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  EFFECTIVE MOLECULAR DIAMETERS FOR THE
  PREDICTION OF THERMODYNAMIC PROPERTIES OF
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  RICE UNIVERSITY, M.S., 1979

RICE UNIVERSITY

EFFECTIVE MOLECULAR DIAMETERS FOR
THE PREDICTION OF THERMODYNAMIC PROPERTIES
OF FLUID MIXTURES

by

FRANK S. S. HWU

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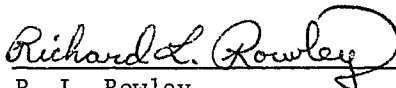REQUIREMENTS FOR THE DEGREE

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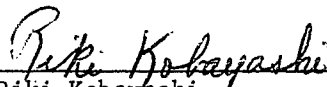

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ABSTRACT

A general method of predicting the effective molecular diameters and the thermodynamic properties for fluid mixtures based on the Hard Sphere Expansion conformal solution theory is developed. The effective diameters are determined from isochoric behavior of pure fluids with unknown intermolecular potentials. Inadequacies in the Hard Sphere Expansion conformal solution theory are offset by this formulation of diameter determination.

Methane-propane mixtures of various composition were selected for testing this approach. Satisfactory results for the compressibility factors and isothermal enthalpies over a wide range of temperature and pressure further demonstrate the applicability of the HSE method. The diameters have been justified to be the optimal ones for use with HSE method by an error analysis of comparing the predicted results with experimental values.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

ACKNOWLEDGMENTS

NOMENCLATURE

Upper Case Letters

A	Helmholtz Free Energy
F,X	Thermodynamic Functions
G	Gibbs Free Energy
H	Enthalpy
K	Vapor-Liquid Equilibrium Constant
N	Number of Molecules, Number of Components
P	Pressure
Q	Configurational Partition Function
R	Gas Constant
T	Temperature
U	Total Potential Function, Internal Energy
V	Volume
VP	Vapor Pressure
Y	Coefficients in Hard Sphere Mixture Equation of State
Z	Compressibility Factor

Lower Case Letters

a	Function defined in Eqn. (4.25)
b.p.	Bubble Point
d	Hard Sphere Diameter
f	Thermodynamic Function, Fugacity
g	Distribution Function
k	Boltzmann Constant
n	Number of moles

NOMENCLATURE (continued)

r	Intermolecular Distance, Reduced Condition
u	Intermolecular Potential Function
x	Molar Fraction in Liquid Phase
y	Molar Fraction in Vapor Phase, Dimensionless Intermolecular Distance

Greek

α	Constant as Defined in Equation (4.30)
Δ	Parameter in Hard Sphere Mixture Equation of State
ϵ	Energy Parameter in Potential Function
ξ	Parameter in Hard Sphere Equation of State, Energy Unlike Pair Parameter
η	Parameter in Hard Sphere Equation of State
θ	Temperature Shape Factor
λ	Volume Unlike Pair Parameter
μ	Chemical Potential
π	3.141592...
ρ	Density
σ	Length Parameter in Potential Function
Σ	Summation
Φ	Volume Shape Factor
ψ	Function as Defined in Equation (4.24)
ω	Acentric Factor
δ	Function as Defined in Equation (4.34)

NOMENCLATURE (continued)

Subscripts and Superscripts

A,B	Indices
b	Bubble Point
c	Critical Condition
ex	Excess Over Hard Sphere Property
exp	Experimental Value
hs	Hard Sphere Property
i,j,k,ℓ	Indices
L	Liquid Phase
M	Mixture
P	Pressure
r	Reference Fluid
ref	Reference
T	Temperature
V	Volume, Vapor Phase
1,2,3,...	Indices, Carbon Number of Paraffin Hydrocarbon
o	Property of Hard Sphere System, Equivalent Condition
(1),(2)	Perturbed Terms
——	Molar Quantity, Average Quantity
',\"	Pseudo Conditions, Derivative
→	Vector
*	Ideal Gas State

CHAPTER 1

INTRODUCTION

Prediction of thermodynamic properties has always been a challenge to both theoreticians and engineers. The classical thermodynamics presents broad interrelations among macroscopic properties, but it is not concerned with quantitative prediction of these properties. The empirical approach, which tries to fit measured values to a preselected equation of state and then calculates other properties by manipulating that equation through thermodynamic relations, is useful in some practical aspects; however, its extrapolation to a range remote from the experimental data used to determine the parameters of the equation is doubtful because of its lack of adequate theoretical background. Another crucial uncertainty is the selection of mixing rules for obtaining the properties of the mixture. Therefore, a theoretically-based principle is needed to guide empirical methods in order to make reasonable extrapolations and extensions.

The theoretical base can be obtained from statistical mechanics, which attempts to establish relationships between macroscopic properties and intermolecular forces. This rigorous approach has demonstrated its predictive power in some simple systems, but there are certain difficulties when it is applied to more complex systems. The major one is the lack of precise knowledge of intermolecular potential between real molecules. Other difficulties are created by the necessary assumptions and approximations made in the derivation and by the computational efforts

involved. These are especially severe if one is concerned about mix-
ture properties. A simpler route to the prediction of thermodynamic
properties is desirable at the expense of a certain amount of rigor.

Realizing the uncertainty in empirical correlation and difficul-
ties in statistical mechanics for real fluid mixtures, Mansoori and Leland[16]
adopted a 'molecular thermodynamics' approach to mixture properties by
which the statistical mechanics is used as a starting point and then
parameters are introduced from pure component data. Their method is
based on a hard sphere expansion (HSE) using a pure fluid as a reference.
Parameters for a pure reference fluid are obtained to evaluate excess
properties over those of a hard sphere fluid for a mixture. These ex-
cess properties are the overall properties less the corresponding hard
sphere properties, and parameters are defined such that these excess
properties are the same for both mixture and reference fluid. The mix-
ture property is then evaluated by adding the excess property of the
reference fluid to the directly calculated hard sphere mixture property.
The method is rather simple and can be applied to systems with any number
of components. The only drawback is that no way of determining the hard
sphere diameters has been developed for this method. Therefore, the
approach as initially described is incomplete.

In this work, we propose a method to determine the effective dia-
meters for use with the HSE theory for real fluids when both the form of
the intermolecular potential and its parameters are unknown, but accurate
equations of state which represent P-V-T behavior over an extensive range
are available for pure components. Presumably other properties derived

from the equations of state are of the same accuracy as well.

Numerical results for compressibility factors, isothermal enthalpy deviations, and fugacity coefficients are presented and compared with experimental data. A flow diagram with sample calculations is given to illustrate the procedures.

CHAPTER 2

CORRESPONDING STATES PRINCIPLE

2.1   Introduction

The principal application of the corresponding states principle

(CSP) is the estimation of unknown thermodynamic properties of many

fluids from the knowledge of the properties of few fluids selected as

the reference substances. This principle has proven to be one of the

most useful tools in correlating and predicting thermodynamic and trans-

port properties for substances of engineering interests.

Historically, the idea of CSP was first introduced by van der Waals

in 1881, and its original theoretical development for 'simple' fluids,

i.e. non-polar fluids with spherical molecules, was presented by Pitzer[19]

in 1939. That work pointed out the molecular requirements which must be

satisfied for a system to obey CSP. They can be summarized as follows:

1. Internal energy states of individual molecules are independent

    of density and depend on temperature only;

2. The molecular energy can be described by classical mechanics,

    i.e. quantum effects can be neglected;

3. The total intermolecular potential energy of the fluid can be

    represented by a sum of pair potentials which can be expressed

    as the product of an energy parameter and a function of dimen-

    sionless separation distances between molecular centers, i.e.

$$U(r) = \epsilon f(\frac{r}{\sigma}) \qquad\qquad (2.1)$$

where ϵ is the minimal energy and σ is the collision diameter.

These assumptions lead directly to the two-parameter CSP. Fluids composed of monatomic or spherically symmetrical molecules satisfy these requirements.

The equation of state derived from statistical mechanics[7,24] using the above assumptions has the form:

$$Z = f(\frac{\epsilon}{kT} , \frac{V}{N\sigma^3})$$ (2.2)

where f is a universal function which is valid for all fluids conforming to the assumptions, k is the Boltzmann constant, V,T, and N are volume, temperature and number of molecules in the system, respectively.

Applying the characteristics of an equation of state at its critical point, i.e. $(\frac{\partial P}{\partial V})_{T=T_c} = 0$ and $(\frac{\partial^2 P}{\partial V^2})_{T=T_c} = 0$, one can express the two-parameters of the equation of state in terms of critical constants

$$Z = f(\frac{T}{T_c}, \frac{V}{V_c})$$ (2.3)

One of the advantages of CSP is that it is not necessary to have an analytical equation of state and one may use instead tabulations of smoothed experimental data in reduced form.

2.2   Deviation from the Simple CSP

The sources of deviation from the simple CSP have been discussed in a review paper by Leland et.al.[4] They classified the pure fluids into five groups accordingly and summarized the attempts made to account for the deviants.

Cook and Rowlinson[6] and Pople[21] have presented the theoretical

basis of a CSP for fluids in which the deviation from simple CSP is

due to an asymmetric force field. From a practical point of view,

among the efforts made to extend simple CSP to 'normal' fluids com-

posed of asymmetrical or slightly polar molecules the use of the empiri-

cal acentric factor and shape factors are most successful. Both have

been widely used in correlating and predicting thermodynamic properties

of hydrocarbons.

The acentric factor, based on vapor pressure deviations, was intro-

duced by Pitzer and Curl[20]. It is defined to be:

$$\omega = -1 - \log_{10}(P_r)_{T_r=.7} \tag{2.4}$$

where the reduced vapor pressure P_r is evaluated at reduced tempera-

ture $T_r=.7$. For simple fluids, the value of ω is essentially zero, but

it becomes larger with increasing polarity or molecular elongation and

smaller as the molecular shape is more spherical. The equation of state

for those fluids can then be expressed as follows:

$$Z = f(\frac{T}{T_c}, \frac{V}{V_c}, \omega) \tag{2.5}$$

The book by Reid et.al[23] contains a broad tabulation of ω values.

The idea of shape factors was theoretically developed by Cook and

Rowlinson[6], and Leach[10]. These parameters multiply the critical pro-

perties of a fluid to give the proper reduced variables for substitution

into a reduced property function for a dissimilar reference fluid. For

example, the equation of state in terms of shape factors is:

$$Z = f(\frac{T}{T_c \theta}, \frac{V}{V_c \phi}) \qquad (2.6)$$

Leach et.al.[11] made practical utilization of shape factors to
the estimation of hydrocarbon properties. The values of shape factors
are generated by simultaneous solution of

$$Z_i = f_r(\frac{T}{T_{c_i} \theta_{ir}}, \frac{V}{V_{c_i} \phi_{ir}}) \qquad (2.7)$$

$$(\frac{f}{P})_i = F_r(\frac{T}{T_{c_i} \theta_{ir}}, \frac{V}{V_{c_i} \phi_{ir}}) \qquad (2.8)$$

where f_r and F_r represent, respectively, the reduced compressibility

factor and fugacity function for a reference fluid r. These shape

factors are designated by two subscripts. The first indicates any given

fluid i and the second a dissimilar reference fluid r. Leach[10] has

derived the functional form of the shape factors in terms of reduced

temperature and density for hydrocarbons.

2.3 Corresponding States Principle for Mixtures

The most important role for CSP is in the prediction of mixture

properties. In engineering practice, the most useful approach has been

through the pseudocritical concept in which the pseudocritical values are

critical properties of a hypothetical pure substance which gives thermo-

dyanmic properties of the mixture when substituted into the pure component equations for the reference. For example, the compressibility factor can be expressed by

$$Z_m = f_r(\frac{T}{T_c'}, \frac{V}{V_c'})$$
(2.9)

or
$$Z_m^{ex} = f_r^{ex}(\frac{T}{T_c''}, \frac{V}{V_c''})$$
(2.10)

where subscripts m and r refer to mixture and reference fluid, respectively, superscript ex indicates "excess property", to be discussed in the next chapter. T_c', V_c' and T_c'', V_c'' are two different types of pseuodocritical constants.

Pseudocritical constants show various forms of composition dependence with different assumptions concerning the solution theory. The ones introduced by Reid and Leland[22] were derived by equating the total mixture property to that of a pure reference fluid as in Eqn. (2.9). In this work, however, the pseudocritical constants are derived from Eqn. (2.10), the equality of the excess over hard sphere mixture property to that of a pure reference fluid. This idea was first proposed by Mansoori and Leland[16].

CHAPTER 3

HARD SPHERE EXPANSION THEORY

Equilibrium thermodynamic properties of a fluid can be predicted

from molecular characteristics by combining an intermolecular potential

function, $U(r)$, and a (radial) distribution function $g_{ij}(r)$ which gives

a measure of the probability of finding two molecules i and j at a dis-

tance r apart. Usually $g(r)$ depends on both density and temperature.

For a pure fluid in which the pair potential $u(r)$ can be written

as $\epsilon f(\frac{r}{\sigma})$, the distribution function can then be expressed in terms of

three dimensionless variables:

$$g(r) = g(\frac{r}{\sigma}, \frac{\epsilon}{kT}, \rho\sigma^3) \tag{3.1}$$

the first two terms show the effect of the characteristics of inter-

acting pair itself on the distribution function, while the last term,

$\rho\sigma^3$, accounts for the molecular environment around the pair created by

the interacting effects of other molecules near it.

For mixtures of conformal components in which all pair poten-

tial functions are factorable in the form of $\epsilon_{ii} f(\frac{r}{\sigma_{ii}})$ for like pairs

and $\epsilon_{ij} f(\frac{r}{\sigma_{ij}})$ for unlike pairs, the distribution function, for a binary

A-B mixture, can be written as:

$$g_{AB}^m(r) = g(\frac{r}{\sigma_{AB}}, \frac{\epsilon_{AB}}{kT}, \frac{\epsilon_{AA}}{kT}, \frac{\epsilon_{BB}}{kT}, \rho_A\sigma_{AA}^3, \rho_A\sigma_{AB}^3, \rho_B\sigma_{BB}^3, \rho_B\sigma_{AB}^3)$$

$$\tag{3.2}$$

It is a complicated function depending on the number density of each

constituent and every conceivable interaction of core molecules and

nearby neighbors.

Assuming spherical central force field and pairwise additivity of

potential functions, and neglecting more-than-two body interactions, one

can show[7] the following relationships between equilibrium properties and

molecular characteristics.

For pure fluids:

$$Z = \frac{P\bar{V}}{RT} = 1 - \frac{2\pi\rho}{3kT} \int_0^\infty \frac{du}{dr} g(r)r^3 \, dr \qquad (3.3)$$

$$\left(\frac{\bar{U}-\bar{U}^*}{RT}\right)_{T,V} = \frac{2\pi\rho}{kT} \int_0^\infty u(r) \, g(r)r^2 \, dr \qquad (3.4)$$

$$\left(\frac{\bar{A}-\bar{A}^*}{RT}\right)_{T,V} = \frac{2\pi\rho}{k} \int_0^{1/T} \int_0^\infty u(r) \, g(r,T)r^2 dr \, d(\frac{1}{T}) \qquad (3.5)$$

For mixtures of N components:

$$Z_m = 1 - \frac{2\pi\rho}{3kT} \sum_i^N \sum_j^N x_i x_j \int_0^\infty \frac{du_{ij}(r)}{dr} g_{ij}(r) \, r^3 dr \qquad (3.6)$$

$$\left(\frac{\bar{U}-\bar{U}^*}{RT}\right)_{m,T,V} = \frac{2\pi\rho}{kT} \sum_i^N \sum_j^N x_i x_j \int_0^\infty u_{ij}(r)g_{ij}(r)^3 \, dr \qquad (3.7)$$

$$\left(\frac{\bar{A}-\bar{A}^*}{RT}\right)_{m,T,V} = \frac{2\pi\rho}{k} \sum_i^N \sum_j^N x_i x_j \int_0^{1/T} \int_0^\infty u_{ij}(r)g_{ij}(r,T)r^3 dr \, d(\frac{1}{T}) \qquad (3.8)$$

For many systems of engineering interests, e.g. dense liquids and

their mixtures, it is very difficult to determine the exact form of

the intermolecular potential and the analytical expression of the dis-

tribution function. Furthermore, the complication of the integrations

which appear in the above equations prohibits one from attempting a

direct computation. It is convenient to resort to a perturbation techni-

que in which the properties of the mixture are calculated from the known

properties of a reference system. However, the reference system must

satisfy two criteria. The first is that the underlying reference system

must be similar to the given system in some sense to insure the rapid con-

vergence; secondly, the properties of the reference system must be known

with sufficient accuracy, either from theory or experiment.

Calculations from equations of state for both pure hard spheres[2]

and hard sphere mixtures[15] are in very good agreement with the data from

machine-calculated Monte Carlo methods and molecular dynamic calculations.

The effectiveness of a hard sphere system as a perturbation reference has

also been tested and justified by many researchers.[26]

In using a hard sphere system as a reference, the choice of the

effective diameter is very important, because the calculated thermodynamic

properties are very sensitive to the diameter. The determination of hard

sphere diameter is discussed in Chapter 4.

3.1   Perturbation Expansion about Hard Sphere Properties

The basic idea of HSE theory is to separate any dimensionless pro-

perty into effects due to repulsive forces and those due to attraction;

the strategy employed starts with separating the intermolecular potential

into two terms. The first is that applicable to hard sphere behavior at

a properly chosen average diameter and a second term accounts for the

attractive forces. With this kind of potential separation, the distribu-

tion function can then be expanded into a power series in $\frac{1}{kT}$ beginning with the hard sphere term. Substitution of separated potential and expanded distribution function into property equations, e.g. Eqns. (3.3) through (3.8), produces another power series of $\frac{1}{kT}$ with the first term containing characteristics of hard spheres only, and the remaining terms arising from the attractive part of the potential function.

To illustrate for a pure fluid of N molecules, divide the total intermolecular potential U into a hard sphere potential U^o and a residual $U^{(1)}$, i.e.

$$U = U^o + U^{(1)} \tag{3.9}$$

where

$$U^o = \sum_{j>i=1}^{N} u^o (r_{ij}, d), \quad u^o (r_{ij}, d) = \begin{cases} 0, & r_{ij} > d \\ \infty, & r_{ij} \leq d \end{cases} \tag{3.10}$$

$$U^{(1)} = \sum_{j>i=1}^{N} u^{(1)}(r_{ij}, d, \varepsilon) = \varepsilon \sum_{j>i=1}^{N} f^{(1)} \left(\frac{r_{ij}}{d}\right) \tag{3.11}$$

The assumptions made in the above equations are (1) pair potential can be represented by $u(r, d, \varepsilon)$ as shown in Fig. 1, (2) additivity of pair potentials holds for both hard sphere and attractive potential, (3) the attractive potential can be factored into the product of an energy parameter and a dimensionless function of $\frac{r}{d}$, and (4) three-body interactions are negligible.

u(r)
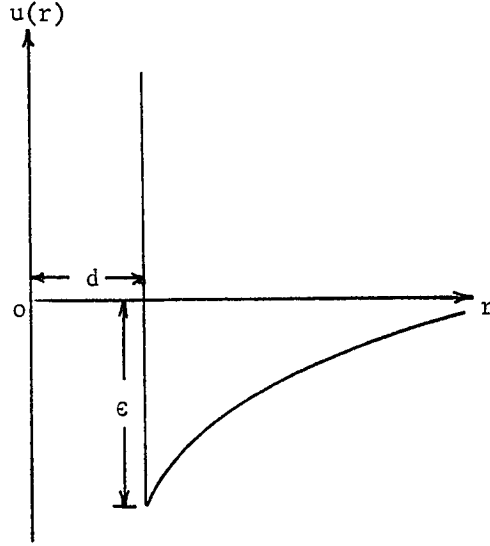
Fig. 1 The HSE Potential

The radial distribution function g(r) for a pure fluid is related to the total intermolecular potential U by

$$g(r) = \frac{V^2}{N!Q} \int \ldots N-2 \ldots \int \exp(-\frac{U}{kT}) \, d\vec{r}_3 \ldots d\vec{r}_N \qquad (3.12)$$

where Q, the configurational partition function, is defined:

$$Q \equiv \frac{1}{N!} \int \ldots N \ldots \int \exp(-\frac{U}{kT}) \, d\vec{r}_1 \ldots d\vec{r}_N \qquad (3.13)$$

V, T, and N are volume, temperature and number of molecules of the system, respectively. The exponential term in both Eqns. (3.12) and (3.13) can be expanded in terms of the hard sphere potential and a series of successive powers of $\frac{1}{kT}$:

$$\exp(-\frac{U}{kT}) = \exp(-\frac{U^0}{kT}) [1 - (\frac{U^{(1)}}{kT}) + \frac{1}{2!} (\frac{U^{(1)}}{kT})^2 - \ldots] \qquad (3.14)$$

Eqn. (3.11) for $U^{(1)}$ is now substituted into Eqn. (3.14) and the result

is placed in Eqn. (3.12) for $g(r)$ and Eqn. (3.13) for Q. The resulting

expansions of the integral and Q in Eqn. (3.12) are each divided by Q^0,

the configurational integral for a hard sphere fluid which can be ob-

tained by replacing U in Eqn. (3.13) by U^0. The distribution function

then becomes:

$$g(r) = g^0 \left(\frac{r}{d},\rho d^3\right)\left[1 + \left(\frac{\epsilon}{kT}\right)g^{(1)}\left(\frac{r}{d},\rho d^3\right) + \left(\frac{\epsilon}{kT}\right)^2 g^{(2)}\left(\frac{r}{d},\rho d^3\right) + \ldots\right] \quad (3.15)$$

The first term g^0 is the distribution function for a hard sphere fluid with

molecules of diameter d. The functions $g^{(1)}$ and $g^{(2)}$ are sums of compli-

cated integrals which are dimensionless functions of $\left(\frac{r}{d}\right)$ and ρd^3. Note that

$g^{(1)}$ and $g^{(2)}$ terms are zero at $r \leq d$.

Substituting this expanded distribution function [Eqn. (3.15)] and

separated potential as in Eqn. (3.9) into the equation of state for a pure

fluid [Eqn. (3.3)] yields a series in $\frac{1}{kT}$ in the form:

$$Z = Z^0 + \left(\frac{\epsilon}{kT}\right)(\rho d^3) Z^{(1)} + \left(\frac{\epsilon}{kT}\right)^2 (\rho d^3) Z^{(2)} + \ldots \quad (3.16)$$

Z^0, the compressibility factor of hard spheres, $Z^{(1)}$ and $Z^{(2)}$ are, respectively,

$$Z^0 = 1 - \frac{2\pi\rho d^3}{3kT} \int_0^\infty \frac{du^0(y)}{dy} g^0(y,\rho d^3) y^3 dy \quad (3.17)$$

$$Z^{(1)} = -\frac{2\pi}{3} \int_0^\infty \frac{df^{(1)}(y,\rho d^3)}{dy} g^0(y,\rho d^3) y^3 dy \quad (3.18)$$

$$z^{(2)} = -\frac{2\pi}{3} \int_0^\infty \frac{df^{(1)}(y,\rho d^3)}{dy} \, g^0(y,\rho d^3) \, g^{(1)}(y,\rho d^3) \, y^3 dy \qquad (3.19)$$

where $y = \frac{r}{d}$.

Similar expanded expressions for internal energy deviation Eqn. (3.4) and Helmholtz free energy deviation Eqn. (3.5) of pure component can be obtained by the same procedures. Note that the internal energy deviation for hard sphere system is zero.

It is necessary now to consider the possibility of developing a similar expansion of the equation of state for a mixture of conformal components. As shown in Eqn. (3.2), the pair distribution function $g_{AB}^m(r)$ in a mixture depends on the force parameters of all kinds of molecular pair interactions and the number densities of every species. It is formidable to attempt direct expansion, but a corresponding states technique called the mean density approximation (MDA)[16] has been used to overcome this difficulty. This approximation assumes

$$g_{AB}^m(r) = g(\frac{r}{\sigma_{AB}}, \frac{\epsilon_{AB}}{kT}, \rho\bar\sigma^3) \qquad (3.20)$$

where ρ is the number density of the mixture. The function g is the pair distribution function for a pure reference fluid, which is conformal with the constituents of the mixture. The first two dimensionless parameters are characteristics of the specific A-B pair interaction. The dimensionless density parameter, however, which describes the effect of the molecular environment around the pair, is an average parameter and depends on the mixture composition. The definition of $\bar\sigma^3$ has dif-

ferent forms for different theories. In the van der Waals one-fluid theory,[22] it is

$$\overline{\sigma}^3 = \sum_i^N \sum_j^N x_i x_j \sigma_{ij}^3 \qquad (3.21)$$

and in HSE conformal solution theory, it is given by:

$$\overline{d}^3 = \frac{[\sum_i^N \sum_j^N x_i x_j d_{ij}^3 \epsilon_{ij}]^2}{\sum_i \sum_j x_i x_j d_{ij}^3 \epsilon_{ij}^2} \qquad (3.22)$$

Derivation of Eqn. (3.22) will be shown in Chapter 4. The effectiveness of MDA for the HSE procedure with Eqn. (3.22) has been justified to some extent by Chang.[3]

Making a similar separation of the intermolecular potential and following the procedure in deriving an expanded distribution function for a pure fluid, one can show that the distribution function for an A-B pair in a mixture is:

$$g_{AB}^m(r) = g_{AB}^0 \left(\frac{r}{d_{AB}}, \rho \overline{d}^3\right)[1 + \frac{\epsilon_{AB}}{kT} g_{AB}^{(1)} \left(\frac{r}{d_{AB}}, \rho \overline{d}^3\right) \qquad (3.23)$$

$$+ \left(\frac{\epsilon_{AB}}{kT}\right)^2 g_{AB}^{(2)} \left(\frac{r}{d_{AB}}, \rho \overline{d}^3\right) + \ldots]$$

where the g_{AB}^0, $g_{AB}^{(1)}$ and $g_{AB}^{(2)}$ are the same as those in Eqn. (3.15) for a pure fluid if d^3 is replaced by $\overline{d}^3$. The $\overline{d}^3$ comes from MDA.

An equation of state for the mixture is then obtained by substituting Eqn. (3.23) into Eqn. (3.6) with the potential separated into the hard sphere and attractive portion. The result is

$$Z_m = Z_m^O + \sum_i^N \sum_j^N (\frac{\epsilon_{ij}}{kT}) \ (\rho d_{ij}^3) \ Z_m^{(1)} + \sum_i^N \sum_j^N (\frac{\epsilon_{ij}}{kT})^2 \ (\rho d_{ij}^3) \ Z_m^{(2)} + \ldots \quad (3.24)$$

where Z_m^O, compressibility factor of hard sphere mixture, is

$$Z_m^O = 1 - \sum_i^N \sum_j^N \frac{2\pi\rho d_{ij}^3}{3kT} \int_0^\infty \frac{du^O(y)}{dy} \ g^O(y, \rho \bar{d}^3) \ y^3 dy \quad (3.25)$$

$Z_m^{(1)}$ is the same as $Z^{(1)}$ and likewise $Z_m^{(2)}$ is the same as $Z^{(2)}$ with d^3 in

Eqns. (3.18) and (3.19) replaced by $\bar{d}^3$. The expanded expression for

internal energy deviation and Helmholtz free energy of the mixture can

be derived by the same procedure.

3.2 Thermodynamic Properties of Mixtures by HSE Method

As shown in the Eqn. (3.16), the compressibility factor is separated

into two parts. One is generated by the repulsive portion of the inter-

molecular potential and the other by the attractive portion. For a pure

fluid, any dimensionless thermodynamic property can be expressed as the

sum of the hard sphere part and the excess part as

$$X_r = X_r^{hs} + X_r^{ex} \quad (3.26)$$

where X represents a dimensionless thermodynamic function such as Z,

$\frac{\bar{U}-\bar{U}^*}{RT}$, $\frac{\bar{H}-\bar{H}^*}{RT}$, $\frac{\bar{A}-\bar{A}^*}{RT}$, $\frac{\bar{G}-\bar{G}^*}{RT}$, $\ln\frac{f}{p}$ or $\ln\frac{f}{\rho RT}$. Subscript r refers to any pure

reference fluid r, and superscripts hs and ex refer to hard sphere and

excess properties, respectively.

Similar expression for mixtures can be obtained by assuming the

mean density approximation as shown in the previous section. This

gives

$$X_m = X_m^{hs} + X_m^{ex} \tag{3.27}$$

where m stands for mixture.

Applying CSP to excess part of pure fluid and mixture, i.e. letting

$X_m^{ex} = X_r^{ex}$, and combining Eqns. (3.26) and (3.27), one obtains the working equation

$$X_m = X_m^{hs} + (X_r - X_r^{hs})_{T^o,\rho^o} \tag{3.28}$$

The total mixture property X_m is the desired function. The hard sphere mixture property X_m^{hs} can be calculated by knowing the individual hard sphere diameter of each component. The reference fluid hard sphere property X_r^{hs} can be evaluated by knowing the equivalent diameter of the mixture. The reference fluid total property x_r is predicted at the equivalent conditions, such as an equivalent temperature T^o and density ρ^o, as will be defined in Chapter 4.

3.2.a) <u>Compressibility Factor</u>

The working equation for obtaining the compressibility factor is

$$Z_m = Z_m^{hs} + (Z_r - Z_r^{hs})_{T^o,\rho^o} \tag{3.29}$$

Carnahan and Starling[2] developed an equation of state for a system of nonattracting hard spheres in the form:

$$z^{hs} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \tag{3.30}$$

where $\eta = \frac{\pi}{6} \rho d^3$, ρ is the particle density and d the diameter of the rigid sphere.

For a hard sphere mixture of N components, Mansoori, et.al.[15] developed the following equation of state.

$$Z_m^{hs} = \frac{1 + (1-3Y_1)\xi_m + (1-3Y_2)\xi_m^2 - Y_3\xi_m^3}{(1 - \xi_m)^3} \qquad (3.31)$$

where

$$\xi_m = \sum_{i=1}^{N} \xi_i = \frac{\pi}{6} \rho_m \sum_{i=1}^{N} x_i d_i^3 \qquad (3.32)$$

$$Y_1 = \sum_{j>i}^{N} \sum_{i=1}^{N} \Delta_{ij}(d_i + d_j)(d_i d_j)^{-\frac{1}{2}} \qquad (3.33)$$

$$Y_2 = \sum_{j>i}^{N} \sum_{i=1}^{N} \Delta_{ij} \sum_{k=1}^{N} (\frac{\xi_k}{\xi_m}) \frac{(d_i d_j)^{\frac{1}{2}}}{d_k} \qquad (3.34)$$

$$Y_3 = [\sum_{i=1}^{N} (\frac{\xi_i}{\xi_m})^{2/3} x_i^{\frac{1}{3}}]^3 \qquad (3.35)$$

and

$$\Delta_{ij} = [(\xi_i \xi_j)^{\frac{1}{2}}/\xi_m][(d_i-d_j)^2/d_i d_j](x_i x_j)^{\frac{1}{2}} \qquad (3.36)$$

If the reference property Z_r is calculated from the BWRS equation of state as shown in Appendix A, one can obtain the compressibility factor for the mixture by substituting Eqns. (3.30) and (3.31) into (3.29).

3.2.b) Isothermal Internal Energy and Enthalpy Deviation

Since no contribution comes from the repulsive part of the poten-
tial to the internal energy deviation, the equation for internal energy
deviation reduces to

$$\left[\left(\frac{\overline{U}-\overline{U}^*}{RT} \right)_m \right]_{T,V} = \left[\left(\frac{\overline{U}-\overline{U}^*}{RT} \right)_r \right]_{T^o, \rho^o} \tag{3.37}$$

and the mixture property is given completely by that of the reference.

The expression for $\left(\frac{\overline{U}-\overline{U}^*}{RT} \right)_r$ from the BWRS equation of state is
derived in Appendix A, and the enthalpy deviation of the mixture is
obtained by the relationship

$$\left(\frac{\overline{H}-\overline{H}^*}{RT} \right)_m = \left(\frac{\overline{U}-\overline{U}^*}{RT} \right)_m + \left(\frac{\overline{PV}}{RT} - \frac{P^*\overline{V}^*}{RT} \right)_m = \left(\frac{\overline{U}-\overline{U}^*}{RT} \right)_m + Z_m - 1 \tag{3.38}$$

Note that $\overline{H}^*$ and $\overline{U}^*$ are functions of temperature only.

3.2.c Free Energies

The working equation for the Helmholtz free energy is

$$\left[\left(\frac{\overline{A}-\overline{A}^*}{RT} \right)_m \right]_{T,V} = \left(\frac{\overline{A}-\overline{A}^*}{RT} \right)_m^{hs} + \left[\left(\frac{\overline{A}-\overline{A}^*}{RT} \right)_r - \left(\frac{\overline{A}-\overline{A}^*}{RT} \right)_r^{hs} \right]_{T^o, \rho^o} \tag{3.39}$$

Expressions for all three terms on the RHS of Eqn. (3.39) can be derived
through Eqn. (3.40) with an appropriate equation of state

$$\left(\frac{\overline{A}-\overline{A}^*}{RT} \right)_{T,V} = \int_o^\rho (Z-1) \frac{d\rho'}{\rho'} \tag{3.40}$$

The results are

$$\left(\frac{\overline{A}-\overline{A}^*}{RT} \right)_m^{hs} = (Y_3 - 1)\, \ell n(1-\xi_m) + \frac{3Y_2 + 2Y_3}{1-\xi_m} + \frac{3}{2} \frac{(1-Y_1-Y_2-Y_3/3)}{(1-\xi_m)^2} - \frac{3}{2}(1-Y_1+Y_2+Y_3)$$

$$\tag{3.41}$$

$$\left(\frac{\overline{A}-\overline{A}^*}{RT}\right)_r^{hs} = \frac{1}{(1-\eta)^2} + \frac{2}{(1-\eta)} - 3 \tag{3.42}$$

and $\left(\dfrac{\overline{A}-\overline{A}^*}{RT}\right)_r$ from BWRS equation of state is derived in Appendix A. All

symbols in the above equations have been defined in section (3.2.a).

From the definition of Gibbs free energy at constant temperature

and volume, one obtains

$$\left(\frac{\overline{G}-\overline{G}^*}{RT}\right)_{T,V} = \left(\frac{\overline{A}-\overline{A}^*}{RT}\right)_{T,V} + \left(\frac{P\overline{V}-P^*\overline{V}^*}{RT}\right) \tag{3.43}$$

Eqn. (3.43) can be expressed in terms of temperature and pressure by:

$$\left(\frac{\overline{G}-\overline{G}^*}{RT}\right)_{T,P} = \left(\frac{\overline{A}-\overline{A}^*}{RT}\right)_{T,V} + (Z-1) + \frac{\overline{G}_{T,P^*}^*}{RT} - \frac{\overline{G}_{T,P}^*}{RT} \tag{3.44}$$

where

$$P^* = \frac{RT}{\overline{V}} \quad \text{and} \quad P = \frac{ZRT}{\overline{V}} \tag{3.45}$$

Integration of the Gibbs free energy of an ideal gas from P^* to P

at constant temperature yields

$$\overline{G}_{T,P}^* - \overline{G}_{T,P^*}^* = \int_{P^*}^{P} d\overline{G}^* = \int_{P^*}^{P} \overline{V}^* \, dP = \int_{P^*}^{P} \frac{RT}{P} \, dP = RT \ln \frac{P}{P^*} = RT \ln Z \tag{3.46}$$

Substituting (3.46) into (3.44), one obtains

$$\left(\frac{\overline{G}-\overline{G}^*}{RT}\right)_{T,P} = \left(\frac{\overline{A}-\overline{A}^*}{RT}\right)_{T,V} + (Z-1) - \ln Z \tag{3.47}$$

Noteworthily, in the process of calculating $\left(\dfrac{\overline{A}-\overline{A}^*}{RT}\right)_m$, one can obtain Z_m

and $(\frac{\overline{U}-\overline{U}^*}{RT})_m$ as well. They are useful in the calculation of the partial

fugacity discussed later but differ from those obtained directly from Z_m

and $(\frac{\overline{U}-\overline{U}^*}{RT})_m$ calculations. We distinguish them by labeling subscript A,

$(Z_A)_m$ and $(\frac{\overline{U}_A-\overline{U}_A^*}{RT})_m$, to indicate that those properties are from $(\frac{\overline{A}-\overline{A}^*}{RT})_m$

calculation.

3.2.d) <u>Fugacity Coefficient of Individual Components and K-values</u>

In this section, we are going to derive an expression for the

fugacity coefficient of an individual component $(\ell n \frac{f_i}{x_i P})$.

The chemical potential of the ith component in the mixture is

defined by

$$\mu_i \equiv (\frac{\partial A}{\partial n_i})_{T,V,n_j} = (\frac{\partial G}{\partial n_i})_{T,P,n_j} \qquad (3.48)$$

the chemical potential departure can then be written as

$$(\mu_i-\mu_i^*)_{T,V} = \frac{\partial}{\partial n_i} [n(\overline{A}-\overline{A}^*)]_{T,V,n_j} \qquad (3.49)$$

where the bar (-) means molar quantity.

Eqn. (3.49) can also be expressed in terms of temperature and

pressure as

$$(\mu_i-\mu_i^*)_{T,V} = (\mu_i-\mu_i^*)_{T,P} + (\mu_i^*)_{T,P} - (\mu_i^*)_{T,P^*} \qquad (3.50)$$

where $P^* = \dfrac{RT}{\overline{V}}$ and $P = \dfrac{ZRT}{\overline{V}}$.

$$\hspace{11cm} (3.51)$$

It is noted that, by definition:

$$[d\mu_i = RT\,d\ell n f_i]_T \hspace{5cm} (3.52)$$

and

$$(\mu_i - \mu_i^*)_{T,P} = RT\, \ell n\, \frac{f_i}{x_i P} \hspace{4cm} (3.53)$$

Integration of the chemical potential Eqn. (3.52) for an ideal gas mixture

from P^* to P at constant temperature yields

$$(\mu_i^*)_{T,P} - (\mu_i^*)_{T,P^*} = \int_{P^*}^{P} d\mu_i = RT \int_{P^*}^{P} d\ell n\, f_i = RT\, \ell n\, \frac{x_i P}{x_i P^*} = RT\, \ell n Z$$

$$\hspace{11cm} (3.54)$$

Substituting Eqns. (3.49), (3.53), and (3.54) into Eqn. (3.50), one

obtains

$$\ell n\, \frac{f_i}{x_i P} = -(\ell n Z)_m + \frac{\partial}{\partial n_i}\, [n(\frac{\overline{A} - \overline{A}^*}{RT})_m]_{T,V,n_j}$$

$$\hspace{11cm} (3.55)$$

$$= -(\ell n Z)_m + [(\frac{\overline{A} - \overline{A}^*}{RT})_m]_{T,V} + n\, \frac{\partial}{\partial n_i}\, [(\frac{\overline{A} - \overline{A}^*}{RT})_m]_{T,V,n_j}$$

The first term $(\ell n Z)_m$ is obtained from the Z_m calculation in section

(3.2.a), the second term from the previous section, and the last term

according to Eqn. (3.39), can be separated into hard sphere part and ex-

cess part. The latter is then replaced by reference fluid. The result is

$$n \frac{\partial}{\partial n_i} \left[\left(\frac{\overline{A} - \overline{A}^*}{RT} \right)_m \right]_{T,V,n_j} = n \frac{\partial}{\partial n_i} \left[\left(\frac{\overline{A} - \overline{A}^*}{RT} \right)_m^{hs} \right]_{T,V,n_j} + \frac{\partial}{\partial n_i} \left[\left(\frac{\overline{A} - \overline{A}^*}{RT} \right)_{r,T^o,\rho^o}^{ex} \right]$$

(3.56)

The composition-dependence of T^o and ρ^o are due to the composition-dependence of pseudocriticals and the definitions of equivalent conditions as shown in Eqns. (4.14) through (4.17). Differentiation of Eqn. (3.40) w.r.t. n_i for a mixture of hard spheres produces the first term on the RHS of Eqn. (3.56).

$$n \frac{\partial}{\partial n_i} \left[\left(\frac{\overline{A} - \overline{A}^*}{RT} \right)_m^{hs} \right]_{T,V,n_j} = n \int_o^\rho \left(\frac{\partial Z}{\partial n_i} \right)_{m,T,V,n_j}^{hs} \frac{d\rho'}{\rho'}$$

(3.57)

Hsu[8] has shown that

$$\int_o^\rho \left(\frac{\partial Z}{\partial n_i} \right)_{m,T,V,n_j}^{hs} \frac{d\rho'}{\rho'} = \left[\frac{3}{2} (Y_{1,i}' - Y_{2,i}' - Y_{3,i}') - \frac{\xi_{m,i}'}{\xi_m} (1-Y_3) \right]$$

$$+ Y_{3,i}' \ln (1-\xi_m) + \frac{1}{1-\xi_m} \left[(1-3Y_2-3Y_3) \frac{\xi_{m,i}'}{\xi_m} + 3Y_{2,i}' + 2Y_{3,i}' \right]$$

$$+ \frac{1}{(1-\xi_m)^2} \left[3 \frac{\xi_{m,i}'}{\xi_m} (-1+Y_1+2Y_2+Y_3) - \frac{3}{2} (Y_{1,i}' + Y_{2,i}' + \frac{1}{3} Y_{3,i}') \right]$$

$$+ \frac{1}{(1-\xi_m)^3} \left[3 \frac{\xi_{m,i}'}{\xi_m} (1 - Y_1 - Y_2 - \frac{1}{3} Y_3) \right]$$

(3.58)

where

$$\xi_{m,i}' = \left(\frac{\partial \xi_m}{\partial n_i} \right)_{T,V,n_j} = \frac{\pi}{6n} \rho d_i^3$$

(3.59)

$$Y_{k,i}' = \left(\frac{\partial Y_k}{\partial n_i} \right)_{T,V,n_j} \quad \text{for } k = 1,2,3$$

(3.60)

and $Y_{1,i}' = \dfrac{\pi\rho}{6n\xi_m} \sum\limits_{j=1}^{N} (d_i + d_j)(d_i - d_j)^2 x_j - (\dfrac{1}{n} + \dfrac{\xi_{m,i}'}{\xi_m})Y_1$ (3.61)

$$Y_{2,i}' = \dfrac{1}{n} [\dfrac{d_i^2}{\sum\limits_{k=1}^{N} x_k d_k^2} - 2\dfrac{n\xi_{m,i}'}{\xi_m} - 1] Y_2$$

$$+ \dfrac{1}{n} (\dfrac{\pi\rho}{6\xi_m})^2 (\sum\limits_{k=1}^{N} x_k d_k^2) [\sum\limits_{j=1}^{N} (d_i d_j)(d_i - d_j)^2 x_j] \quad (3.62)$$

$$Y_{3,i}' = \dfrac{1}{n} [\dfrac{3d_i^2}{\sum\limits_{j=1}^{N} x_j d_j^2} - 2\dfrac{n\xi_{m,i}'}{\xi_m} - 1] Y_3 \quad (3.63)$$

n_i and x_i are, respectively, the number of moles and the molar fraction of ith component, n is the total number of moles, N is the number of components in the mixture, while other quantities ξ_m, Y_1, Y_2 and Y_3 have been defined in section (3.2.a).

Let us now work on the last term of Eqn. (3.56); it is the 'excess' Helmholtz free energy of the reference substance r at the equivalent temperature T^0 and equivalent density ρ^0. For convenience, the subscript r has been omitted in the following derivations. Performing the differentiation yields

$$n \dfrac{\partial}{\partial n_i} [(\dfrac{\overline{A}-\overline{A}^*}{RT})_{T^0,\rho^0}] = n \dfrac{\partial}{\partial T^0} [(\dfrac{\overline{A}-\overline{A}^*}{RT})_{\rho^0}^{ex}] (\dfrac{\partial T^0}{\partial n_i})_{n_j}$$

$$+ n \dfrac{\partial}{\partial \rho^0} [(\dfrac{\overline{A}-\overline{A}^*}{RT})_{T^0}^{ex}] (\dfrac{\partial \rho^0}{\partial n_i})_{n_j}$$

      (3.64)

Differentiating Eqn. (3.40) w.r.t. temperature and density separately, one can show that

$$\frac{\partial}{\partial T^o} \left(\frac{\overline{A}-\overline{A}^*}{RT}\right)^{ex}_{\rho^o} = \int_0^{\rho^o} \left(\frac{\partial Z}{\partial T^o}\right)^{ex}_{\rho'} \frac{d\rho'}{\rho'} = -\frac{1}{T^o} \left(\frac{\overline{U}_A-\overline{U}_A^*}{RT}\right)^{ex}_{T^o,\rho^o} \tag{3.65}$$

and

$$\frac{\partial}{\partial \rho^o} \left(\frac{\overline{A}-\overline{A}^*}{RT}\right)^{ex}_{T^o} = \frac{1}{\rho^o} (Z_A-1)^{ex}_{T^o,\rho^o} \tag{3.66}$$

Note, as mentioned in the previous section, we add subscript A to indi-cate the quantities are obtained from $\left(\dfrac{\overline{A}-\overline{A}^*}{RT}\right)_m$ calculation.

The equivalent temperature and density are functions of pseudo-critical temperature and volume as shown in Eqns. (4.16) and (4.17), one can then write

$$\left(\frac{\partial T^o}{\partial n_i}\right)_{n_j} = \left(\frac{\partial T^o}{\partial T_c''}\right)_{V_c''} \left(\frac{\partial T_c''}{\partial n_i}\right)_{n_j} \tag{3.67}$$

$$\left(\frac{\partial \rho^o}{\partial n_i}\right)_{n_j} = \left(\frac{\partial \rho^o}{\partial V_c''}\right)_{T_c''} \left(\frac{\partial V_c''}{\partial n_i}\right)_{n_j} \tag{3.68}$$

and

$$\left(\frac{\partial T^o}{\partial T_c''}\right)_{V_c''} = -\frac{T\,T_c}{T_c''^2} \tag{3.69}$$

$$\left(\frac{\partial \rho^o}{\partial V_c''}\right)_{T_c''} = \frac{\rho}{V_c} \tag{3.70}$$

Substituting Eqns. (3.65) through (3.70) into (3.64), one obtains

$$n \frac{\partial}{\partial n_i} \left[\left(\frac{\overline{A} - \overline{A}^*}{RT} \right)^{ex}_{T^o, \rho^o} \right] = \left(\frac{\overline{U}_A - \overline{U}_A^*}{RT} \right)^{ex}_{T^o, \rho^o} \cdot \frac{n}{T_c''} \left(\frac{\partial T_c''}{\partial n_i} \right)_{n_j}$$

$$+ (Z_A - 1)^{ex}_{T^o, \rho^o} \cdot \frac{n}{V_c''} \left(\frac{\partial V_c''}{\partial n_i} \right)_{n_j} \qquad (3.71)$$

the expressions for $n \left(\frac{\partial T_c''}{\partial n_i} \right)_{n_j}$ and $n \left(\frac{\partial V_c''}{\partial n_i} \right)_{n_j}$ are derived in Appendix B.

Substition of Eqns. (3.57) and (3.71) into Eqn. (3.55) yields the fugacity coefficient of individual component in the mixture

$$\ell n \frac{f_i}{x_i P} = - (\ell n Z)_m + \left[\left(\frac{\overline{A} - \overline{A}^*}{RT} \right)_m \right]_{T,V} + \left[\left(\frac{\overline{U}_A - \overline{U}_A^*}{RT} \right)_r \right]_{T^o, \rho^o} \cdot \frac{n}{T_c''} \left(\frac{\partial T_c''}{\partial n_i} \right)_{n_j}$$

$$+ \left[(Z_A - Z_A^{hs})_r \right]_{T^o, \rho^o} \cdot \frac{n}{V_c''} \left(\frac{\partial V_c''}{\partial n_i} \right)_{n_j} + n \int_0^\rho \left(\frac{\partial Z}{\partial n_i} \right)^{hs}_{m,T,V,n_j} \frac{d\rho}{\rho}$$

$$(3.72)$$

The last integral term was expressed in Eqn. (3.58).

The k-value can be obtained from

$$\ell n K_i = \left(\ell n \frac{f_i}{x_i P} \right)_L - \left(\ell n \frac{f_i}{y_i P} \right)_V = \ell n \frac{y_i}{x_i} \qquad (3.73)$$

where subscripts L and V refer to liquid and vapor phases at the equilibrium temperature and pressure, respectively.

CHAPTER 4

APPLICATION OF CSP AND HSE TO HYDROCARBON MIXTURES

4.1 Defining Equations of Pseudoforce Parameters for HSE Method

As mentioned in the previous chapter, a dimensionless mixture thermodynamic property is obtained by adding a directly calculated hard sphere mixture property to an excess over hard sphere mixture property. The latter is set to equal to the corresponding pure reference fluid property calculated by substituting pseudoforce parameter $\bar{\epsilon}$ and $\bar{d}^3$ into a pure reference fluid equation. A detailed treatment of the development of the pseudoforce parameter defining equation is given by Mansoori and Leland[16].

The equation of state for the pure reference fluid can be rewritten from Eqn. (3.16) by replacing ϵ and d^3 with $\bar{\epsilon}$ and $\bar{d}^3$, respectively, as follows

$$Z_r = Z^0 + (\frac{\bar{\epsilon}}{kT})(\rho\bar{d}^3)\ Z^{(1)} + (\frac{\bar{\epsilon}}{kT})^2(\rho\bar{d}^3)\ Z^{(2)} + 0[(\frac{\bar{\epsilon}}{kT})^3] \qquad (4.1)$$

$\bar{\epsilon}$ and $\bar{d}^3$ are the two pseudoforce parameters of the mixture, they, or the pseudo-criticals derived thereafter, will be used to predict the mixture property from the pure reference fluid at the same conditions as the mixture is.

Subtracting Eqn. (4.1) from Eqn. (3.24), regrouping terms of like powers in $(\frac{1}{kT})$, one obtains

$$Z_m - Z_r = (Z_m^o - Z_r^o) + (\frac{1}{kT}) \rho \; (\sum_i^N \sum_j^N \epsilon_{ij} d_{ij}^3 - \overline{\epsilon} \; \overline{d}^3) \; Z^{(1)}$$

$$(4.2)$$

$$+ (\frac{1}{kT})^2 \; \rho \; (\sum_i^N \sum_j^N \epsilon_{ij}^2 \; d_{ij}^3 - \overline{\epsilon}^2 \; \overline{d}^3) Z^{(2)} + 0 \; [(\frac{1}{kT})^3]$$

The first two terms on the RHS of Eqn. (4.2) are, respectively, hard-sphere compressibility factors of the mixture and reference fluid which are calculated from equations of states for hard sphere systems by using appropriately chosen effective diameters. The last two terms are set to be zero by making

$$\overline{\epsilon} \; \overline{d}^3 = \sum_i^N \sum_j^N x_i x_j \; \epsilon_{ij} d_{ij}^3 \qquad (4.3)$$

$$\overline{d}^3 \; \overline{\epsilon}^2 = \sum_i^N \sum_j^N x_i x_j \; \epsilon_{ij}^2 d_{ij}^3 \qquad (4.4)$$

or
$$\overline{d}^3 = \frac{[\sum_i^N \sum_j^N x_i x_j \; \epsilon_{ij} d_{ij}^3]^2}{\sum_i^N \sum_j^N x_i x_j \; \epsilon_{ij}^2 d_{ij}^3} \qquad (4.5)$$

$$\overline{\epsilon} = \frac{\sum_i^N \sum_j^N x_i x_j \; \epsilon_{ij}^2 d_{ij}^3}{\sum_i^N \sum_j^N x_i x_j \; \epsilon_{ij} d_{ij}^3} \qquad (4.6)$$

Eqn. (4.2) then reduces to the working equation for the compressibility factor

$$Z_m(T,\rho) = Z_m^{hs}(\rho, d_i\text{'s}) + [Z_r(T_r^o, \rho_r^o) - Z_r^{hs}(\rho, \overline{d})] \qquad (4.7)$$

where d_i's are diameters of components in the mixture, T_r^o and ρ_r^o are, respectively equivalent temperature and density, to be defined later, of the reference fluid. For other dimensionless thermodynamic properties, $(\frac{\bar{U}-\bar{U}^*}{RT})_m$ and $(\frac{\bar{A}-\bar{A}^*}{RT})_m$, one can obtain the same expressions of pseudoforce parameters.

We have extended the prediction of properties to the second order of $\frac{1}{kT}$ as shown in Eqn. (4.2) and should therefore obtain better results than those predicted by the van der Waals 1-fluid theory which rigorously makes the expansion only to the first order of $\frac{1}{kT}$.

Eqns. (4.5) and (4.6) show the composition dependence of pseudoforce parameters $\bar{d}^3$ and $\bar{\varepsilon}$ in which ε_{ii} and d_{ii}^3 describe interactions between like pairs of molecules and ε_{ij} and d_{ij}^3 describe interactions between unlike molecular pairs. Because the interaction between unlike molecules is not completely understood, we adopt the following equations similar to those proposed by Mollerup and Rowlinson[18] for the van der Waals 1-fluid theory.

$$\varepsilon_{ij} = \xi_{ij}(\varepsilon_{ii}\varepsilon_{jj})^{\frac{1}{2}} \qquad (4.8)$$

$$d_{ij}^3 = \lambda_{ij} [\frac{1}{2}(d_{ii}^3 + d_{jj}^3)] \qquad (4.9)$$

where ξ_{ij} and λ_{ij} are the unlike pair parameters which can be empirically adjusted to give better mixture property prediction. For most unlike hydrocarbon pairs, it has been shown[5,18] that ξ_{ij} and λ_{ij} are close to

unity, and their effect on property prediction is appreciably large, especially for equilibrium calculations.

For engineering applications, it is more convenient to express pseudo-parameters in terms of critical constants. In general, the direct proportionality of ϵ_{ii} to T_{c_i} and d^3_{ii} to V_{c_i} for simple fluids can be shown by applying $(\frac{\partial P}{\partial V})_{T=T_c} = 0$ and $(\frac{\partial^2 P}{\partial V^2})_{T=T_c} = 0$. Leach[10] introduced the shape factors to account for the nonconformity of molecules due to non-central force field and/or slight polarity. He assumed

$$\epsilon_{ii} \propto \theta_i T_{c_i} \tag{4.10}$$

$$d^3_{ii} \propto \Phi_i V_{c_i} \tag{4.11}$$

and also for reference fluid at pseudo conditions with the same proprotional constants

$$\bar{\epsilon} \propto \theta_r T_c^{''} \tag{4.12}$$

$$\bar{d} \propto \Phi_r V_c^{''} \tag{4.13}$$

where subscript r stands for reference fluid and $T_c^{''}$ and $V_c^{''}$ are the pseudocritical temperature and volume, respectively.

Substituting Eqns. (4.10) through (4.13) into Eqns. (4.5) and (4.6), using relations (4.8) and (4.9) for unlike pair interactions, and canceling out proportional constants, one obtains

$$T_c'' = \frac{\sum\limits_i^N \sum\limits_j^N x_i x_j (\bar{\Phi}_{ir} V_{c_i} + \bar{\Phi}_{jr} V_{c_j}) \frac{\lambda_{ij}}{2} (\theta_{ir} T_{c_i} \theta_{jr} T_{c_j})\xi_{ij}^2}{\sum\limits_i^N \sum\limits_j^N x_i x_j (\bar{\Phi}_{ir} V_{c_i} + \bar{\Phi}_{jr} V_{c_j}) \frac{\lambda_{ij}}{2} (\theta_{ir} T_{c_i} \theta_{jr} T_{c_j})^{\frac{1}{2}}\xi_{ij}} \tag{4.14}$$

and

$$V_c'' = \frac{[\sum\limits_i^N \sum\limits_j^N x_i x_j (\bar{\Phi}_{ir} V_{c_i} + \bar{\Phi}_{jr} V_{c_j}) \frac{\lambda_{ij}}{2} (\theta_{ir} T_{c_i} \theta_{jr} T_{c_j})^{\frac{1}{2}}\xi_{ij}]^2}{\sum\limits_i^N \sum\limits_j^N x_i x_j (\bar{\Phi}_{ir} V_{c_i} + \bar{\Phi}_{jr} V_{c_j}) \frac{\lambda_{ij}}{2} (\theta_{ir} T_{c_i} \theta_{jr} T_{r_j}) \xi_{ij}^2} \tag{4.15}$$

where $\bar{\Phi}_{ir}$'s and θ_{ir}'s are shape factors for component i relative to the reference r.

The equivalent temperature and density of the reference fluid are defined in such a way that the excess properties of mixture and reference fluid over the hard-sphere properties are equal when both are at the same reduced conditions, i.e. at

$$T_r^o = \frac{T_m}{T_c''} T_{c_r} \tag{4.16}$$

and

$$\rho_r^o = \frac{\rho_m V_c''}{V_{c_r}} \tag{4.17}$$

Based on Leach and Leland's idea of shape factors, one can define an equivalent temperature and density for each component in a conformal solution in the sense of the equalities of total property and hard sphere property of individual component to those of reference fluid, i.e.

$$X_i(T_i^o, \rho_i^o) = X_r(T_r^o, \rho_r^o) \qquad (4.18)$$

and

$$X_i^{hs}(T_i^o, \rho_i^o) = X_r^{hs}(T_r^o, \rho_r^o) \qquad (4.19)$$

The definitions of equivalent temperature and density of each component are then as follows:

$$T_i^o = \frac{T_r^o}{T_{c_r}} T_{c_i} \theta_{ir} \qquad (4.20)$$

and

$$\rho_i^o = \frac{\rho_r^o V_{c_r}}{V_{c_i} \theta_{ir}} \qquad (4.21)$$

Substituting Eqns. (4.16) and (4.17) into Eqns. (4.20) and (4.21), one can obtain equivalent conditions in terms of mixture properties as

$$T_i^o = \frac{T_m}{T_c''} T_{c_i} \theta_{ir} \qquad (4.22)$$

$$\rho_i^o = \frac{\rho_m V_c''}{V_{c_i} \phi_{ir}} \ . \qquad (4.23)$$

4.2 Choice of Reference Fluid

Inspecting the desired Eqn. (3.7), one notices that the successful prediction of mixture properties depends on the accuracy of the pure reference fluid property, obtained either from experimental data or

from a smoothed equation of state, and the way in which the effective diameters are determined.

As a rule, the error due to an inaccurate reference fluid can be reduced to a minimum by using the most reliable experimental data or equation of state available. Nevertheless, the consideration of conformity of each component to the reference fluid is also very important. In other words, the more conformal the components to the preselected reference fluid, the better the prediction.

In this work, ethane is chosen as the reference fluid for methane-propane mixtures of various compositions. The choice is based on the closeness of its acentric factor to the molar average acentric factor of the components in the mixture. The properties of the reference fluid are generated from BWRS equation of state.

4.3   Determination of Hard Sphere Diameter

The major problem of applying CSP and HSE method to real mixtures is the question of how to determine the diameter in the hard sphere potential function. Different criteria for the choice of the hard sphere diameter have been proposed from theoretical and phenomenological approaches. The theoretical determinations of the diameter are for use with perturbation and/or variational techniques. A review paper by Smith[26] summarizes and compares the different formulations for diameter determination. The effectiveness of the theoretically-determined diameter has been justified to some extent in the prediction of properties of model systems, e.g. the machine calculated Lennard-Jones molecules and soft-sphere molecules. However, the direct application of these formulations to real fluids has

been delayed because of the lack of knowledge of potential functions be-
tween real molecules. Recently, a work has been undertaken by Jones[9] to
find the best set of parameters for the Mie potential by lease-square fit
of second varial coefficients of hydrocarbons over a wide range of tempera-
tures. Hopefully the Mie potential function with the parameters obtained
can represent the true potential function of hydrocarbons in some respects.

In this section, we will discuss the problem of determining effect-
ive diameters for use with the HSE theory for real fluids when both the
form of the intermolecular potential and its parameters are unknown, but
accurate equations of state representing the P-V-T behavior over an exten-
sive range are available for the pure components.

The following analyses are applicable for every dimensionless pro-
perty of concern, but we will take compressibility factor as an example to
show how the diameters are determined. For convenience, the compressibility
factor of a pure component, i.e. Eqn. (3.15), is written as

$$Z = Z^{hs}(\rho d^3) + \psi(\rho d^3, \frac{\varepsilon}{kT}) \qquad (4.24)$$

The form of the ψ function is unspecified but its value is always less
than zero.

Criteria for the Effective Diameters

As we have shown in the derivation of HSE method, any dimensionless
thermodynamic property can be expanded into a power series of 1/T with
the property of a corresponding hard sphere system as the leading term.
The terms of orders $(1/T)^3$ and higher are assumed to be the same for the

mixture and the reference fluid, or they are assumed to be relatively

small in comparison with lower order terms so that they can be included

in the leading term by properly choosing an effective diameter of the

hard sphere molecule. Therefore, it is possible to enumerate criteria

which the diameters should fulfill for a fluid with an unknown potential.

The diameters should be chosen for each fluid so that:

1. The ψ function for each fluid at a constant density is repre-

sented as closely as possible by a quadratic form:

$$\psi \cong \frac{a_1(\rho)}{T} + \frac{a_2(\rho)}{T^2} \tag{4.25}$$

where $a_1(\rho)$ and $a_2(\rho)$ are functions of density only.

2. The $a_1(\rho)$ and $a_2(\rho)$ coefficients in Eqn. (4.25) involve the

effects of intermolecular attraction only.

3. The z^{hs} term in Eqn. (4.24) accounts for all repulsion effects

plus the effects due to attraction which have higher order temperature

dependence than $(\frac{1}{T})^2$ and cannot be accounted for in Eqn. (4.25).

4. At high densities where three body interactions begin to make

contributions to the ψ of the order $(\frac{1}{T})^2$, as much as possible of the con-

tribution of these effects is removed from the $\frac{a_2(\rho)}{T^2}$ term and included

in the z^{hs} term.

These criteria are ideal conditions which cannot be realized com-

pletely by altering the value of d. In order to find the diameters which

these criteria approach as closely as possible, it is necessary to have

an accurate representation of the constant density isochoric behavior of

each pure component over as wide a temperature range as possible.

Effective Diameters from A Pure Component Equation of State

In this study the BWRS equation of state was used primarily because it has been fitted to a wide range of pure components. For some components there are some equations which represent isochoric behavior much better. However, the effect of the HSE procedure for mixtures when pure component equations of state are known is to generate in the reference fluid equation of state a more rigorous composition dependence. The BWRS equation for mixtures has an empirical composition dependence which works well in some cases, particularly for hydrocarbon mixtures, but not so well for others, especially when non-hydrocarbons are involved. When the BWRS equation is used for all pure component properties, it is of interest to compare the theoretically based composition dependence induced by the HSE theory with its empirical form in the BWRS mixture equation.

For a pure component the BWRS equation, or any empirical equation of state which has been fitted over the widest possible range of temperatures and density conditions, can be represented conceptually as follows:

$$Z = Z(\rho) + [Z^+(\rho,T) + Z^-(\rho,T)] \qquad (4.26)$$

where Z is the compressibility factor. The term in brackets in Eqn. (4.26) includes all the temperature dependence and has the same value of the ψ term in Eqn. (4.24). If represented at a constant density by an expansion in powers of $\frac{1}{T}$ it would need many terms of higher order than $(\frac{1}{T})^2$ if the empirical equation of state was valid over the widest possible range of temperatures at this density. Consequently, the ψ term in Eqn. (4.26) is defined as

$$\psi_\infty = Z^+(\rho,T) + Z^-(\rho,T) \ . \qquad\qquad (4.27)$$

The ∞ subscript indicates that in an expanded form it would include all order of (1/T) in representing the value of ψ over the widest possible temperature range.

If the equation of state in Eqn. (4.26) were generated by an imaginary Kihara type potential, the $Z(\rho)$ term would represent the contribution of the hard core. Because the molecules with this type of potential also have a soft repulsion at separation distances slightly greater than the hard core diameter, the $Z(\rho)$ term does not include all repulsion effects. The soft repulsive potential contributions to the compressibility factor are positive and temperature dependent. As the ψ term includes all of the temperature dependence of Z, the soft repulsive contributions are included in it and are designated by $Z^+(\rho,T)$ in Eqn. (4.27). The major source of temperature dependence in the ψ term is due to contributions from the attractive portion of the unknown intermolecular potential. These contributions, designated as $Z^-(\rho,T)$ in Eqn. (4.27) are large and negative, causing the value of ψ_∞ to be always negative.

It is important to point out that although any empirical equation of state fitted to a wide range of P-V-T properties can give the value of $Z^-(\rho,T), Z^+(\rho,T)$, and $Z(\rho)$, the term $Z^+(\rho,T)$ has no relation to and cannot be identified as a sum of the positive temperature dependent terms which appear in the empirical equation. Likewise, $Z^-(\rho,T)$ has no relation to the combined negative temperature dependent terms.

If it were possible to separate ψ precisely into the true $Z^+(\rho,T)$ and $Z^-(\rho,T)$ contributions, the optimum diameter to meet the criteria discussed above should be given by the solution of:

$$Z^{hs}(\rho d^3) = Z(\rho) + Z^+(\rho,T) + \alpha Z^-(\rho,T) \qquad (4.28)$$

where α is the fraction of $Z^-(\rho,T)$ due to the sum of all attractive terms of order $(\frac{1}{T})^3$ and higher plus all 3-body attraction terms of the order $(\frac{1}{T})^2$ in an expansion of $Z^-(\rho,T)$ in powers of $(\frac{1}{T})$. The diameter is then obtained by evaluating $Z^{hs}(\rho d^3)$ from Eqn. (4.28) and equating the result to the hard sphere equation of state, Eqn. (3.30), and solving for diameter d.

A method of approximating the right side of Eqn. (4.28) in order to solve for d in this way was developed in this study. From the equation of state only the $Z(\rho)$ term is obtainable. For example, from the BWRS equation:

$$Z(\rho) = 1 + B_o\rho + b_o\rho \qquad (4.29)$$

Special procedures must be used to estimate the other terms in Eqn. (4.28). The value of these terms can be determined directly in two limiting cases. The first of these is a high density limit and was studied by Bienkowski and Chao.[1] As they have shown, in this limit:

$$\underset{P \to \infty}{\text{Lim}} \; [Z(\rho) + Z^+(\rho,T)] \gg \alpha Z^-(\rho,T)$$

and in this limit $Z^-(\rho,T)$ in Eqn. (4.26) is also negligible in comparison with $Z^+(\rho,T)$. Consequently, the solution for values of d from Eqns. (4.28) and (3.30) should approach the diameters obtained by Bienkowski and Chao. Unfortunately, conditions of interest are very far from this limit

and it appears that the optimal diameters do not approach the limiting

values monotonically.

The other limiting case is at a high temperature limit where

$$\text{Lim} \; [Z^+(\rho,T) + \alpha Z^-(\rho,T)] = 0 \qquad (4.31)$$
$$(\tfrac{1}{T}) \to 0$$

In this case the right side of (4.28) becomes only $Z(\rho)$, which is fur-

nished directly by the equation of state as in Eqn. (4.29). This is

called the high temperature limit and at some temperature conditions of

interest, especially at low densities, the optimal diameters approach it

closely. These diameters are always smaller than the high density limit

of Bienkowski and Chao.

These limits are very nearly upper and lower bounds for the optimal

diameters although they do not closely approach the upper bound at any

conceivable density of interest. A few cases at low density showed the

optimal diameter very slightly below the high temperature limit. The

discrepancy is easily within the experimental uncertainty, however.

Determination of Effective Diameters from Isochores

We must now consider a more general method for use when these limit-

ing conditions are not applicable. Determining $Z^{hs}(\rho d^3)$ with the optimal

diameters at a given finite temperature and density is carried out by con-

sidering a limited temperature range along an isochore at the given density.

This temperature range is selected to locate the given temperature as

near to the center of the range as possible. Isochores extrapolate

smoothly into the two phase region and in the liquid phase at lower tempera-

tures in the range these extrapolations may even produce negative

compressibility factors without adverse effects to the solution for

the diameters. Properties along the isochore can be obtained either

from direct experimental data or from an equation of state which repre-

sents isochoric behavior well. If such an equation of state is used,

the temperature range selected must be shifted to higher values if neces-

sary to insure that $(\frac{\partial P}{\partial \rho})_T$ as calculated by the equation is positive at

each temperature value within the range.

The width of the range is selected ideally to determine at a given

temperature and density, T and ρ, the first and second derivatives of the

dimensionless property with respect to inverse temperatures and to pre-

dict the property at each temperature in the range with an accuracy within

its experimental error by a quadratic function. For example, if the com-

pressibility factor is being evaluated, the values of z at ρ at each point

in the range about T are fit by least squares to:

$$Z = a_o(\rho) + \frac{a_1(\rho)}{T} + \frac{a_2(\rho)}{T^2} \qquad (4.32)$$

In this work a range was selected consisting of 11 temperatures, 10° F

apart, including the given temperature. If $(\frac{\partial P}{\partial \rho})_r$ is positive at each tem-

perature, the range then consists of 5 temperatures above and 5 below the

given value, otherwise the range is shifted upward so that the lower tem-

perature in the range is nearer to the given temperature. If $(\frac{\partial P}{\partial \rho})_T$ is

negative at the given temperature the method is inoperable at the given

conditions.

It was found that varying the width of the range did not affect the results as long as the conditions described for it are met. Eqn. (4.32) at every density studied gave excellent reproduction of z values along the 100° range as defined here.

The value of ψ for the quadratic fit of the isochore in this limited range is defined as ψ_2 to indicate that it contains two inverse temperature terms. Consequently, from Eqn. (4.32):

$$\psi_2 = \frac{a_1(\rho)}{T} + \frac{a_2(\rho)}{T^2} \tag{4.33}$$

We can find the temperature dependence not accounted for by the quadratic fit by comparing ψ_2 with ψ_∞ which presumably describes the maximum possible range of temperatures. The difference defined as

$$\delta = \psi_\infty - \psi_2 \tag{4.34}$$

since the HSE pseudo critical values for the excess over the hard sphere behavior were derived by considering only terms in $(\frac{1}{T})$ and $(\frac{1}{T})^2$ in its expansion. Furthermore, these terms involved only pairwise contributions from the attractive portion of the intermolecular potential. Consequently, at conditions where the coefficients a_1 and a_2 in Eqn. (4.33) contain predominantly attractive contributions of this type, the $\alpha Z^-(\rho,T)$ term in Eqn. (4.28) contains no triplet potential effects of order $(\frac{1}{T})^2$ and is consequently entirely included among the interactions of order $(\frac{1}{T})^3$ in the ψ_∞ expression. If an expression of $Z^+(\rho,T)$ in powers of $\frac{1}{T}$ gives coefficients of $(\frac{1}{T})$ and $(\frac{1}{T})^2$ which are negligible in comparison to the attractive contributions of these terms, their presence will not

appreciably affect the $\bar{\epsilon}$ pseudo attraction parameter predicted by the HSE theory. Consequently, the only soft sphere contributions which need to be included in the hard sphere term by adjusting the diameter are those in terms of order $(\frac{1}{T})^3$ and higher in the ψ_∞ term.

In this case, the difference between ψ_∞ and ψ_2 represents all terms of higher order than $(\frac{1}{T})^3$ which need to be combined into the hard sphere result. This difference defines the δ parameter in Eqn. (4.34). If all terms of order $(\frac{1}{T})^3$ were zero, the best $Z^{hs}(\rho d^3)$ value at these conditions would be the a_0 leading term in Eqn. (4.32) for the quadratic fit. With corrections for the higher order terms, the best $Z^{hs}(\rho d^3)$ value is then:

$$Z^{hs}(\rho d^3) = a_0 + \delta \qquad (4.35)$$

Eqn. (4.35) may be regarded as the best approximation to Eqn. (4.28) under these conditions.

The limits of validity of Eqn. (4.35) are indicated by the magnitude of the ψ_2 term in Eqn. (4.33). The assumptions leading to Eqn. (4.35) become invalid at high densities. At the lowest densities below $\rho V_c \cong 0.6$, $\delta \cong 0$ and $a_0 \cong Z(\rho)$, the high temperature limit of the equation of state in Eqn. (4.29). As densities increase above $\rho V_c = 0.6$, $a_1(\rho)$ in Eqn. (4.33) becomes more negative and $a_2(\rho)$ begins to increase, but the sum of them, ψ_2 keeps increasing in negative magnitude. Presumably this means an attraction contribution is being represented. Positive contributions of the soft repulsion are apparently still negligible and Eqn. (4.35), which requires this, is still valid. This causes

the value of δ in Eqn. (4.34) to be positive and z^{hs} in Eqn. (4.35) increases.

As density increases further the absolute value of ψ_2 begins to decrease, because a_2 term keeps becoming less negative and at $\rho V_c \approx 1.2$ it becomes positive while δ approaches a maximum. The a_2 term starting to become less negative in this way is considered to be caused by the onset of the positive contributions of soft repulsion which at these densities begins to affect the coefficient of $(\frac{1}{T})^2$. This maximum in δ occurs at a reduced density of about 1.6.

The reduced density of 1.6 is considered to be the upper limit of the validity of Eqn. (4.35). At densities higher than this δ decreases rapidly and a_1 becomes less negative, interpreted as the appearance of positive soft repulsion effects in $\frac{1}{T}$ term. Diameters from Eqn. (4.35) give poor results in this region. There is no way that these soft effects can be separated from attraction effects and the optimal diameter cannot be calculated.

The diameters can be predicted once more at very high densities where ψ_2 has become very small although still negative, indicating more effects of soft repulsion. It is also very likely that three body contributions to $(\frac{1}{T})^2$ term are no longer negligible by the fact that a_2 begins to drop. The optimal diameters are then obtained by placing all of the second order $(\frac{1}{T})^2$ term in the hard sphere equation.

The temperature range used for the quadratic fit is reduced from $100°$ to $50°$F with the given temperature near the center of this shorter

range. The objective is now to obtain an accurate representation of each z value in the range by

$$Z = a_o^{'}(\rho) + \frac{a_1^{'}(\rho)}{T} \qquad (4.36)$$

The $a_1^{'}$ term is always negative at readily accessible densities. Since none of the negative $\frac{1}{T}$ dependence should appear in the hard sphere equation and Eqn. (4.36) represents the z values accurately in the shorter range, the best z^{hs} result is:

$$z^{hs}(\rho d^3) = a_o^{'}(\rho) \qquad (4.37)$$

Eqn. (4.37) is then solved for the diameter. This linear fit method gives excellent results for the optimal diameter at reduced densities of about 2.4 and higher.

The reduced density region between 1.6 and 2.4 is thus an indeterminant region. As a first approximation, the best $z^{hs}(\rho d^3)$ values in this region were assumed to be given by a spline fit interpolation between points at $\rho_R > 2.4$ and those at $\rho_R < 1.6$. For liquids at low temperatures the indeterminant region is lengthened because the liquid no longer can be extrapolated to reduced densities near 1.6 because of the stability limit. Low density values at $\rho_R < 0.6$ are still obtainable by equating $z^{hs}(\rho d^3)$ to the high temperature limit of the equation of state.

The behavior of the quadratic and linear fit methods is shown in Figure 2. It is found that the quadratic fit method below $\rho_R = 1.6$ and the linear fit method at $\rho_R > 2.4$ give excellent results for the optimal

Figure 2

Computation of Z^{HS}
From BWRS Equation

CH_4 at $\frac{T}{T_c} = 1.0$
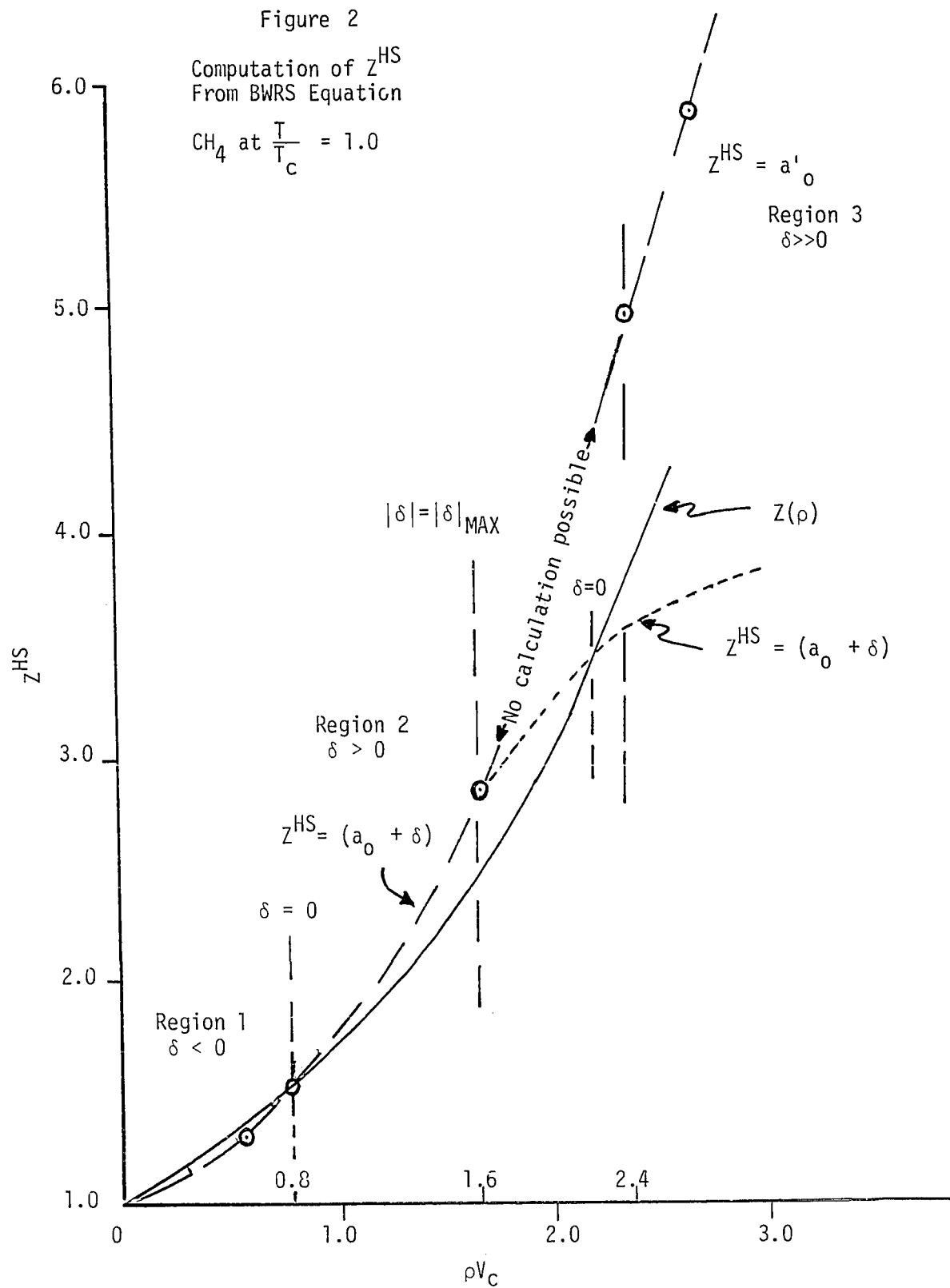
diameter. This was checked by increasing and decreasing $Z^{hs}(\rho d^3)$ about the predicted value and noting the effect on the predicted mixture properties. The weakest prediction for $Z^{hs}(\rho d^3)$ is in the spline fit region. Some typical results of this test on the predicted value are shown in Table 10.

Although only the determination of diameters for the compressibility factor calculations is shown here and is used as an example in the explanation of the method, other properties can be predicted equally well. Because of the temperature and density dependence of the diameters and shape factors which relate them to critical constants, it is best to determine separate values of them for each component.

The determination of diameters for Z and $\dfrac{\bar{A}-\bar{A}^*}{RT}$ calculations are exactly the same. For $\dfrac{\bar{U}-\bar{U}^*}{RT}$ no hard sphere property calculations are made and the a_o term of the quadratic fit along the compressibility factor isochores can be equated to $Z^{hs}(\rho d^3)$. This is then solved for the diameter used in the pseudo parameter computations.

4.4 Procedures of Calculation

A program in FORTRAN IV is written for an IBM 370/155 digital computer; a flow diagram for the computer program is shown in Fig. 3. The program can calculate both total mixture properties; Z, $\dfrac{\bar{U}-\bar{U}^*}{RT}$, and $\dfrac{\bar{A}-\bar{A}^*}{RT}$, and individual component property $\ln\dfrac{f_i}{x_i P}$. A property index IZUF is read in the computer with other input information to indicate which property is the desired one.

Input Information
exp
T, P , $x_1, \ldots x_n$

Data Base
critical constants: T_c, V_c, P_c
acentric factors: ω
normal b.p. : T_b
11 constants of BWRS eq.

Trial Values
$\theta_{ir}=1, \bar{\phi}_{ir}=1$

Calc. T_c'', V_c''

Estimate ρ

Calc. T_i^o, ρ_i^o

Determine
Z_i^{hs}

Solve $\bar{\phi}_{ir}, \theta_{ir}$

Calculate
$T_{c\ new}'', V_{c\ new}''$

Is $T_{c\ new}'' \approx T_c''$
$V_{c\ new}'' \approx V_c''$

NO

YES

Calculate $d_i, \bar{d}$

Calc. Z_r, Z_r^{hs}, Z_m^{hs}

Calc. Z_m, P_m

Set $\rho_{new} = \rho + \Delta\rho$

NO

Is $P_m \approx P^{exp}$

YES

Print Out Data
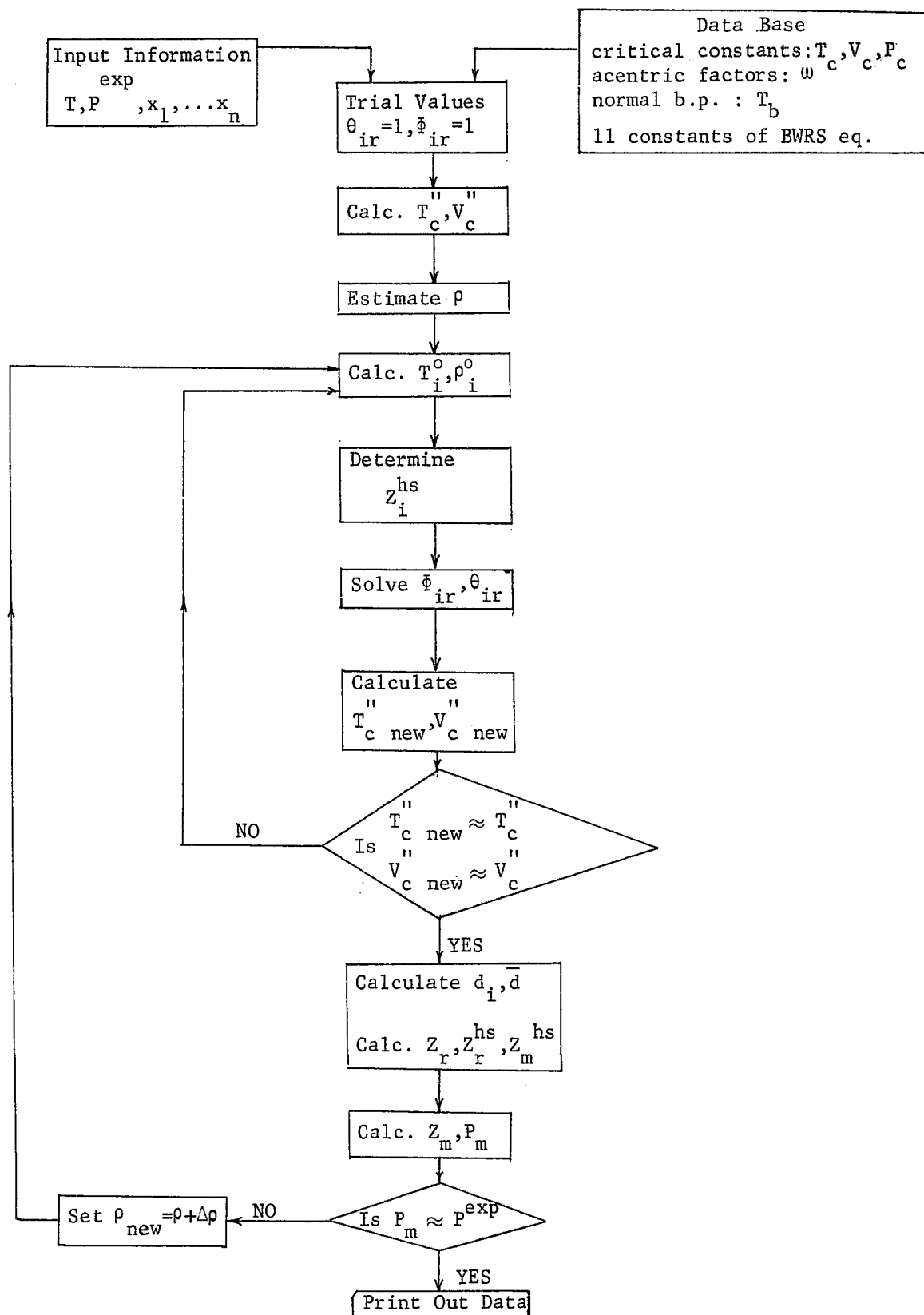
Fig. 3   Flow Diagram of HSE Procedure

(a) IZUF = 1, Z calculation only;

(b) IZUF = 2, Z and $\dfrac{\overline{U}-\overline{U}^{\ast}}{RT}$ calculations;

(c) IZUF = 3, Z and $\dfrac{\overline{A}-\overline{A}^{\ast}}{RT}$ calculations;

(d) IZUF = 4, Z, $\dfrac{\overline{A}-\overline{A}^{\ast}}{RT}$ and $\ln\dfrac{f_i}{x_i P}$ calculations.

For cases (b) and (c), although $\dfrac{\overline{U}-\overline{U}^{\ast}}{RT}$ and $\dfrac{\overline{A}-\overline{A}^{\ast}}{RT}$ are, respectively,

the desired properties, the compressibility factor Z must be calculated

first. Because it is in the Z calculation that one can obtain a consistent

mixture density at the given temperature, pressure and compositions of

the mixture. The more practically used properties, $(\overline{H}-\overline{H}^{\ast})$ and $\ln\dfrac{f}{P}$

are readily obtained by Eqns. (3.38) and (.347), respectively. In case

(d), Z calculation gives consistent mixture density and $\dfrac{\overline{A}-\overline{A}^{\ast}}{RT}$ calculation

provides the required pseudocriticals and shape factors for use in .

$\ln\dfrac{f_i}{x_i P}$ calculation as indicated in Eqn. (3.72).

Two kinds of information are required to proceed the computation;

characteristic properties and state properties. The former includes criti-

cal constants, T_c, V_c and P_c, acentric factors ω, normal boiling tempera-

tures T_b and 11 constants for BWRS equation of state, the values used are

listed in Tables 1 and 2, which are part of the computer program. State

properties comprise temperature, pressure, composition and number of compon-

ents in the mixture. For CH_4-C_3H_8 mixture, the energy unlike pair para-

meter ξ_{ij} = .97 is taken from Mollerup and Rowlinson's work[18], and volume

unlike pair parameter λ_{ij} is set to be unity as suggested by Hsu[8].

In this work, temperature and density are used as the independent variables in the computation scheme. Because temperature and pressure are more popularly adopted in most engineering practices, an initial estimation of the mixture density from input mixture temperature and pressure is then necessary.

Equivalent pressure can be defined in a similar manner to the definition for equivalent temperature and density as in Eqns. (4.16) and (4.17), i.e.

$$P^o_r = \frac{P_m}{P''_c} P_{c_r} \tag{4.38}$$

where $P_{c_r} = \dfrac{Z_{c_r} R T_{c_r}}{V_{c_r}}$ and $P''_c = \dfrac{Z''_c R T''_c}{V''_c}$, Z_{c_r} and Z''_c are compressibility factors at critical and pseudocritical conditions for reference fluid and mixture, respectively.

Substituting P_{c_r} and P''_c into Eqn. (4.38), one obtains

$$P^o_r = \frac{P_m V''_c}{T''_c} \frac{T_{c_r}}{V_{c_r}} \frac{Z_{c_r}}{Z''_c} \tag{4.39}$$

we know every quantity except Z''_c on the RHS of Eqn. (4.39). A trial-and-error on the value of $\dfrac{Z_{c_r}}{Z''_c}$ has been studied, we found that first setting $\dfrac{Z_{c_r}}{Z''_c} = 1$, then choosing route according to following criteria can give a reasonable first trial mixture density.

(1) if $\dfrac{T_r^o}{T_{c_r}} < 1$ and $P_r^o > VP_r$, then $\rho_r^o = Z_r\ (T_r^o,\ VP_r + 0.1\ P_r^o)$

(2) if $\dfrac{T_r^o}{T_{c_r}} < 1$ and $P_r^o < VP_r$, then $\rho_r^o = Z_r(T_r^o,\ P_r^o)$

(3) if $\dfrac{T_r^o}{T_{c_r}} \geq 1$ and $P_r^o \leq 1.5\ P_{c_r}$, then $\rho_r^o = Z_r(T_r^o,\ .9P_r^o)$

(4) if $\dfrac{T_r^o}{T_{c_r}} \geq 1$ and $1.5\ P_{c_r} < P_r^o \leq 6.5\ P_{c_r}$, then $\rho_r^o = Z_r(T_r^o,\ P_r^o)$

(5) if $\dfrac{T_r^o}{T_{c_r}} \geq 1$ and $P_r^o > 6.5\ P_{c_r}$, then $\rho_r^o = (T_r^o,\ .9P_r^o)$

where the equivalent temperature T_r^o is defined in Eqn. (4.12), VP_r stands

for the vapor pressure of the reference fluid at T_r^o, it is estimated by

using Lee-kesler vapor pressure equation[12]. $\rho_r^o = Z_r(T_r^o,\ P_r^o)$ implies

that ρ_r^o is obtained by solving BWRS equation of state at T_r^o and P_r^o

The initial mixture density is then calculated from Eqn. (4.40)

$$\rho_m = \dfrac{\rho_r}{V_c''}\ V_{c_r} \qquad\qquad (4.40)$$

It should be pointed out that the first trial mixture density is import-

ant to the computation. The closer the first trial value to the experi-

mental density, the faster the computation converges.

A sample calculation is presented below, it shows the step-by-step

procedure for compressibility factor calculations.

<u>Sample calculation</u>:

Equimolar binary mixture of methane and propane at 160° F and 3000

psia. For convenience, the indices 1 and 3 denote, respectively, CH_4,

and C_3H_8, corresponding to the number of carbon atoms in the compounds,

and let r stand for the reference fluid C_2H_6.

a) At first, the relative shape factors are set to be unity,

$$\Phi_{1r} = \Phi_{3r} = 1, \ \theta_{1r} = \theta_{3r} = 1$$

b) The trial values $T_c^{''}$ and $V_c^{''}$ are calculated from Eqns. (4.14) and

(4.15),

$$T_c^{''} = 538.1^{\circ}R, \ V_c^{''} = 2.279 \ ft^3/\ell b\text{-mole}$$

c) The trial mixture density is estimated from Eqns. (4.38) through

(4.40),

$$\rho_m = .7369 \ \ell b\text{-mole}/ft^3$$

d) The equivalent temperature and density are calculated from Eqns.

(4.22) and (4.23),

$$T_1^o = 395.3^{\circ}R \ , \ \rho_1^o = 1.053 \ \ell b\text{-mole}/ft^3$$

$$T_3^o = 766.6^{\circ}R \ , \ \rho_3^o = \ .524 \ \ell b\text{-mole}/ft^3$$

$$T_r^o = 633.1^{\circ}R \ , \ \rho_r^o = \ .717 \ \ell b\text{-mole}/ft^3$$

e) The hard sphere property is determined from Eqn. (4.35) or (4.37)

at the above equivalent temperature and density,

$$z_1^{hs} = 2.906, \ z_3^{hs} = 3.751, \ z_r^{hs} = 3.360$$

53

f) The relative volume shape factors Φ_{ir}'s are solved from Eqns. (4.19) and (4.21),

$$\Phi_{1r} = .872, \quad \Phi_{3r} = 1.121$$

g) The relative temperature shape factors Φ_{ir}'s are solved from Eqns. (4.18) and (4.20),

$$\theta_{1r} = .930, \quad \theta_{3r} = 1.037$$

h) The process from steps b to g are repeated until the pseudo-criticals T_c'' and V_c'' converge to relatively unchanged values,

$$T_c'' = 554.6^0 R, \quad V_c = 2.325 \ ft^3/\ell b\text{-mole}$$

Only 7 iterations are needed for the fractional deviations of two consecutive iterations to be less than 1×10^{-3}. At this point, each component is conformal with reference fluid by using the relative shape factors obtained.

i) The diameters are calculated from Eqns. (3.30),

$$d_1 = 3.552 \overset{o}{A}, \quad d_3 = 4.819 \overset{o}{A}, \quad d_r = 4.200 \overset{o}{A}$$

j) Hard sphere properties of the mixture and reference fluid are obtained from Eqns. (3.30) and (3.31),

$$Z_r^{hs} = 3.469 \qquad Z_m^{hs} = 3.689$$

k) Total mixture property Z_m is calculated from Eqn. (3.29) and P_m from $P_m = Z_m \rho_m RT$,

$$Z_m = .7808 \qquad P_m = 3827 \ psia$$

Now a complete total mixture property calculation is accomplished.

ℓ) The calculated P_m is compared with experimental mixture pressure P_{exp}, P_m is then adjusted by a numerical method called 'false position', and steps d through i are repeated until $P_m \approx P_{exp}$. 9 iterations are needed to make $\left| \dfrac{P_m - P_{exp}}{P_{exp}} \right| \leq 1.5 \times 10^{-3}$ and the final results are

$$T_c'' = 549.2^\circ R, \quad V_c'' = 2.322 \ ft^3/\ell b\text{-mole}$$

$$T_1^0 = 369.0^\circ R, \quad \rho_1^0 = 1.134 \ \ell b\text{-mole}/ft^3, \quad \Phi_{1r} = .8705, \quad \theta_{1r} = .9527$$

$$T_3^0 = 765.0^\circ R, \quad \rho_3^0 = .445 \ \ell b\text{-mole}/ft^3, \quad \Phi_{3r} = 1.1036, \ \theta_{3r} = 1.0185$$

$$T_r^0 = 620.3^\circ R, \quad \rho_r^0 = .672 \ \ell b\text{-mole}/ft^3,$$

$$d_1 = 3.558 \overset{\circ}{A}, \quad d_3 = 4.860 \overset{\circ}{A}, \quad d_r = 4.236 \overset{\circ}{A}$$

$$P_m = 2997 \ psia, \quad \rho_m = .6779 \ \ell b\text{-mole}/ft^3, \ Z_m = .6646$$

Comparing to experimental value $Z = .6676$, the error for compressibility factor prediction is 0.4%.

4.5   Results and Discussion

Tables 4, 5, and 6 contain the predicted compressibility factors of binary mixture of methane and propane for several compositions at $160^\circ F$, $280^\circ F$, and $400^\circ F$. The pressure range is from 400 psia to 9000 psia. The average deviation is .7%. The poorer results at some conditions have been studied. Most of them are due to the weakness in the BWRS reference equation of state at the equivalent conditions, a few are due to the spline-fit approximation in the indeterminant region.

Results of isothermal enthalpy deviations are shown in Tables

7 and 8. The agreements are generally good. For the mixture of 23.8%

methane-76.2% propane, HSE method does not show much improvement over

the van der Waals one-fluid theory studied by Mollerup.[17] The theore-

tical advantages of the HSE method for enthalpy predictions may be off-

set here by the use of a generally poorer reference equation of state

than that used by Mollerup.

Tables 9 compares the predicted fugacity coefficients of equimolar

methane and propane mixture with experimental data which are calculated

by numerical integration of the partial volume from Sage and Lacey's[25]

data. The discrepancies are apparently due to the failure of the BWRS

equation of state to generate accurate $(\frac{\overline{A}-A^*}{RT})$ for the reference fluid

ethane, which is required by the HSE method and other CSP theories, as

one can see from Table 3, which shows the difference between the experi-

mental data and those from the BWRS equation of state for the pure ethane.

In this work, no attempts have been made to change the unlike pair

interaction parameters in order to give better predictions.

CHAPTER 5

CONCLUSION

The HSE theory incorporated with the method of determining effect-
ive diameters is applied to predict the thermodynamic properties of
hydrocarbon mixtures. Although the determination of diameters for
fluids with unknown potential functions with this method is not possible
at all densities, enough calculations can be made to allow a correla-
tion by fitting the results to the Verlet-Weis equation for the optimal
diameter with the perturbation theory.

There are several advantages of using the HSE method with the
effective diameters. It is rather simple and straightforward. The
method first utilizes the knowledge of pure component properties, the
shape factors are then generated internally to insure conformality of
each constituent with the reference fluid, and the diameters are deter-
mined at the same time. The mixture properties are then calculated read-
ily. No data correlation is needed to obtain the necessary composition
dependence.

The theoretical merit of the HSE method is the separation of the
overall properties into different contributions which allows us to treat
the short range repulsive interactions more precisely, and the long range
attraction effects are accounted for by the well-developed CSP. It is
believed that the HSE method should extend the predictions to lower tem-
peratures than previous CSP methods did, because the second order of
inverse temperature has been taken into account.

The theoretically-based HSE method can safely be extrapolated to new regions of pressure and temperature and its extension to multicomponent systems is straightforward as well.

APPENDIX A

BWRS EQUATION OF STATE AND DERIVED THERMODYNAMIC FUNCTIONS

The BWRS equation of state is an 11-parameter, modified BWR (Benedict-Webb-Rubin) equation proposed by Starling.[27] It has the form of

$$P = \rho RT + (B_o RT - A_o - C_o/T^2 + D_o/T^3 - E_o/T^4)\, \rho^2$$

$$+ (bRT - a - d/T)\, \rho^3 + \alpha(a + d/T)\, \rho^6 \qquad (A\text{-}1)$$

$$+ c\rho^3/T^2\, (1 + \gamma\rho^2)\, \exp(-\gamma\rho^2)$$

where P is the absolute pressure in psia, T the absolute temperature in ^oR, ρ the molar density in ℓb.-mole/cu.ft., and R the universal gas constant (= 10.7335 psi-ft.^{3}/ℓb.-mole ^oR).

The values of the 11 parameters for several natural gas systems, which are listed in Table 2, are obtained by Lin and Hopke[14] through a multiproperty regression analysis procedure in which they used experimental density, enthalpy, vapor pressure and K-value data of both pure component and mixture to generate the optimal set of parameters.

Compressibility

Dividing through Eqn. (A-1) by ρRT, one obtains the compressibility factor form of the equation of state:

$$Z = \frac{P}{\rho RT} = 1 + (B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} + \frac{D_o}{RT^4} - \frac{E_o}{RT^5})\,\rho$$

$$+ (b - \frac{a}{RT} - \frac{d}{RT^2})\,\rho^2 + \alpha\,(\frac{a}{RT} + \frac{d}{RT^2})\,\rho^5 \qquad \text{(A-2)}$$

$$+ \frac{c\rho^2}{RT^3}\,(1 + \gamma\rho^2)\,\exp(-\gamma\rho^2)$$

Internal Energy Deviation

The expression for internal energy deviation is derived by using the relationship

$$\left(\frac{\bar{U}-\bar{U}^*}{RT}\right)_{T,V} = -T \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_{\rho'} \frac{d\rho'}{\rho'} \qquad \text{(A-3)}$$

the result is

$$\left(\frac{\bar{U}^*-\bar{U}}{RT}\right)_{T,V} = \left(\frac{A_o}{RT} + \frac{3C_o}{RT^3} - \frac{4D_o}{RT^4} + \frac{5E_o}{RT^5}\right)\rho + \frac{1}{2}\left(\frac{a}{RT} + \frac{2d}{RT^2}\right)\rho^2$$

$$\text{(A-4)}$$

$$- \frac{\alpha}{5}\left(\frac{a}{RT} + \frac{2d}{RT^2}\right)\rho^5 + \frac{3c}{\gamma RT^3}\left[1 + \frac{1}{2}(\gamma\rho^2)\right]e^{-\gamma\rho^2} - \frac{3c}{\gamma RT^3}$$

Helmholtz Free Energy Deviation

The Helmholtz free energy deviation is derived by using the following relationship

$$\left(\frac{\bar{A}-\bar{A}^*}{RT}\right)_{T,V} = \int_0^\rho (Z-1)\,\frac{d\rho'}{\rho'} \qquad \text{(A-5)}$$

the result is

$$\left(\frac{\overline{A}-\overline{A}^*}{RT}\right)_{T,V} = \left(B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3} + \frac{D_o}{RT^4} - \frac{E_o}{RT^5}\right)\rho + \frac{1}{2}\left(b - \frac{a}{RT} - \frac{d}{RT^2}\right)\rho^2$$

<div align="right">(A-6)</div>

$$+ \frac{\alpha}{5}\left(\frac{a}{RT} + \frac{d}{RT^2}\right)\rho^5 + \frac{c}{\gamma RT^3}\left[1 - \left(1 + \frac{\gamma\rho^2}{2}\right)e^{-\gamma\rho^2}\right]$$

APPENDIX B

EXPRESSIONS OF $\quad n(\dfrac{\partial T_c''}{\partial n_k})_{T,V,n_\ell} \quad$ AND $\quad n(\dfrac{\partial V_c''}{\partial n_k})_{T,V,n_\ell}$

The pseudocritical temperature T_c'' and volume V_c'' can be expressed, respectively, in terms of number of moles of the components as follows

$$T_c'' = \frac{\sum\limits_{i}^{N}\sum\limits_{j}^{N} n_i n_j \dfrac{\lambda_{ij}}{2}(V_{c_i}\Phi_{ir}+V_{c_j}\Phi_{jr})\,\xi_{ij}^{2}\,(\theta_{ir}T_{c_i}\theta_{jr}T_{c_j})}{\sum\limits_{i}^{N}\sum\limits_{j}^{N} n_i n_j \dfrac{\lambda_{ij}}{2}(V_{c_i}\Phi_{ir}+V_{c_j}\Phi_{jr})\,\xi_{ij}\,(\theta_{ir}T_{c_i}\theta_{jr}T_{c_j})^{\frac{1}{2}}} \tag{B-1}$$

$$V_c'' = \frac{[\sum\limits_{i}^{N}\sum\limits_{j}^{N} n_i n_j \dfrac{\lambda_{ij}}{2}(V_{c_i}\Phi_{ir}+V_{c_j}\Phi_{jr})\,\xi_{ij}\,(\theta_{ir}T_{c_i}\theta_{jr}T_{c_j})^{\frac{1}{2}}]^{2}}{n^{2}\sum\limits_{i}^{N}\sum\limits_{j}^{N} n_i n_j \dfrac{\lambda_{ij}}{2}(V_{c_i}\Phi_{ir}+V_{c_j}\Phi_{jr})\,\xi_{ij}^{2}\,(\theta_{ir}T_{c_i}\theta_{jr}T_{c_j})} \tag{B-2}$$

where n_i and n_j are, respectively, number of moles of ith and j^{th} components, n is the total number of moles of the mixture, and N is the number of components.

For convenience, let us represent the numerator of T_c'' by N and the denominator by D, i.e.

$$N = \sum\limits_{i}^{N}\sum\limits_{j}^{N} n_i n_j \dfrac{\lambda_{ij}}{2}(V_{c_i}\Phi_{ir}+V_{c_j}\Phi_{jr})\,\xi_{ij}^{2}\,(\theta_{ir}T_{c_i}\theta_{jr}T_{c_j}) \tag{B-3}$$

$$D = \sum\limits_{i}^{N}\sum\limits_{j}^{N} n_i n_j \dfrac{\lambda_{ij}}{2}(V_{c_i}\Phi_{ir}+V_{c_j}\Phi_{jr})\,\xi_{ij}\,(\theta_{ir}T_{c_i}\theta_{jr}T_{c_j})^{\frac{1}{2}} \tag{B-4}$$

Eqns. (B-1) and (B-2) then become

$$T_c'' = \frac{N}{D} \qquad\qquad (B-5)$$

$$V_c'' = \frac{D^2}{n^2 N} \qquad\qquad (B-6)$$

Differentiating Eqns. (B-3) through (B-6) by n_k and keeping T,V, and n_ℓ constant, one obtains

$$\left(\frac{\partial T_c''}{\partial n_k}\right)_{T,V,n_\ell} = \frac{D\left(\frac{\partial N}{\partial n_k}\right)_{T,V,n_\ell} - N\left(\frac{\partial D}{\partial n_k}\right)_{T,V,n_\ell}}{D^2} \qquad (B-7)$$

$$\left(\frac{\partial V_c''}{\partial n_k}\right)_{T,V,n_\ell} = \frac{2n^2 DN\left(\frac{\partial D}{\partial n_k}\right)_{T,V,n_\ell} - n^2 D^2 \left(\frac{\partial N}{\partial n_k}\right)_{T,V,n_\ell} - 2nD^2 N}{n^4 N^2} \qquad (B-8)$$

$$\left(\frac{\partial N}{\partial n_k}\right)_{T,V,n_\ell} = A_k + B\left(\frac{\partial T_c''}{\partial n_k}\right)_{T,V,n_\ell} + C\left(\frac{\partial V_c''}{\partial n_k}\right)_{T,V,n_\ell} \qquad (B-9)$$

$$\left(\frac{\partial D}{\partial n_k}\right)_{T,V,n_\ell} = E_k + F\left(\frac{\partial T_c''}{\partial n_k}\right)_{T,V,n_\ell} + G\left(\frac{\partial V_c''}{\partial n_k}\right)_{T,V,n_\ell} \qquad (B-10)$$

where

$$A_k = 2 \sum_i^N n_i \frac{\lambda_{ik}}{2} (\beta_i + \beta_k) \xi_{ik}^2 (\alpha_i \alpha_k) \qquad (B-11)$$

$$B = \sum_i^N \sum_j^N n_i n_j \frac{\lambda_{ij}}{2} \xi_{ij} \left\{ \left[\left(\frac{\partial \beta_i}{\partial T_c''}\right)_{V_c''} + \left(\frac{\partial \beta_j}{\partial T_c''}\right)_{V_c''} \right] \alpha_i \alpha_j \right.$$

$$\left. + 2 (\beta_i + \beta_j) \alpha_j \left(\frac{\partial \alpha_i}{\partial T_c''}\right)_{V_c''} \right\} \qquad (B-12)$$

$$-C = \sum_i^N \sum_j^N n_i n_j \frac{\lambda_{ij}}{2} \xi_{ij}^2 \left\{ \left[\left(\frac{\partial \beta_i}{\partial V_c} \right)_{T_c''} + \left(\frac{\partial \beta_j}{\partial V_c} \right)_{T_c''} \right] \alpha_i \alpha_j \right.$$

(B-13)

$$\left. + 2 (\beta_i + \beta_j) \alpha_j \left(\frac{\partial \alpha_i}{\partial V_c} \right)_{T_c''} \right\}$$

$$E_k = 2 \sum_i^N n_i \frac{\lambda_{ik}}{2} (\beta_i + \beta_k) \xi_{ik} (\alpha_i \alpha_k)^{\frac{1}{2}}$$

(B-14)

$$F = \sum_i^N \sum_j^N n_i n_j \frac{\lambda_{ij}}{2} \xi_{ij} \left\{ \left[\left(\frac{\partial \beta_i}{\partial T_c} \right)_{V_c''} + \left(\frac{\partial \beta_j}{\partial T_c} \right)_{V_c''} \right] (\alpha_i \alpha_j)^{\frac{1}{2}} \right.$$

(B-15)

$$\left. + (\beta_i + \beta_j) \left(\frac{\alpha_j}{\alpha_i} \right)^{\frac{1}{2}} \left(\frac{\partial \alpha_i}{\partial T_c} \right)_{V_c''} \right\}$$

$$G = \sum_i^N \sum_j^N n_i n_j \frac{\lambda_{ij}}{2} \xi_{ij} \left\{ \left[\left(\frac{\partial \beta_i}{\partial V_c} \right)_{T_c''} + \left(\frac{\partial \beta_j}{\partial V_c} \right)_{T_c''} \right] (\alpha_i \alpha_j)^{\frac{1}{2}} \right.$$

(B-16)

$$\left. + (\beta_i + \beta_j) \left(\frac{\alpha_j}{\alpha_i} \right)^{\frac{1}{2}} \left(\frac{\partial \alpha_i}{\partial V_c} \right)_{T_c''} \right\}$$

and $\alpha_i = T_{c_i} \theta_{ir}$, $\beta_i = V_{c_i} \Phi_{ir}$.

Multiplying Eqn. (B-7) by $\frac{n}{T_c''}$ and Eqn. (B-8) by $\frac{n}{V_c''}$, and substituting

Eqns. (B-5) and (B-6) into the resulting equations, one obtains

$$\frac{n}{T_c''} \left(\frac{\partial T_c''}{\partial n_k}\right) = \frac{n}{N} \left(\frac{\partial N}{\partial n_k}\right) - \frac{n}{D} \left(\frac{\partial D}{\partial n_k}\right) \tag{B-17}$$

$$\frac{n}{V_c''} \left(\frac{\partial V_c''}{\partial n_k}\right) = \frac{2n}{D} \left(\frac{\partial D}{\partial n_k}\right) - \frac{n}{N} \left(\frac{\partial N}{\partial n_k}\right) - 2 \tag{B-18}$$

or
$$\frac{n}{V_c''} \left(\frac{\partial V_c''}{\partial n_k}\right) = \frac{n}{D} \left(\frac{\partial D}{\partial n_k}\right) - \frac{n}{T_c''} \left(\frac{\partial T_c''}{\partial n_k}\right) - 2 \tag{B-19}$$

the subscripts T, V and n_ℓ have been dropped for convenience.

Substitution of Eqns. (B-9) and (B-10) into Eqns. (B-17) and (B-19) and rearrangement of the resulting equations produce

$$\left(\frac{1}{T_c''} - \frac{B}{N} + \frac{F}{D}\right) n\left(\frac{\partial T_c''}{\partial n_k}\right) + \left(\frac{G}{D} - \frac{C}{N}\right) n\left(\frac{\partial V_c''}{\partial n_k}\right) = n\left(\frac{A_k}{N} - \frac{E_k}{D}\right) \tag{B-20}$$

$$\left(\frac{1}{T_c''} - \frac{F}{D}\right) n\left(\frac{\partial T_c''}{\partial n_k}\right) + \left(\frac{1}{V_c''} - \frac{G}{D}\right) n\left(\frac{\partial V_c''}{\partial n_k}\right) = n\left(\frac{E_k}{D}\right) - 2 \tag{B-21}$$

$n\left(\frac{\partial T_c''}{\partial n_k}\right)_{T,V,n_\ell}$ and $n\left(\frac{\partial V_c''}{\partial n_k}\right)_{T,V,n_\ell}$ can then be solved readily.

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TABLE 1

Physical Properties of Pure Components

Component	Molecular Weight	Critical Temp., °F	Critical Volume cu.ft./lb.-mole	Critical Pressure, psia	Normal Boiling Temp., °F	Acentric Factor, ω
Methane	16.042	-116.43	1.5939	673.1	-263.5	.013
Ethane	30.068	90.07	2.3419	708.3	-127.8	.105
Propane	44.094	205.99	3.2041	617.4	- 44.0	.152

TABLE 2

THE BWRS-EXXON Constants

	CH_4	C_2H_6	C_3H_8
B_o	0.696663	0.940341	1.15091
$A_o/10^4$	0.703241	1.50851	2.20325
$C_o/10^8$	3.31272	26.0615	75.3232
γ	1.39930	3.04152	5.50137
b	0.861307	2.69564	6.36610
$a/10^3$	2.75239	17.3349	55.8356
a	0.453145	1.03845	2.17606
$c/10^9$	0.508281	5.94592	23.3092
$D_o/10^{10}$	1.41063	20.7312	75.6999
$d/10^5$	0.684469	5.98254	18.7440
$E_o/10^{11}$	1.26531	90.0981	437.431

TABLE 3

The Analysis of The Accuracy of Reference Fluid C_2H_6

$$T = 160^\circ F$$

Pressure (psia)	z^+_{expt}	z_{BWRS}	$\left(\dfrac{\bar{A}^* - \bar{A}}{RT}\right)^+_{T,V,expt}$	$\left(\dfrac{\bar{A}^* - \bar{A}}{RT}\right)_{T,V,BWRS}$
400	.8594	.8548	.1454	.1508
800	.6878	.6768	.3446	.3591
1000	.5881	.5737	.4820	.5045
3000	.6134	.6064	1.0129	1.0361
5000	.9024	.8937	1.0519	1.0693
7000	1.1793	1.1732	1.0478	1.0678
9000	1.4454	1.4442	1.0333	1.0546

$$T = 220^\circ F$$

Pressure (psia)	z^+_{expt}	z_{BWRS}	$\left(\dfrac{\bar{A}^* - \bar{A}}{RT}\right)^+_{T,V,expt}$	$\left(\dfrac{\bar{A}^* - \bar{A}}{RT}\right)_{T,V,BWRS}$
400	.8999	.8963	.1035	.1073
800	.7939	.7850	.2244	.2341
1000	.7394	.7285	.2924	.3065
3000	.6579	.6538	.7315	.7495
5000	.9030	.8941	.7785	.7989
7000	1.1548	1.1453	.7744	.7983
9000	1.4016	1.3922	.7594	.7835

$$T = 280^\circ F$$

Pressure (psia)	z^+_{expt}	z_{BWRS}	$\left(\dfrac{\bar{A}^* - \bar{A}}{RT}\right)^+_{T,V,expt}$	$\left(\dfrac{\bar{A}^* - \bar{A}}{RT}\right)_{T,V,BWRS}$
400	.9267	.9236	.0758	.0786
800	.8541	.8471	.1580	.1655
1000	.8194	.8103	.2011	.2113
3000	.7218	.7208	.5198	.5363
5000	.9184	.9105	.5747	.5939
7000	1.1439	1.1325	.5726	.5930
9000	1.3698	1.3559	.5547	.5760

+ Sage and Lacey, Ref. 25.

TABLE 4

Predicted Compressibility Factors for 70% CH_4 - 30% C_3H_8 Mixture

(Pure C_2H_6 is used as the reference fluid)

P (psia)	160°F		280°F		400°F	
	Z_{expt}^{++}	Z_{cal}	Z_{expt}^{++}	Z_{cal}	Z_{expt}^{++}	Z_{cal}
400	.9222	.9211	.9590	.9593	.9791	.9782
800	.8473	.8430	.9229	.9231	.9614	.9607
1000	.8126	.8091	.9078	.9074	.9542	.9537
3000	.7430	.7271	.8734	.8626	.9518	.9489
5000	.9473	.9313	.9964	.9844	1.0416	1.0404
7000	1.1715	1.1616	1.1657	1.1577	1.1745	1.1735
9000	1.4047	1.3903	1.3514	1.3390	1.3218	1.3238

++Sage and Lacey, Ref. 25.

TABLE 5

Predicted Compressibility Factors 50% CH_4 - 50% C_3H_8 Mixture

(Pure C_2H_6 is used as the reference fluid)

P (psia)	160° F		280° F		400° F	
	Z_{expt}^{++}	Z_{cal}	Z_{expt}^{++}	Z_{cal}	Z_{expt}^{++}	Z_{cal}
400	.8962	.8696	.9281	.9317	.9608	.9613
800	.7313	.7228	.8640	.8661	.9277	.9273
1000	.6670	.6448	.8365	.8393	.9146	.9126
3000	.6676	.6645	.7849	.7721	.8887	.8833
5000	.9454	.9446	.9694	.9626	1.0118	1.0106
7000	1.2189	1.2191	1.1878	1.1839	1.1844	1.1853
9000	1.4886	1.4866	1.4093	1.4050	1.3657	1.3696

++Sage and Lacey, Ref. 25.

TABLE 6

·Predicted Compressibility Factors For

30% CH_4 - 70% C_3H_8 Mixture

Pure C_2H_6 Is Used As The Reference Fluid

$T = 160^\circ F$

P (psia)	Z_{expt}^{++}	Z_{cal}
400	.7923	.7991
600	.6552	.6673
1500	.3980	.3948
3000	.6415	.6476
5000	.9736	.9758
7000	1.2873	1.2919
9000	1.5888	1.5965

$T = 280^\circ F$

400	.8928	.8964
800	.7880	.7879
1000	.7416	.7354
3000	.7097	.7112
5000	.9637	.9645
7000	1.2266	1.2276
9000	1.4829	1.4837

$T = 400^\circ F$

400	.9391	.9403
800	.8862	.8844
1000	.8639	.8670
3000	.8204	.8174
5000	.9912	.9949
7000	1.2041	1.2113
9000	1.4213	1.4277

++ Sage and Lacey, ref. 25

TABLE 7

Predicted Enthalpy Deviation For 23.4% CH_4 - 76.6% C_3H_8

(Pure C_2H_6 Is Used As The Reference Fluid)

Temp. ($^\circ$ F)	Pressure (psia)	$(\bar{H}^*-\bar{H})^{++}_{expt.}$ (Btu/lb)	$(\bar{H}^*-\bar{H})_{HSE}$ (Btu/lb)	$(\bar{H}^*-\bar{H})^+_{CSP}$ (Btu/lb)
200	250	12.4	12.4	12.2
	750	50.0	49.5	47.7
	1250	97.6	98.9	98.7
	1750	111.6	111.7	112.1
100	250	20.4	19.3	18.5
	1250	142.4	144.0	142.4
	1750	143.6	144.4	143.1
50	750	157.1	156.8	154.9
	1250	156.1	156.3	154.8
	1750	155.5	156.0	154.3
0	750	169.3	168.3	167.1
	1250	168.5	167.4	166.2
	1750	167.1	166.5	165.1
-50	750	180.7	178.4	178.6
	1250	179.3	177.1	177.2
	1750	178.0	176.0	175.8

++Yesavage, Ref. 29.
+ Mollerup, Ref. 17.

TABLE 8

Predicted Enthalpy Deviation For 49.4% Methane - 50.6% Propane

Pure Ethane Is Used As The Reference Fluid

Temp. (^{o}F)	Pressure (psia)	$(\bar{H}^* - \bar{H})^{++}$ expt. (Btu/lb)	$(\bar{H}^* - \bar{H})_{HSE}$ (Btu/lb)
200	250	9.8	9.4
	500	20.7	19.7
	1000	44.9	43.8
	1500	69.3	70.4
	2000	86.9	88.9
100	250	14.5	13.9
	1500	119.8	123.2
	2000	126.9	127.2
0	1000	158.6	160.4
	1500	158.8	160.5
	2000	158.5	159.6
-50	1000	173.5	173.0
	1500	172.7	172.1
	2000	171.4	171.0

++ Yesavage, Ref. 29.

TABLE 9

Predicted Fugacity Coefficients For 50% Methane - 50% Propane Mixture

Pure Ethane Is Used As The Reference Fluid

$$T = 160^\circ F$$

Pressure (psia)	$(\ln \frac{f}{P})_{expt.}$ [++]	$(\ln \frac{f}{P})_{HSE}$
200	0^+	0^+
1000	-.2649	-.2593
2000	-.5601	-.5896
3000	-.7209	-.7616
5000	-.8261	-.8687
7000	-.8006	-.8453
9000	-.7132	-.7590

$$T = 220^\circ F$$

200	0^+	0^+
1000	-.1874	-.1773
2000	-.3874	-.4024
3000	-.5156	-.5435
5000	-.6065	-.6419
7000	-.5836	-.6214
9000	-.5043	-.5452

++ Sage and Lacey, Ref. 25.

+ $(\ln \frac{f}{P})_{T,P = 200\ psia} = 0$ is the datum point.

TABLE 10.

Effect on Z^{HS} on Calculated Z

In the Incalculable Region for Z^{HS}

50% CH_4

50% C_3H_8

$T = 160°F$

$P = 5000$ psia

Z^{HS}	% Error
2.73	5.31
3.39	1.77

$(a_o + \delta) = 3.48 \rightarrow$

3.68*	0.29
3.74+	0
3.94	-0.99
4.21	-2.23

*By spline fit between Z^{HS} at $\rho_R > 2.4$ and Z^{HS} at $\rho_R < 1.6$

+Predicted by interpolation to 0 % Error.