),PHIV_H(KKK),PHIV_MH(KKK),PHIL1_H(KKK),
     @                    PHIL1_MH(KKK),PHIV1_H(KKK),PHIV1_MH(KKK),VSTARL(KKK)

          COMMON/CA/CUBIC,ACT
          COMMON/PHUG/PHIV,PHIL
          COMMON/XY/X,Y
          COMMON/ALV/AEL,AEV
          COMMON/GLV/GAMMAV,GAMMAL
          COMMON/CRIT/BT
          COMMON/RN/RUN,QUN,VSTARL
          COMMON/KK/KK
          COMMON/ICO/ICOUNT


          DO 1 I=1,KK
          PHI(I)=0.
          PHIL(I)=0.
          PHIV(I)=0.
          X1(I)=0.
    1     CONTINUE
          SIT(1)=1.E37
          NSD=0.
    26    CONTINUE
          DO 3000 I=2,MAXIT
          SIT(I)=0.
    3000  CONTINUE
          DO 24 ITER=2,MAXIT
          DO 27 I=1,KK
          X1(I)=X(I,ICOUNT)
    27    CONTINUE
          CALL MXEOSPAR(T,X1,BINARY)
          CALL MXACT(T,X1,GAMMA,AE)
          DO 3131 I=1,KK
          GAMMAL(I)=GAMMA(I)
    3131  CONTINUE
          AEL=AE
          CALL MXMIX(T,BINARY,CROSS,X1,AE)
          CALL MXVOL(T,P,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 29 I=1,KK
          PHIL(I)=PHI(I)
    29    CONTINUE
          H=0.001
          P1=P+H
          CALL MXVOL(T,P1,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P1,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
```

```
          DO 291 I=1,KK
          PHIL_H(I)=PHI(I)
291       CONTINUE
          P2=P-H
          CALL MXVOL(T,P2,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P2,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 292 I=1,KK
          PHIL_MH(I)=PHI(I)
292       CONTINUE
          DO 13 K=1,KK
          HH=H
          ADERL(1,1)=(PHIL_H(K)-PHIL_MH(K))/(2.0*HH)
          ERR1=BIG
          DO 12 I=2,NTAB
          HH=HH/CON
          P11=P+HH
          CALL MXVOL(T,P11,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P11,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 302 I1=1,KK
          PHIL1_H(I1)=PHI(I1)
302       CONTINUE
          P22=P-HH
          CALL MXVOL(T,P22,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P22,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 303 I2=1,KK
          PHIL1_MH(I2)=PHI(I2)
303       CONTINUE
          ADERL(1,I)=(PHIL1_H(K)-PHIL1_MH(K))/(2.0*HH)
          FAC=CON2
          DO 11 J=2,I
          ADERL(J,I)=(ADERL(J-1,I)*FAC-ADERL(J-1,I-1))/(FAC-1.)
          FAC=CON2*FAC
          ERRT1=MAX(ABS(ADERL(J,I)-ADERL(J-1,I)),ABS(ADERL(J,I)-ADERL
   @      (J-1,I-1)))
          IF (ERRT1.LE.ERR1) THEN
          ERR1=ERRT1
          DPHIDPL(K)=ADERL(J,I)
          ENDIF
11        CONTINUE
          IF(ABS(ADERL(I,I)-ADERL(I-1,I-1)).GE.SAFE*ERR1) GOTO 4
12        CONTINUE
4         CONTINUE
13        CONTINUE
          NSD=NSD+ICOUNT
          IF (NSD.EQ.ICOUNT) THEN
          DO 210 I=1,KK
          X1(I)=Y(I,ICOUNT-1)
210       CONTINUE
          ELSE
          DO 213 I=1,KK
          X1(I)=Y(I,ICOUNT)
```

```
213     CONTINUE
        ENDIF
        CALL MXEOSPAR(T,X1,BINARY)
        CALL MXACT(T,X1,GAMMA,AE)
        DO 3133 I=1,KK
        GAMMAV(I)=GAMMA(I)
3133    CONTINUE
        AEV=AE
        CALL MXMIX(T,BINARY,CROSS,X1,AE)
        CALL MXVOL(T,P,VL,VG)
        V=VG
        CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 211 I=1,KK
        PHIV(I)=PHI(I)
211     CONTINUE
        P_V=P+H
        CALL MXVOL(T,P,VL,VG)
        V=VG
        CALL MXFUGACITY1(T,P_V,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 2211 I=1,KK
        PHIV_H(I)=PHI(I)
2211    CONTINUE
        P_VH=P-H
        CALL MXVOL(T,P_VH,VL,VG)
        V=VG
        CALL MXFUGACITY1(T,P_VH,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 2311 I=1,KK
        PHIV_MH(I)=PHI(I)
2311    CONTINUE
        DO 133 K=1,KK
        HH1=H
        ADERV(1,1)=(PHIV_H(K)-PHIV_MH(K))/(2.0*HH1)
        ERR22=BIG
        DO 123 I=2,NTAB
        HH1=HH1/CON
        P33=P+HH1
        CALL MXVOL(T,P33,VL,VG)
        V=VG
        CALL MXFUGACITY1(T,P33,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 2511 I3=1,KK
        PHIV1_H(I3)=PHI(I3)
2511    CONTINUE
        P44=P-HH1
        CALL MXVOL(T,P44,VL,VG)
        V=VG
        CALL MXFUGACITY1(T,P44,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 2411 I4=1,KK
        PHIV1_MH(I4)=PHI(I4)
2411    CONTINUE
        ADERV(1,I)=(PHIV1_H(K)-PHIV1_MH(K))/(2.0*HH1)
        FAC=CON2
        DO 113 J=2,I
        ADERV(J,I)=(ADERV(J-1,I)*FAC-ADERV(J-1,I-1))/(FAC-1.)
        FAC=CON2*FAC
```

```
           ERRT2=MAX(ABS(ADERV(J,I)-ADERV(J-1,I)),
     @     ABS(ADERV(J,I)-ADERV(J-1,I-1)))
           IF (ERRT2.LE.ERR22) THEN
           ERR22=ERRT2
           DPHIDPV(K)=ADERV(J,I)
           ENDIF
 113       CONTINUE
           IF(ABS(ADERV(I,I)-ADERV(I-1,I-1)).GE.SAFE*ERR22) GOTO 43
 123       CONTINUE
 43        CONTINUE
 133       CONTINUE
           DO 212 I=1,KK
           DK(I)=EXP(PHIL(I))/EXP(PHIV(I))
 212       CONTINUE
           DO 31 I=1,KK
           DKDP(I)=DK(I)*(DPHIDPL(I)-DPHIDPV(I))
 31        CONTINUE
           SSS=0.
           DO 22 I=1,KK
           SS=X(I,ICOUNT)*DKDP(I)
           SSS=SSS+SS
           SI=DK(I)*X(I,ICOUNT)
           SIT(ITER)=SIT(ITER)+SI
 22        CONTINUE
           DO 23 I=1,KK
           Y(I,ICOUNT)=DK(I)*X(I,ICOUNT)/SIT(ITER)
 23        CONTINUE
           PN=P-(-1.+SIT(ITER))/SSS
           IF (ABS(PN-P).LT.ERR) THEN
           P=PN
           RETURN
           ELSE
           P=PN
           GOTO 26
           ENDIF
 24        CONTINUE
           RETURN
           END

           SUBROUTINE  MXDEWP(T,P,BINARY,CROSS,VL,VG)
           IMPLICIT DOUBLE PRECISION (A-H,O-Z)
           PARAMETER (MAXIT=200,ERR=1.E-3,ERRR=1.E-5)
           PARAMETER (R = 83.1439, Z=10, KKK=8)
           PARAMETER (CON=1.4,CON2=CON*CON,BIG=1.E30,NTAB=10,SAFE=2.)
           PARAMETER (NDATA=1000)
           DIMENSION X(KKK,NDATA),Y(KKK,NDATA),X1(KKK),
     @     PAR1(KKK,KKK),PAR2(KKK,KKK),
     @                BINARY(KKK,KKK),CROSS(KKK,KKK),
     @                GAMMA(KKK),PHIL(KKK),
     @                PHIV(KKK),PHI(KKK),DK(KKK),SIT(MAXIT),
     @                GAMMAV(KKK),GAMMAL(KKK),DPHIDP(KKK),
     @                DPHIDPV(KKK),DPHIDPL(KKK),DKDP(KKK),
     @                ADERL(NTAB,NTAB),ADERV(NTAB,NTAB),PHIL_H(KKK),
     @                PHIL_MH(KKK),PHIV_H(KKK),PHIV_MH(KKK),PHIL1_H(KKK),
```

```
@              PHIL1_MH(KKK),PHIV1_H(KKK),PHIV1_MH(KKK),VSTARL(KKK)

         COMMON/CA/CUBIC,ACT
         COMMON/PHUG/PHIV,PHIL
         COMMON/XY/X,Y
         COMMON/ALV/AEL,AEV
         COMMON/GLV/GAMMAV,GAMMAL
         COMMON/CRIT/BT
         COMMON/RN/RUN,QUN,VSTARL
         COMMON/KK/KK
         COMMON/ICO/ICOUNT


         DO 1 I=1,KK
         PHI(I)=0.
         PHIL(I)=0.
         PHIV(I)=0.
         X1(I)=0.
 1       CONTINUE
         SIT(1)=1.E37
         NSD=0.
 26      CONTINUE
         DO 3000 I=2,MAXIT
         SIT(I)=0.
 3000    CONTINUE
         DO 24 ITER=2,MAXIT
         DO 27 I=1,KK
         X1(I)=Y(I,ICOUNT)
 27      CONTINUE
         CALL MXEOSPAR(T,X1,BINARY)
         CALL MXACT(T,X1,GAMMA,AE)
         DO 3131 I=1,KK
         GAMMAV(I)=GAMMA(I)
 3131    CONTINUE
         AEV=AE
         CALL MXMIX(T,BINARY,CROSS,X1,AE)
         CALL MXVOL(T,P,VL,VG)
         V=VG
         CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
         DO 29 I=1,KK
         PHIV(I)=PHI(I)
 29      CONTINUE
         H=0.001
         P1=P+H
         CALL MXVOL(T,P1,VL,VG)
         V=VG
         CALL MXFUGACITY1(T,P1,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
         DO 291 I=1,KK
         PHIV_H(I)=PHI(I)
 291     CONTINUE
         P2=P-H
         CALL MXVOL(T,P2,VL,VG)
         V=VG
```

```
          CALL MXFUGACITY1(T,P2,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 292 I=1,KK
          PHIV_MH(I)=PHI(I)
 292      CONTINUE
          DO 13 K=1,KK
          HH=H
          ADERV(1,1)=(PHIV_H(K)-PHIV_MH(K))/(2.0*HH)
          ERR1=BIG
          DO 12 I=2,NTAB
          HH=HH/CON
          P11=P+HH
          CALL MXVOL(T,P11,VL,VG)
          V=VG
          CALL MXFUGACITY1(T,P11,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 302 I1=1,KK
          PHIV1_H(I1)=PHI(I1)
 302      CONTINUE
          P22=P-HH
          CALL MXVOL(T,P22,VL,VG)
          V=VG
          CALL MXFUGACITY1(T,P22,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 303 I2=1,KK
          PHIV1_MH(I2)=PHI(I2)
 303      CONTINUE
          ADERV(1,I)=(PHIV1_H(K)-PHIV1_MH(K))/(2.0*HH)
          FAC=CON2
          DO 11 J=2,I
          ADERV(J,I)=(ADERV(J-1,I)*FAC-ADERV(J-1,I-1))/(FAC-1.)
          FAC=CON2*FAC
          ERRT1=MAX(ABS(ADERV(J,I)-ADERV(J-1,I)),ABS(ADERV(J,I)-ADERV
    @     (J-1,I-1)))
          IF (ERRT1.LE.ERR1) THEN
          ERR1=ERRT1
          DPHIDPV(K)=ADERV(J,I)
          ENDIF
11        CONTINUE
          IF(ABS(ADERV(I,I)-ADERV(I-1,I-1)).GE.SAFE*ERR1) GOTO 4
12        CONTINUE
4         CONTINUE
13        CONTINUE
          NSD=NSD+ICOUNT
          IF (NSD.EQ.ICOUNT) THEN
          DO 210 I=1,KK
          X1(I)=X(I,ICOUNT-1)
 210      CONTINUE
          ELSE
          DO 213 I=1,KK
          X1(I)=X(I,ICOUNT)
 213      CONTINUE
          ENDIF
          CALL MXEOSPAR(T,X1,BINARY)
          CALL MXACT(T,X1,GAMMA,AE)
          DO 3133 I=1,KK
          GAMMAL(I)=GAMMA(I)
```

```
3133      CONTINUE
          AEL=AE
          CALL MXMIX(T,BINARY,CROSS,X1,AE)
          CALL MXVOL(T,P,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 211 I=1,KK
          PHIL(I)=PHI(I)
211       CONTINUE
          P_L=P+H
          CALL MXVOL(T,P_L,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P_L,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 2211 I=1,KK
          PHIL_H(I)=PHI(I)
2211      CONTINUE
          P_LH=P-H
          CALL MXVOL(T,P_LH,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P_LH,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 2311 I=1,KK
          PHIL_MH(I)=PHI(I)
2311      CONTINUE
          DO 133 K=1,KK
          HH1=H
          ADERL(1,1)=(PHIL_H(K)-PHIL_MH(K))/(2.0*HH1)
          ERR22=BIG
          DO 123 I=2,NTAB
          HH1=HH1/CON
          P33=P+HH1
          CALL MXVOL(T,P33,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P33,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 2511 I3=1,KK
          PHIL1_H(I3)=PHI(I3)
2511      CONTINUE
          P44=P-HH1
          CALL MXVOL(T,P44,VL,VG)
          V=VL
          CALL MXFUGACITY1(T,P44,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 2411 I4=1,KK
          PHIL1_MH(I4)=PHI(I4)
2411      CONTINUE
          ADERL(1,I)=(PHIL1_H(K)-PHIL1_MH(K))/(2.0*HH1)
          FAC=CON2
          DO 113 J=2,I
          ADERL(J,I)=(ADERL(J-1,I)*FAC-ADERL(J-1,I-1))/(FAC-1.)
          FAC=CON2*FAC
          ERRT2=MAX(ABS(ADERL(J,I)-ADERL(J-1,I)),
  @       ABS(ADERL(J,I)-ADERL(J-1,I-1)))
          IF (ERRT2.LE.ERR22) THEN
          ERR22=ERRT2
          DPHIDPL(K)=ADERL(J,I)
          ENDIF
```

```
113         CONTINUE
            IF(ABS(ADERL(I,I)-ADERL(I-1,I-1)).GE.SAFE*ERR22) GOTO 43
123         CONTINUE
 43         CONTINUE
133         CONTINUE
            DO 212 I=1,KK
            DK(I)=EXP(PHIL(I))/EXP(PHIV(I))
 212        CONTINUE
            DO 31 I=1,KK
            DKDP(I)=DK(I)*(DPHIDPL(I)-DPHIDPV(I))
 31         CONTINUE
            SSS=0.
            DO 22 I=1,KK
            SS=-Y(I,ICOUNT)*DKDP(I)/DK(I)**2.
            SSS=SSS+SS
            SI=Y(I,ICOUNT)/DK(I)
            SIT(ITER)=SIT(ITER)+SI
 22         CONTINUE
            DO 23 I=1,KK
            X(I,ICOUNT)=Y(I,ICOUNT)/DK(I)/SIT(ITER)
 23         CONTINUE
            PN=P-(-1.+SIT(ITER))/SSS
            IF (ABS(PN-P).LT.ERR) THEN
            P=PN
            RETURN
            ELSE
            P=PN
            GOTO 26
            ENDIF
 24         CONTINUE
            RETURN
            END

            SUBROUTINE  MXBUBBLET(T,P,BINARY,CROSS,VL,VG)
            IMPLICIT DOUBLE PRECISION (A-H,O-Z)
            PARAMETER (MAXIT=200,ERR=1.E-3,ERRR=1.E-5)
            PARAMETER (R = 83.1439, Z=10, KKK=8)
            PARAMETER (CON=1.4,CON2=CON*CON,BIG=1.E30,NTAB=10,SAFE=2.)
            PARAMETER (NDATA=1000)
            DIMENSION X(KKK,NDATA),Y(KKK,NDATA),X1(KKK),
   @        PAR1(KKK,KKK),PAR2(KKK,KKK),
   @                  BINARY(KKK,KKK),CROSS(KKK,KKK),
   @                  GAMMA(KKK),PHIL(KKK),
   @                  PHIV(KKK),PHI(KKK),DK(KKK),SIT(MAXIT),
   @                  GAMMAV(KKK),GAMMAL(KKK),DPHIDP(KKK),
   @                  DPHIDTV(KKK),DPHIDTL(KKK),DKDT(KKK),
   @                  ADERL(NTAB,NTAB),ADERV(NTAB,NTAB),PHIL_H(KKK),
   @                  PHIL_MH(KKK),PHIV_H(KKK),PHIV_MH(KKK),PHIL1_H(KKK),
   @                  PHIL1_MH(KKK),PHIV1_H(KKK),PHIV1_MH(KKK),VSTARL(KKK)


            COMMON/CA/CUBIC,ACT
            COMMON/PHUG/PHIV,PHIL
            COMMON/XY/X,Y
```

```
        COMMON/ALV/AEL,AEV
        COMMON/GLV/GAMMAV,GAMMAL
        COMMON/CRIT/BT
        COMMON/RN/RUN,QUN,VSTARL
        COMMON/KK/KK
        COMMON/ICO/ICOUNT


        DO 1 I=1,KK
        PHI(I)=0.
        PHIL(I)=0.
        PHIV(I)=0.
        X1(I)=0.
1       CONTINUE
        SIT(1)=1.E37
        NSD=0.
26      CONTINUE
        DO 3000 I=2,MAXIT
        SIT(I)=0.
3000    CONTINUE
        DO 24 ITER=2,MAXIT
        DO 27 I=1,KK
        X1(I)=X(I,ICOUNT)
27      CONTINUE
        CALL MXEOSPAR(T,X1,BINARY)
        CALL MXACT(T,X1,GAMMA,AE)
        DO 3131 I=1,KK
        GAMMAL(I)=GAMMA(I)
3131    CONTINUE
        AEL=AE
        CALL MXMIX(T,BINARY,CROSS,X1,AE)
        CALL MXVOL(T,P,VL,VG)
        V=VL
        CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 29 I=1,KK
        PHIL(I)=PHI(I)
29      CONTINUE
        H=0.001
        T1=T+H
        CALL MXEOSPAR(T1,X1,BINARY)
        CALL MXACT(T1,X1,GAMMA,AE)
        CALL MXMIX(T1,BINARY,CROSS,X1,AE)
        CALL MXVOL(T1,P,VL,VG)
        V=VL
        CALL MXFUGACITY1(T1,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 291 I=1,KK
        PHIL_H(I)=PHI(I)
291     CONTINUE
        T2=T-H
        CALL MXEOSPAR(T2,X1,BINARY)
        CALL MXACT(T2,X1,GAMMA,AE)
        CALL MXMIX(T2,BINARY,CROSS,X1,AE)
        CALL MXVOL(T2,P,VL,VG)
        V=VL
```

```
            CALL MXFUGACITY1(T2,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 292 I=1,KK
            PHIL_MH(I)=PHI(I)
 292        CONTINUE
            DO 13 K=1,KK
            HH=H
            ADERL(1,1)=(PHIL_H(K)-PHIL_MH(K))/(2.0*HH)
            ERR1=BIG
            DO 12 I=2,NTAB
            HH=HH/CON
            T11=T+HH
            CALL MXEOSPAR(T11,X1,BINARY)
            CALL MXACT(T11,X1,GAMMA,AE)
            CALL MXMIX(T11,BINARY,CROSS,X1,AE)
            CALL MXVOL(T11,P,VL,VG)
            V=VL
            CALL MXFUGACITY1(T11,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 302 I1=1,KK
            PHIL1_H(I1)=PHI(I1)
 302        CONTINUE
            T22=T-HH
            CALL MXEOSPAR(T22,X1,BINARY)
            CALL MXACT(T22,X1,GAMMA,AE)
            CALL MXMIX(T22,BINARY,CROSS,X1,AE)
            CALL MXVOL(T22,P,VL,VG)
            V=VL
            CALL MXFUGACITY1(T22,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 303 I2=1,KK
            PHIL1_MH(I2)=PHI(I2)
 303        CONTINUE
            ADERL(1,I)=(PHIL1_H(K)-PHIL1_MH(K))/(2.0*HH)
            FAC=CON2
            DO 11 J=2,I
            ADERL(J,I)=(ADERL(J-1,I)*FAC-ADERL(J-1,I-1))/(FAC-1.)
            FAC=CON2*FAC
            ERRT1=MAX(ABS(ADERL(J,I)-ADERL(J-1,I)),ABS(ADERL(J,I)-ADERL
   @        (J-1,I-1)))
            IF (ERRT1.LE.ERR1) THEN
            ERR1=ERRT1
            DPHIDTL(K)=ADERL(J,I)
            ENDIF
11          CONTINUE
            IF(ABS(ADERL(I,I)-ADERL(I-1,I-1)).GE.SAFE*ERR1) GOTO 4
12          CONTINUE
4           CONTINUE
13          CONTINUE
            NSD=NSD+ICOUNT
            IF (NSD.EQ.ICOUNT) THEN
            DO 210 I=1,KK
            X1(I)=Y(I,ICOUNT-1)
 210        CONTINUE
            ELSE
            DO 213 I=1,KK
            X1(I)=Y(I,ICOUNT)
```

```
213         CONTINUE
            ENDIF
            CALL MXEOSPAR(T,X1,BINARY)
            CALL MXACT(T,X1,GAMMA,AE)
            DO 3133 I=1,KK
            GAMMAV(I)=GAMMA(I)
3133        CONTINUE
            AEV=AE
            CALL MXMIX(T,BINARY,CROSS,X1,AE)
            CALL MXVOL(T,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 211 I=1,KK
            PHIV(I)=PHI(I)
211         CONTINUE
            T_V=T+H
            CALL MXEOSPAR(T_V,X1,BINARY)
            CALL MXACT(T_V,X1,GAMMA,AE)
            CALL MXMIX(T_V,BINARY,CROSS,X1,AE)
            CALL MXVOL(T_V,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T_V,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 2211 I=1,KK
            PHIV_H(I)=PHI(I)
2211        CONTINUE
            T_VH=T-H
            CALL MXEOSPAR(T_VH,X1,BINARY)
            CALL MXACT(T_VH,X1,GAMMA,AE)
            CALL MXMIX(T_VH,BINARY,CROSS,X1,AE)
            CALL MXVOL(T_VH,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T_VH,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 2311 I=1,KK
            PHIV_MH(I)=PHI(I)
2311        CONTINUE
            DO 133 K=1,KK
            HH1=H
            ADERV(1,1)=(PHIV_H(K)-PHIV_MH(K))/(2.0*HH1)
            ERR22=BIG
            DO 123 I=2,NTAB
            HH1=HH1/CON
            T33=T+HH1
            CALL MXEOSPAR(T33,X1,BINARY)
            CALL MXACT(T33,X1,GAMMA,AE)
            CALL MXMIX(T33,BINARY,CROSS,X1,AE)
            CALL MXVOL(T33,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T33,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 2511 I3=1,KK
            PHIV1_H(I3)=PHI(I3)
2511        CONTINUE
            T44=T-HH1
            CALL MXEOSPAR(T44,X1,BINARY)
            CALL MXACT(T44,X1,GAMMA,AE)
```

```
      CALL MXMIX(T44,BINARY,CROSS,X1,AE)
      CALL MXVOL(T44,P,VL,VG)
      V=VG
      CALL MXFUGACITY1(T44,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
      DO 2411 I4=1,KK
      PHIV1_MH(I4)=PHI(I4)
2411  CONTINUE
      ADERV(1,I)=(PHIV1_H(K)-PHIV1_MH(K))/(2.0*HH1)
      FAC=CON2
      DO 113 J=2,I
      ADERV(J,I)=(ADERV(J-1,I)*FAC-ADERV(J-1,I-1))/(FAC-1.)
      FAC=CON2*FAC
      ERRT2=MAX(ABS(ADERV(J,I)-ADERV(J-1,I)),
    @ ABS(ADERV(J,I)-ADERV(J-1,I-1)))
      IF (ERRT2.LE.ERR22) THEN
      ERR22=ERRT2
      DPHIDTV(K)=ADERV(J,I)
      ENDIF
113   CONTINUE
      IF(ABS(ADERV(I,I)-ADERV(I-1,I-1)).GE.SAFE*ERR22) GOTO 43
123   CONTINUE
43    CONTINUE
133   CONTINUE
      DO 212 I=1,KK
      DK(I)=EXP(PHIL(I))/EXP(PHIV(I))
212   CONTINUE
      DO 31 I=1,KK
      DKDT(I)=DK(I)*(DPHIDTL(I)-DPHIDTV(I))
31    CONTINUE
      SSS=0.
      DO 22 I=1,KK
      SS=X(I,ICOUNT)*DKDT(I)
      SSS=SSS+SS
      SI=DK(I)*X(I,ICOUNT)
      SIT(ITER)=SIT(ITER)+SI
22    CONTINUE
      DO 23 I=1,KK
      Y(I,ICOUNT)=DK(I)*X(I,ICOUNT)/SIT(ITER)
23    CONTINUE
      TN=T-(-1.+SIT(ITER))/SSS
      IF (ABS(TN-T).LT.ERR) THEN
      T=TN
      RETURN
      ELSE
      T=TN
      GOTO 26
      ENDIF
24    CONTINUE
      RETURN
      END

      SUBROUTINE  MXDEWT(T,P,BINARY,CROSS,VL,VG)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (MAXIT=200,ERR=1.E-3,ERRR=1.E-5)
```

```
        PARAMETER (R = 83.1439, Z=10, KKK=8)
        PARAMETER (CON=1.4,CON2=CON*CON,BIG=1.E30,NTAB=10,SAFE=2.)
        PARAMETER (NDATA=1000)
        DIMENSION X(KKK,NDATA),Y(KKK,NDATA),X1(KKK),
   @    PAR1(KKK,KKK),PAR2(KKK,KKK),
   @                BINARY(KKK,KKK),CROSS(KKK,KKK),
   @                GAMMA(KKK),PHIL(KKK),
   @                PHIV(KKK),PHI(KKK),DK(KKK),SIT(MAXIT),
   @                GAMMAV(KKK),GAMMAL(KKK),DPHIDP(KKK),
   @                DPHIDTV(KKK),DPHIDTL(KKK),DKDT(KKK),
   @                ADERL(NTAB,NTAB),ADERV(NTAB,NTAB),PHIL_H(KKK),
   @                PHIL_MH(KKK),PHIV_H(KKK),PHIV_MH(KKK),PHIL1_H(KKK),
   @                PHIL1_MH(KKK),PHIV1_H(KKK),PHIV1_MH(KKK),VSTARL(KKK)


        COMMON/CA/CUBIC,ACT
        COMMON/PHUG/PHIV,PHIL
        COMMON/XY/X,Y
        COMMON/ALV/AEL,AEV
        COMMON/GLV/GAMMAV,GAMMAL
        COMMON/CRIT/BT
        COMMON/RN/RUN,QUN,VSTARL
        COMMON/KK/KK
        COMMON/ICO/ICOUNT


        DO 1 I=1,KK
        PHI(I)=0.
        PHIL(I)=0.
        PHIV(I)=0.
        X1(I)=0.
  1     CONTINUE
        SIT(1)=1.E37
        NSD=0.
  26    CONTINUE
        DO 3000 I=2,MAXIT
        SIT(I)=0.
  3000  CONTINUE
        DO 24 ITER=2,MAXIT
        DO 27 I=1,KK
        X1(I)=Y(I,ICOUNT)
  27    CONTINUE
        CALL MXEOSPAR(T,X1,BINARY)
        CALL MXACT(T,X1,GAMMA,AE)
        DO 3131 I=1,KK
        GAMMAV(I)=GAMMA(I)
  3131  CONTINUE
        AEV=AE
        CALL MXMIX(T,BINARY,CROSS,X1,AE)
        CALL MXVOL(T,P,VL,VG)
        V=VG
        CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
        DO 29 I=1,KK
        PHIV(I)=PHI(I)
```

```
29          CONTINUE
            H=0.001
            T1=T+H
            CALL MXEOSPAR(T1,X1,BINARY)
            CALL MXACT(T1,X1,GAMMA,AE)
            CALL MXMIX(T1,BINARY,CROSS,X1,AE)
            CALL MXVOL(T1,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T1,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 291 I=1,KK
            PHIV_H(I)=PHI(I)
291         CONTINUE
            T2=T-H
            CALL MXEOSPAR(T2,X1,BINARY)
            CALL MXACT(T2,X1,GAMMA,AE)
            CALL MXMIX(T2,BINARY,CROSS,X1,AE)
            CALL MXVOL(T2,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T2,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 292 I=1,KK
            PHIV_MH(I)=PHI(I)
292         CONTINUE
            DO 13 K=1,KK
            HH=H
            ADERV(1,1)=(PHIV_H(K)-PHIV_MH(K))/(2.0*HH)
            ERR1=BIG
            DO 12 I=2,NTAB
            HH=HH/CON
            T11=T+HH
            CALL MXEOSPAR(T11,X1,BINARY)
            CALL MXACT(T11,X1,GAMMA,AE)
            CALL MXMIX(T11,BINARY,CROSS,X1,AE)
            CALL MXVOL(T11,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T11,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 302 I1=1,KK
            PHIV1_H(I1)=PHI(I1)
302         CONTINUE
            T22=T-HH
            CALL MXEOSPAR(T22,X1,BINARY)
            CALL MXACT(T22,X1,GAMMA,AE)
            CALL MXMIX(T22,BINARY,CROSS,X1,AE)
            CALL MXVOL(T22,P,VL,VG)
            V=VG
            CALL MXFUGACITY1(T22,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 303 I2=1,KK
            PHIV1_MH(I2)=PHI(I2)
303         CONTINUE
            ADERV(1,I)=(PHIV1_H(K)-PHIV1_MH(K))/(2.0*HH)
            FAC=CON2
            DO 11 J=2,I
            ADERV(J,I)=(ADERV(J-1,I)*FAC-ADERV(J-1,I-1))/(FAC-1.)
            FAC=CON2*FAC
            ERRT1=MAX(ABS(ADERV(J,I)-ADERV(J-1,I)),ABS(ADERV(J,I)-ADERV
```

```
   @        (J-1,I-1)))
            IF (ERRT1.LE.ERR1) THEN
            ERR1=ERRT1
            DPHIDTV(K)=ADERV(J,I)
            ENDIF
11          CONTINUE
            IF(ABS(ADERV(I,I)-ADERV(I-1,I-1)).GE.SAFE*ERR1) GOTO 4
12          CONTINUE
4           CONTINUE
13          CONTINUE
            NSD=NSD+ICOUNT
            IF (NSD.EQ.ICOUNT) THEN
            DO 210 I=1,KK
            X1(I)=X(I,ICOUNT-1)
 210        CONTINUE
            ELSE
            DO 213 I=1,KK
            X1(I)=X(I,ICOUNT)
 213        CONTINUE
            ENDIF
            CALL MXEOSPAR(T,X1,BINARY)
            CALL MXACT(T,X1,GAMMA,AE)
            DO 3133 I=1,KK
            GAMMAL(I)=GAMMA(I)
 3133       CONTINUE
            AEL=AE
            CALL MXMIX(T,BINARY,CROSS,X1,AE)
            CALL MXVOL(T,P,VL,VG)
            V=VL
            CALL MXFUGACITY1(T,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 211 I=1,KK
            PHIL(I)=PHI(I)
 211        CONTINUE
            T_V=T+H
            CALL MXEOSPAR(T_V,X1,BINARY)
            CALL MXACT(T_V,X1,GAMMA,AE)
            CALL MXMIX(T_V,BINARY,CROSS,X1,AE)
            CALL MXVOL(T_V,P,VL,VG)
            V=VL
            CALL MXFUGACITY1(T_V,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 2211 I=1,KK
            PHIL_H(I)=PHI(I)
 2211       CONTINUE
            T_VH=T-H
            CALL MXEOSPAR(T_VH,X1,BINARY)
            CALL MXACT(T_VH,X1,GAMMA,AE)
            CALL MXMIX(T_VH,BINARY,CROSS,X1,AE)
            CALL MXVOL(T_VH,P,VL,VG)
            V=VL
            CALL MXFUGACITY1(T_VH,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
            DO 2311 I=1,KK
            PHIL_MH(I)=PHI(I)
 2311       CONTINUE
            DO 133 K=1,KK
```

```
          HH1=H
          ADERL(1,1)=(PHIL_H(K)-PHIL_MH(K))/(2.0*HH1)
          ERR22=BIG
          DO 123 I=2,NTAB
          HH1=HH1/CON
          T33=T+HH1
          CALL MXEOSPAR(T33,X1,BINARY)
          CALL MXACT(T33,X1,GAMMA,AE)
          CALL MXMIX(T33,BINARY,CROSS,X1,AE)
          CALL MXVOL(T33,P,VL,VG)
          V=VL
          CALL MXFUGACITY1(T33,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 2511 I3=1,KK
          PHIL1_H(I3)=PHI(I3)
2511      CONTINUE
          T44=T-HH1
          CALL MXEOSPAR(T44,X1,BINARY)
          CALL MXACT(T44,X1,GAMMA,AE)
          CALL MXMIX(T44,BINARY,CROSS,X1,AE)
          CALL MXVOL(T44,P,VL,VG)
          V=VL
          CALL MXFUGACITY1(T44,P,CROSS,V,X1,PHI,GAMMA,BINARY,AE)
          DO 2411 I4=1,KK
          PHIL1_MH(I4)=PHI(I4)
2411      CONTINUE
          ADERL(1,I)=(PHIL1_H(K)-PHIL1_MH(K))/(2.0*HH1)
          FAC=CON2
          DO 113 J=2,I
          ADERL(J,I)=(ADERL(J-1,I)*FAC-ADERL(J-1,I-1))/(FAC-1.)
          FAC=CON2*FAC
          ERRT2=MAX(ABS(ADERL(J,I)-ADERL(J-1,I)),
     @    ABS(ADERL(J,I)-ADERL(J-1,I-1)))
          IF (ERRT2.LE.ERR22) THEN
          ERR22=ERRT2
          DPHIDTL(K)=ADERL(J,I)
          ENDIF
113       CONTINUE
          IF(ABS(ADERL(I,I)-ADERL(I-1,I-1)).GE.SAFE*ERR22) GOTO 43
123       CONTINUE
43        CONTINUE
133       CONTINUE
          DO 212 I=1,KK
          DK(I)=EXP(PHIL(I))/EXP(PHIV(I))
212       CONTINUE
          DO 31 I=1,KK
          DKDT(I)=DK(I)*(DPHIDTL(I)-DPHIDTV(I))
31        CONTINUE
          SSS=0.
          DO 22 I=1,KK
          SS=-Y(I,ICOUNT)*DKDT(I)/DK(I)**2.
          SSS=SSS+SS
          SI=Y(I,ICOUNT)/DK(I)
          SIT(ITER)=SIT(ITER)+SI
22        CONTINUE
```

```
            DO 23 I=1,KK
            X(I,ICOUNT)=Y(I,ICOUNT)/DK(I)/SIT(ITER)
23          CONTINUE
            TN=T-(-1.+SIT(ITER))/SSS
            IF (ABS(TN-T).LT.ERR) THEN
            T=TN
            RETURN
            ELSE
            T=TN
            GOTO 26
            ENDIF
24          CONTINUE
            RETURN
            END

            FUNCTION ZBRENT(FUNC,X1,X2,TOL)
            IMPLICIT DOUBLE PRECISION (A-H,O-Z)
            INTEGER ITMAX
            REAL*8 ZBRENT,TOL,X1,X2,FUNC,EPS
            EXTERNAL FUNC
            PARAMETER (ITMAX=100,EPS=3.E-8)
            INTEGER ITER
            REAL*8 B,C,D,FA,FB,FC,P,R,S,TOL1,XM,A,E,Q
            A=X1
            B=X2
            FA=FUNC(A)
            FB=FUNC(B)
            IF((FA.GT.0..AND.FB.GT.0.).OR.(FA.LT.0..AND.FB.LT.0.))PAUSE
    *       'ROOT MUST BE BRACKETED FOR ZBRENT'
            C=B
            FC=FB
            DO 11 ITER=1,ITMAX
            IF((FB.GT.0..AND.FC.GT.0.).OR.(FB.LT.0..AND.FC.LT.0.))THEN
            C=A
            FC=FA
            D=B-A
            E=D
            ENDIF
            IF(ABS(FC).LT.ABS(FB)) THEN
            A=B
            B=C
            C=A
            FA=FB
            FB=FC
            FC=FA
            ENDIF
            TOL1=2.*EPS*ABS(B)+0.5*TOL
            XM=.5*(C-B)
            IF(ABS(XM).LE.TOL1 .OR. FB.EQ.0.)THEN
            ZBRENT=B
            RETURN
            ENDIF
            IF(ABS(E).GE.TOL1 .AND. ABS(FA).GT.ABS(FB)) THEN
            S=FB/FA
```

```
            IF(A.EQ.C) THEN
            P=2.*XM*S
            Q=1.-S
            ELSE
            Q=FA/FC
            R=FB/FC
            P=S*(2.*XM*Q*(Q-R)-(B-A)*(R-1.))
            Q=(Q-1.)*(R-1.)*(S-1.)
            ENDIF
            IF(P.GT.0.) Q=-Q
            P=ABS(P)
            IF(2.D0*P .LT. MIN(3.D0*XM*Q-ABS(TOL1*Q),ABS(E*Q))) THEN
            E=D
            D=P/Q
            ELSE
            D=XM
            E=D
            ENDIF
            ELSE
            D=XM
            E=D
            ENDIF
            A=B
            FA=FB
            IF(ABS(D) .GT. TOL1) THEN
            B=B+D
            ELSE
            B=B+SIGN(TOL1,XM)
            ENDIF
            FB=FUNC(B)
11          CONTINUE
            PAUSE 'ZBRENT EXCEEDING MAXIMUM ITERATIONS'
            ZBRENT=B
            RETURN
            END

            SUBROUTINE ZRHQR(A,M,RTR,RTI)
            IMPLICIT DOUBLE PRECISION (A-H,O-Z)
            INTEGER M,MAXM
            REAL*8 A(M+1),RTR(M),RTI(M)
            PARAMETER (MAXM=50)
CU     USES BALANC,HQR
            INTEGER J,K
            REAL*8 HESS(MAXM,MAXM),XR,XI
            IF (M.GT.MAXM.OR.A(M+1).EQ.0.) PAUSE 'BAD ARGS IN ZRHQR'
            DO 12 K=1,M
            HESS(1,K)=-A(M+1-K)/A(M+1)
            DO 11 J=2,M
            HESS(J,K)=0.
11          CONTINUE
            IF (K.NE.M) HESS(K+1,K)=1.
12          CONTINUE
            CALL BALANC(HESS,M,MAXM)
            CALL HQR(HESS,M,MAXM,RTR,RTI)
```

```
      DO 14 J=2,M
      XR=RTR(J)
      XI=RTI(J)
      DO 13 K=J-1,1,-1
      IF(RTR(K).LE.XR)GOTO 1
      RTR(K+1)=RTR(K)
      RTI(K+1)=RTI(K)
13    CONTINUE
      K=0
1     RTR(K+1)=XR
      RTI(K+1)=XI
14    CONTINUE
      RETURN
      END

      SUBROUTINE HQR(A,N,NP,WR,WI)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      INTEGER N,NP
      REAL*8 A(NP,NP),WI(NP),WR(NP)
      INTEGER I,ITS,J,K,L,M,NN
      REAL*8 ANORM,P,Q,R,S,T,U,V,W,X,Y,Z
      ANORM=ABS(A(1,1))
      DO 12 I=2,N
      DO 11 J=I-1,N
      ANORM=ANORM+ABS(A(I,J))
11    CONTINUE
12    CONTINUE
      NN=N
      T=0.
1     IF(NN.GE.1)THEN
      ITS=0
2     DO 13 L=NN,2,-1
      S=ABS(A(L-1,L-1))+ABS(A(L,L))
      IF(S.EQ.0.)S=ANORM
      IF(ABS(A(L,L-1))+S.EQ.S)GOTO 3
13    CONTINUE
      L=1
3     X=A(NN,NN)
      IF(L.EQ.NN)THEN
      WR(NN)=X+T
      WI(NN)=0.
      NN=NN-1
      ELSE
      Y=A(NN-1,NN-1)
      W=A(NN,NN-1)*A(NN-1,NN)
      IF(L.EQ.NN-1)THEN
      P=0.5*(Y-X)
      Q=P**2+W
      Z=SQRT(ABS(Q))
      X=X+T
      IF(Q.GE.0.)THEN
      Z=P+SIGN(Z,P)
      WR(NN)=X+Z
      WR(NN-1)=WR(NN)
```

```
          IF(Z.NE.0.)WR(NN)=X-W/Z
          WI(NN)=0.
          WI(NN-1)=0.
          ELSE
          WR(NN)=X+P
          WR(NN-1)=WR(NN)
          WI(NN)=Z
          WI(NN-1)=-Z
          ENDIF
          NN=NN-2
          ELSE
          IF(ITS.EQ.30)PAUSE 'TOO MANY ITERATIONS IN HQR'
          IF(ITS.EQ.10.OR.ITS.EQ.20)THEN
          T=T+X
          DO 14 I=1,NN
          A(I,I)=A(I,I)-X
14        CONTINUE
          S=ABS(A(NN,NN-1))+ABS(A(NN-1,NN-2))
          X=0.75*S
          Y=X
          W=-0.4375*S**2
          ENDIF
          ITS=ITS+1
          DO 15 M=NN-2,L,-1
          Z=A(M,M)
          R=X-Z
          S=Y-Z
          P=(R*S-W)/A(M+1,M)+A(M,M+1)
          Q=A(M+1,M+1)-Z-R-S
          R=A(M+2,M+1)
          S=ABS(P)+ABS(Q)+ABS(R)
          P=P/S
          Q=Q/S
          R=R/S
          IF(M.EQ.L)GOTO 4
          U=ABS(A(M,M-1))*(ABS(Q)+ABS(R))
          V=ABS(P)*(ABS(A(M-1,M-1))+ABS(Z)+ABS(A(M+1,M+1)))
          IF(U+V.EQ.V)GOTO 4
15        CONTINUE
4         DO 16 I=M+2,NN
          A(I,I-2)=0.
          IF (I.NE.M+2) A(I,I-3)=0.
16        CONTINUE
          DO 19 K=M,NN-1
          IF(K.NE.M)THEN
          P=A(K,K-1)
          Q=A(K+1,K-1)
          R=0.
          IF(K.NE.NN-1)R=A(K+2,K-1)
          X=ABS(P)+ABS(Q)+ABS(R)
          IF(X.NE.0.)THEN
          P=P/X
          Q=Q/X
          R=R/X
```

```
                ENDIF
                ENDIF
                S=SIGN(SQRT(P**2+Q**2+R**2),P)
                IF(S.NE.0.)THEN
                IF(K.EQ.M)THEN
                IF(L.NE.M)A(K,K-1)=-A(K,K-1)
                ELSE
                A(K,K-1)=-S*X
                ENDIF
                P=P+S
                X=P/S
                Y=Q/S
                Z=R/S
                Q=Q/P
                R=R/P
                DO 17 J=K,NN
                P=A(K,J)+Q*A(K+1,J)
                IF(K.NE.NN-1)THEN
                P=P+R*A(K+2,J)
                A(K+2,J)=A(K+2,J)-P*Z
                ENDIF
                A(K+1,J)=A(K+1,J)-P*Y
                A(K,J)=A(K,J)-P*X
17              CONTINUE
                DO 18 I=L,MIN(NN,K+3)
                P=X*A(I,K)+Y*A(I,K+1)
                IF(K.NE.NN-1)THEN
                P=P+Z*A(I,K+2)
                A(I,K+2)=A(I,K+2)-P*R
                ENDIF
                A(I,K+1)=A(I,K+1)-P*Q
                A(I,K)=A(I,K)-P
18              CONTINUE
                ENDIF
19              CONTINUE
                GOTO 2
                ENDIF
                ENDIF
                GOTO 1
                ENDIF
                RETURN
                END

                SUBROUTINE BALANC(A,N,NP)
                IMPLICIT DOUBLE PRECISION (A-H,O-Z)
                INTEGER N,NP
                REAL*8 A(NP,NP),RADIX,SQRDX
                PARAMETER (RADIX=2.,SQRDX=RADIX**2)
                INTEGER I,J,LAST
                REAL*8 C,F,G,R,S
1               CONTINUE
                LAST=1
                DO 14 I=1,N
                C=0.
```

```
      R=0.
      DO 11 J=1,N
      IF(J.NE.I)THEN
      C=C+ABS(A(J,I))
      R=R+ABS(A(I,J))
      ENDIF
11    CONTINUE
      IF(C.NE.0..AND.R.NE.0.)THEN
      G=R/RADIX
      F=1.
      S=C+R
2     IF(C.LT.G)THEN
      F=F*RADIX
      C=C*SQRDX
      GOTO 2
      ENDIF
      G=R*RADIX
3     IF(C.GT.G)THEN
      F=F/RADIX
      C=C/SQRDX
      GOTO 3
      ENDIF
      IF((C+R)/F.LT.0.95*S)THEN
      LAST=0
      G=1./F
      DO 12 J=1,N
      A(I,J)=A(I,J)*G
12    CONTINUE
      DO 13 J=1,N
      A(J,I)=A(J,I)*F
13    CONTINUE
      ENDIF
      ENDIF
14    CONTINUE
      IF(LAST.EQ.0)GOTO 1
      RETURN
      END

      SUBROUTINE XSOLVE(T,Y,XIJR)
C
C   THIS SUBROUTINE EMPLOYS A FIXED POINT ITERATION
C    METHOD TO SOLVE FOR THE R RATIOS, AND THEN
C    CALCULATES THE LOCAL COMPOSITIONS XIJ THAT
C    R-VALUES REPRESENT.
C
      IMPLICIT REAL*8(A-H,O-Z)
      PARAMETER (RR = 83.1439, Z=10, KKK=8)
      LOGICAL TEST
      DIMENSION Y(KKK),XIJR(KKK,KKK)
      DIMENSION C(KKK,KKK),CSQRT(KKK,KKK),PAR2(KKK,KKK),PAR1(KKK,KKK)
      DIMENSION R(KKK),RNEW(KKK)
      COMMON/PRA/PAR1,PAR2
      COMMON/KK/KK
```

```
            DATA EPS/1.0D-06/
            ITMAX=25.

            DO 44 I=1,KK
            DO 45 J=1,KK
            C(I,J)=EXP(-PAR1(I,J)*10000./RR/T)
 45         CONTINUE
            C(I,I)=1.
 44         CONTINUE
            IT=-1
            K=1
C
C    DETERMINE KEY COMPONENT BY LARGEST COMPOSITION VALUE
C
            DO 1 I=1,KK
            IF(Y(I).GT.Y(K)) K=I
  1         CONTINUE
            SUM=0.0D0

C
C    CALCULATION OF INITIAL GUESSES.  WE DO SO BY IGNORING
C      THE PRESENCE OF ALL COMPONENTS OTHER THAN THE KEY
C      COMPONENT AND THE COMPONENT FOR WHICH WE ARE
C      OBTAINING AN INITIAL GUESS.
C    WE ALSO CALCULATE THE CSQRT VALUES HERE TO SAVE NEEDLESS
C      REPITITION IN THE ITERATION LOOP.
C
            DO 5 I=1,KK
            IF(I.EQ.K) GO TO 2
            IF(Y(I).EQ.0.0D0) GO TO 3
            T1=Y(I)/Y(K)
            T2=1.0D0+T1
            T3=(C(I,K)-1.0D00)/C(I,K)
            R(I)=2.0D0*T1/(1.0D0+T1+DSQRT(T2*T2-4.0D0*T1*T3))
            SUM=SUM+R(I)
            GO TO 6
  2         R(I)=1.0D0
            SUM=SUM+R(I)
            GO TO 6
  3         R(I)=0.0D0
            SUM=SUM+R(I)
  6         DO 5 J=1,KK
            CSQRT(I,J)=DSQRT(C(I,J)/(C(I,K)*C(J,K)))
  5         CONTINUE
            IT=0
C
C    ENTER ITERATIVE LOOP
C
  4         DO 9 I=1,KK
            SUMJ=0.0D0
            DO 8 J=1,KK
            SUMJ=SUMJ+R(J)*CSQRT(I,J)
  8         CONTINUE
            RNEW(I)=(Y(I)/Y(K))*SUM/SUMJ
```

```
            IF(I.EQ.K) RNEW(I)=1.0D0
  9         CONTINUE
            TEST=.TRUE.
            DO 10 I=1,KK
            IF(DABS(RNEW(I)-R(I)).GT.EPS) TEST=.FALSE.
  10        CONTINUE
            IF(TEST) GO TO 50
  11        DO 12 I=1,KK
            R(I)=RNEW(I)
  12        CONTINUE
            IT=IT+1
            IF(IT.GT.ITMAX) GO TO 50
            SUM=0.0D0
            DO 7 L=1,KK
            SUM=SUM+R(L)
  7         CONTINUE
            GO TO 4
C
C   HAVE EXITED LOOP;  WE NOW CALCULATE THE XIJ VALUES
C
  50        DO 51 I=1,KK
            SUMJ=0.0D0
            DO 52 J=1,KK
            SUMJ=SUMJ+R(J)*CSQRT(I,J)
  52        CONTINUE
            DO 51 J=1,KK
            XIJR(I,J)=R(J)*CSQRT(I,J)/SUMJ
  51        CONTINUE
            IF(IT.GT.ITMAX) WRITE(*,53)
  53        FORMAT('-MAXIMUM NUMBER OF ITERATIONS EXCEEDED')
            DO 54 I=1,KK
            DO 54 J=1,KK
            IF (XIJR(I,J) .LT. 0.0D0) GO TO 55
  54        CONTINUE
            RETURN
  55        WRITE(*,56) (R(I),I=1,KK)
  56        FORMAT('- R-VALUES ARE:',3X,8E13.6)
            WRITE(*,57) (Y(I),I=1,KK)
  57        FORMAT('- Y-VALUES ARE:',3X,8E13.6/'- C-VALUES ARE:')
            DO 58 I=1,KK
            WRITE(*,59) (C(I,J),J=1,KK)
  59        FORMAT('0',8E13.6)
  58        CONTINUE
            STOP
            END
```

APPENDIX D-3

Sample Program for R134a-Propane

```
      SUBROUTINE FOFX(ID,XD,BINARY,YD,ZZZ)
C PRESSURE IS IN BARS AND MOLAR VOLUME IN CC/MOLE,AE IS IN UNITS C
BARS*CC/MOLE
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      PARAMETER (R = 83.1439, Z=10, KKK=3)
      PARAMETER(LINIT=9)
      PARAMETER(LSPEC=6,LCRIT=7,LNRTL=8)

      DIMENSION X(KKK),X1(KKK),Y(KKK),BINARY(50)

      REAL ZZZ

      COMMON/CA/CUBIC,ACT
      COMMON/XY/X,Y
      COMMON/PR/PRE,TEM
      COMMON/EQU/ROT
      COMMON/ZLO/ZLZ
      COMMON/PP/PRES
      COMMON/IC/ICOUNT
      COMMON/IT/ITER

C     IDD=ID+14
      IDD=ID
C     IF (ID.GE.8) THEN
C     IDD=ID+23
C     ENDIF

      ICOUNT=IDD

      IF ((ROT.EQ.1).OR.(ROT.EQ.2)) THEN
      IF(IDD.LE.70) THEN
      X(1)=XD
      X(2)=1-XD
      X1(1)=X(1)
      X1(2)=X(2)
      ENDIF
      ENDIF

C R134A-PROPANE

      IF (IDD.LE.23) THEN
      ZLZ=3
      ENDIF
      IF (IDD.GE.24.AND.IDD.LE.46) THEN
      ZLZ=1
      ENDIF

      IF (IDD.EQ.1.OR.IDD.EQ.24) THEN
      Y(1)=0.25
```

```
Y(2)=1.-Y(1)
P=3.1
ENDIF

IF (IDD.EQ.8.OR.IDD.EQ.31) THEN
Y(1)=0.23
Y(2)=1.-Y(1)
P=6.
ENDIF

IF (IDD.EQ.15.OR.IDD.EQ.38) THEN
Y(1)=0.21
Y(2)=1.-Y(1)
P=11.
ENDIF

IF (IDD.GE.1.AND.IDD.LE.7) THEN
T=255.
ENDIF
IF (IDD.GE.8.AND.IDD.LE.14) THEN
T=275.
ENDIF
IF (IDD.GE.15.AND.IDD.LE.23) THEN
T=298.
ENDIF
IF (IDD.GE.24.AND.IDD.LE.30) THEN
T=255.
ENDIF
IF (IDD.GE.31.AND.IDD.LE.37) THEN
T=275.
ENDIF
IF (IDD.GE.38.AND.IDD.LE.46) THEN
T=298.
ENDIF

CALL MXEOSPAR (T,X1,BINARY)

SWITCH=1.
CALL MXBUBBLE(T,P,BINARY,VL,VG,ZZ)

IF (ZLZ.EQ.1) THEN
IF(IDD.LE.84) THEN
ZZZ=Y(1)
ENDIF
ENDIF

IF (ZLZ.EQ.2) THEN
ZZZ=X(1)
ENDIF

IF ((ROT.EQ.1).OR.(ROT.EQ.3)) THEN
IF (ZLZ.EQ.3) THEN
ZZZ=P
ENDIF
```

```
ENDIF
IF ((ROT.EQ.2).OR.(ROT.EQ.4)) THEN
IF (ZLZ.EQ.4) THEN
ZZZ=T
ENDIF
ENDIF
IF (ZLZ.EQ.5) THEN
ZZZ=ZZ/R/T
ENDIF

END
```

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