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MIXING RULES AND UNLIKE INTERACTION PARAMETER CORRELATIONS FOR CHARACTERIZATION PARAMETERS IN A THREE-PARAMETER CORRESPONDING-STATES THERMODYNAMIC PROPERTIES CORRELATION

The University of Oklahoma PH.D. 1981

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MIXING RULES AND UNLIKE INTERACTION PARAMETER CORRELATIONS FOR CHARACTERIZATION PARAMETERS IN A THREE-PARAMETER CORRESPONDING-STATES THERMODYNAMIC PROPERTIES CORRELATION

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TAE JONG LEE

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MIXING RULES AND UNLIKE INTERACTION PARAMETER CORRELATIONS FOR CHARACTERIZATION PARAMETERS IN A THREE-PARAMETER CORRESPONDING-STATES THERMODYNAMIC PROPERTIES CORRELATION

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TABLE OF CONTENTS

Page

Page

LIST OF TABLES

Table Page

LIST OF ILLUSTRATIONS

ABSTRACT

The conformal solution method is used as the basis for developing mixing rules for the characteristic parameters appearing in a three-parameter, corresponding-states correlation of thermodynamic properties. A logical extension of the van der Waals (VDW) one-fluid rules from two to three parameters, referred to herein as the modified VDW one-fluid mixing rules, is shown to yield accurate predictions of vapor-liquid equilibrium (VLE) for binary mixtures of paraffin hydrocarbons with similar size molecules but poor VLE predictions for mixtures of paraffin hydrocarbons wih highly dissimilar molecular sizes. Therefore, semiempirical exponent mixing rules were developed to obtain improved VLE predictive capability. In order to predict unlike interaction parameters from the characteristic properties of pure components alone, new correlations were formulated. The semiempirical exponent mixing rules, in conjunction with the correlations developed herein for unlike interaction parameters, gave predicted VLE accuracy standing about in the middle between the modified VDW one-fluid and semiempirical exponent mixing rules using individual unlike interaction parameters for each pair of paraffin hydrocarbons. The overall average absolute deviation of predicted methane K-values from experimental binary mixture data for methane with heavier normal paraffin hydrocarbons ranging from ethane through normal decane was 4.1% using the semiempirical exponent mixing rules compared with 11.0% for the modified VDW one-fluid rules (both using individual unlike interaction parameters for each fluid pair) and 7.78% for the semiempirical exponent mixing rules using the correlations for unlike interaction parameters. The three methods provide accurate predictions of bulk properties for the methane binaries. When tested for other light hydrocarbons and natural gas mixtures, the semiempirical exponent mixing rules show significantly better accuracy for VLE predictions for multicomponent mixtures involving light hydrocarbons, slightly better accuracy for binary mixtures involving light hydrocarbons and nitrogen and comparable accuracy for binary and multicomponent mixtures containing hydrogen sulfide and carbon dioxide (when compared to the modified VDW one-fluid mixing rules). Both mixing rules exhibit reasonably accurate predictions of VLE and bulk properties for these systems. The semiempirical exponent mixing rules with the correlations for unlike interaction parameters yield acceptable predictions of VLE and bulk properties for all mixtures studied except the hydrogen sulfide-carbon dioxide and ethane-ethylene systems.

MIXING RULES AND UNLIKE INTERACTION PARAMETER CORRELATIONS FOR CHARACTERIZATION PARAMETERS IN A THREE PARAMETER CORRESPONDING STATES THERMODYNAMIC PROPERTIES CORRELATION

CHAPTER I

INTRODUCTION

The purpose of the research presented in this dissertation was to develop new mixing rules for the characteristic parameters appearing in the three-parameter conformal solution model utilized at the University of Oklahoma. Also, correlations were developed for the unlike interaction parameters appearing in the mixing rules for binary fluid pairs involving hydrocarbons, carbon dioxide, hydrogen sulfide and nitrogen.

The use of conformal solution theory models for the prediction of mixture thermodynamic behavior is becoming increasingly popular for industrial calculations. The attractiveness of the conformal solution approach stems largely from the fact that it is faster computationally than purely theoretical methods and yet has a sufficiently good basis in theory to allow extension to complex molecular interactions (e.g., multipole, dispersion and steric effects), which would be difficult using purely empirical methods.

The formulation of conformal solution theory which has received widest use to date is the so-called van der Waals one-fluid theory (45). Strictly, the van der Waals one-fluid theory applies to mixtures of similar size molecules for which all pair potentials can be expressed in the form $u_{ij} = \varepsilon_{ij} \phi(r_{ij}/\sigma_{ij})$. Unfortunately, for many industrial mixtures molecular size difference can be large and orientation effects make important contributions to the pair potentials. Thus, aside from the approximations inherent to conformal solution theory, factors which adversely affect the accuracy of the van der Waals one-fluid theory for the complex molecular systems encountered industrially include (1) the use of the two parameter (ε_{ij} and σ_{ij}) pair potential and (2) the requirement of similar molecular size for the mixture components. Chapter II discusses previous work related to mixing rules and correlations for unlike pair interaction parameters.

Efforts are in progress at the University of Oklahoma to develop a multiparameter corresponding states framework for correlation of thermodynamic properties, taking into account the various orientation contributions to pair interactions (e.g., dipole-dipole, quadrupole-quadrupole, dipole-quadrupole, and higher multipole effects, as well as dispersion and steric effects). Preliminary research (41) in this direction has involved lumping the collective effects of orientation contributions into a single term in the pair potential and the resultant expressions for the thermodynamic properties from the Pople perturbation theory (53). This approach leads to the three-parameter corresponding-states correlation framework reported in recent work (41) and utilized herein. The three characterization parameters in this correlation framework are the characteristic molecular size/separation parameter, σ, the characteristic molecular energy parameter, ε, and the characteristic orientation parameter, γ. Within this three parameter corresponding states framework it is possible to derive, along the lines of the method used by Smith (79), a three parameter conformal solution model, which is presented in section III-1. In the derivation of the three parameter conformal solution theory, certain parameters (exponents) in the mixing rules for three characterization parameters are arbitrary. The use of the van der Waals one-fluid rules for the energy and separation parameters, along with a mixing rule for the orientation parameter, derived along the lines of the van der Waals one-fluid theory, yields the so called modified van der Waals mixing rules discussed in section III-2. The theoretical basis of the Berthelot rules used as starting formulas for development of new correlations of unlike pair interaction parameters is discussed in section III-3. The methodology for the thermodynamic properties calculations presented herein is presented in Chapter IV. It is shown in section V-1 that the use of the modified van der Waals one-fluid mixing rules yields accurate predictions of mixture thermodynamic behavior for mixtures of molecules with dissimilarities as great as methane and propane, but that the accuracy of prediction decays for larger molecular dissimilarities. In section V-2, the exponents in the modified van der Waals one-fluid mixing rules are varied empirically; the resultant mixing rules, referred to herein as semiempirical exponent mixing rules, yield significantly improved predictions for mixtures with components as dissimilar as methane and normal decane.

The development of satisfactory correlations for unlike interaction parameters in terms of characterization parameters of pure components alone has been one of prime concerns for most generalized correlations. In Chapter VI, two correlations are formulated so that mixture properties and phase compositions may be calculated at any conditions of T and P only from pure component parameters without requiring binary interaction parameters which must be evaluated from binary mixture data. One of the correlations, which was developed for binaries of methane with other n-paraffins, was applied to other paraffin-paraffin binaries with satisfactory results and to unsaturated-paraffin hydrocarbon binaries with acceptable predictions. The other correlation is for nonhydrocarbon-hydrocarbon interactions involving nitrogen, carbon dioxide and hydrogen sulfide. Constants in this correlation vary depending on the nonhydrocarbons involved. Chapter VII presents comparisons among the modified VDW one-fluid, the semiempirical exponent, and the semiempirical exponent mixing rules using the correlations for unlike interaction parameters (in the latter case) for prediction of binary mixture thermodynamic behavior. The optimum and estimated binary interaction parameters used in the prediction calculations are presented in Chapter VII. Data used for the comparisons of predicted properties for both binary and multicomponent mixtures are summarized in Chapter VII. In Chapter VIII the predicted multicomponent thermodynamic behavior obtained using the semiempirical exponent mixing rules with and without the correlations for unlike interaction parameters is compared with predictions using the modified VDW one-fluid rules.

CHAPTER II

REVIEW OF LITERATURE

2.1 Previous Work Related to Mixing Rules

Several representative mixing theories which have been proposed in the past are discussed here. They are the random mixture approximation (56), the average potential model (55), and the one-, two-, and three-fluid van der Waals theories (72). Recently, a generalized conformal solution theory (42) has been developed. None of these mixture theories has reached a stage of development sufficiently adequate for application to all types of mixtures. Instead, each theory seems to be restricted to a particular class of solutions. The random mixture approximation was formulated by Prigogine (56), Scott (77), and Byers Brown (9). This theory is limited to molecules of equal size. Since it does not account for the effect of component molecular size differences on mixture properties, it is inadequate. To improve the random mixture approximation, perturbation and two-fluid models were considered. An improved mixture model is the average potential model studied by Prigogine (55) and Scott (77). This model is more accurate than the random mixture model but still can not handle the effect of component molecular size differences on the properties of the mixture. The van der Waals one-, two-, and three-fluid theories (72) make use of the so called van der Waals approximation to relate the interaction parameters for the mixture to the parameters associated with individual like and unlike interactions. They differ in their choice of the number of hypothetical pure fluids utilized. For example, the van der Waals one-fluid theory, utilized by Leland and colleagues (44), equates the mixture properties to those of a hypothetical single pure fluid. The van der Waals one-fluid model appears to provide the best results among the n-fluid van der Waals theories (27). To improve mixture property predictions over the two parameter van der Waals one-fluid theory, a generalized conformal solution model was utilized by Lee and Starling (42). They used a perturbation technique in conjuction with three-parameter corresponding states theory. Their conformal solution model is discussed in Chapter III. Two equations of state are noted here as examples to show how mixing rules and combining rules are employed. The first is the simple two parameter equation of state of Redlich and Kwong (64); the second is the more complicated three parameter Lee-Kesler equation of state (40).

The Redlich-Kwong equation of state can be written in the form

$$p=\frac{RT}{V-b}-\frac{a}{T^{1/2}V(V+b)} \qquad \text{(II-1)}$$

where a and b are constants. This equation can be rearranged in terms of the compressibility factor Z as

$$Z^3-Z^2+(A^*-B^{*2}-B^*)Z-A^*B^*=0 \qquad \text{(II-2)}$$

A* and B* are determined from:

$$A^*=\frac{\Omega_a P_r}{T_r^{2.5}} \qquad \text{(II-3)}$$

$$B^*=\frac{\Omega_b P_r}{T_r} \qquad \text{(II-4)}$$

where $\Omega_a=[9(2^{1/3}-1)]^{-1}=0.427480...$ (II-5)

$$\Omega_b=(27\Omega_a)^{-1}=0.086640... \qquad \text{(II-6)}$$

Equation (II-2) can be extended to mixtures by employing the pseudocritical rules (65) defined as

$$T_{c_m}=\left\{\frac{\left[\sum_i x_i(T_{c_i}^{5/2}/P_{c_i})^{1/2}\right]^2}{\sum_i x_i(T_{c_i}/P_{c_i})}\right\}^{2/3} \qquad \text{(II-7)}$$

$$P_{c_m}=\frac{T_{c_m}}{\sum_i x_i(T_{c_i}/P_{c_i})} \qquad \text{(II-8)}$$

Since the pseudocritical temperature and pseudocritical pressure are the two characterization parameters required in this two parameter formulation of the Redlich-Kwong equation, all mixture thermodynamic properties can be calculated using Eqs. (II-1) through (II-8).

Lee and Kesler (40) proposed an analytical approach to relate the compressibility factor of a real fluid to properties of a simple fluid and those of a reference fluid. The compressibility factor of a fluid with acentric factor ω is represented by Lee and Kesler using the relation

$$Z = Z^{(0)} + \left(\frac{\omega}{\omega^{(R)}}\right)\left(Z^{(R)} - Z^{(0)}\right) \qquad \text{(II-9)}$$

The compressibility factor for both the simple fluid $Z^{(0)}$ and the reference fluid $Z^{(R)}$ are derived from the following reduced form of a modified Benedict-Webb-Rubin equation:

$$Z^{(0 \text{ or } R)} = \left(\frac{P_r V_r}{T_r}\right) = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^3}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \qquad \text{(II-10)}$$

where $B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3}$ (II-11)

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \qquad D = d_1 + \frac{d_2}{T_r} \qquad \text{(II-12)}$$

and b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, β and γ are constants.

$$Z^{(0)} = \frac{P_r V_r^{(0)}}{T_r} \qquad \text{(II-13)}$$

and

$$Z^{(R)} = \frac{P_r V_r^{(R)}}{T_r} \qquad \text{(II-14)}$$

The mixing rules recommended by Lee and Kesler (40) are as follows:

$$T_{c_m} = \frac{1}{8V_{c_m}} \sum_{i}\sum_{j} x_i x_j (V_{c_i}^{1/3} + V_{c_j}^{1/3})^3 (T_{c_i} T_{c_j})^{1/2} \qquad \text{(II-15)}$$

$$V_{c_m} = \frac{1}{8} \sum_{i}\sum_{j} x_i x_j (V_{c_i}^{1/3} + V_{c_j}^{1/3})^3 \qquad \text{(II-16)}$$

$$V_{c_i} = \frac{(0.2905 - 0.085\ \omega_i)\ RT_{c_i}}{P_{c_i}} \qquad \text{(II-17)}$$

$$\omega_m = \sum_{i} x_i \omega_i \qquad \text{(II-18)}$$

$$P_{c_m} = \frac{(0.2905 - 0.085\ \omega_m)\ RT_{c_m}}{V_{c_m}} \qquad \text{(II-19)}$$

These mixing rules for T_{c_m} and V_{c_m} imply the following combining rules for σ_{ij} and ε_{ij}, provided σ_{ii}^3 is proportional to V_{c_i} and ε_{ii} is proportional to T_{c_i},

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \qquad \text{(II-20)}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \qquad \text{(II-21)}$$

It is seen that Lee and Kesler use the van der Waals one-fluid mixing rules for T_{c_m} and V_{c_m} along with the additivity of acentric factors of constituents on a molar basis for the mixture acentric factor and use the arithmetic combining rule for σ_{ij} and the geometric combining rule for ε_{ij}.

2.2 Previous Work Related to Combining Rules

Combining rules relate unlike interaction parameters, such as $\varepsilon_{ij}, \sigma_{ij}, \gamma_{ij}$, to the parameters for pure components. For the estimation of unlike interaction parameters, various combining rules have been proposed. The most commonly adopted combining rules are shown in section 2.1 and are repeated below:

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \qquad \text{(II-22)}$$

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \qquad \text{(II-23)}$$

Equation (II-22), called Lorentz's rule (48), can be derived from the hard sphere repulsion approximation. The geometric mean rule of Berthelot (5), Equation (II-23), follows from London's (47) description of the dispersion forces of two unlike molecules having nearly the same size and ionization potential.

These formulas appear to give good results for simple molecules of similar size. When components are dissimilar, mixture thermodynamic property calculation accuracy diminishes when the Lorentz-Berthelot rules are used, leading to the following modifications.

$$\sigma_{ij} = \eta_{ij}(\sigma_{ii} + \sigma_{jj})/2 \tag{II-24}$$

$$\varepsilon_{ij} = \zeta_{ij}(\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{II-25}$$

η_{ij} and ζ_{ij}, called binary interaction parameters, are measures of deviations from the Lorentz-Berthelot rules. The binary interaction parameters are evaluated from binary data. If σ_{ii} and ε_{ii} are proportional to V_{c_i} and T_{c_i} respectively, Equations (II-24) and (II-25) can be expressed in terms of critical properties:

$$V_{c_{ij}} = \eta_{ij} \frac{\left(V_{c_i}{}^{1/3} + V_{c_j}{}^{1/3}\right)^3}{8} \tag{II-26}$$

$$T_{c_{ij}} = \zeta_{ij} \left(T_{c_i} T_{c_j}\right)^{1/2} \tag{II-27}$$

Lin and Robinson (46) tested a variety of combining rules for ε_{ij} for predicting rare-gas interactions by fitting second virial coefficients along with the potential function of Dymond and Alder. In their study the harmonic mean, $2\varepsilon_{ii}\varepsilon_{jj}/(\varepsilon_{ii} + \varepsilon_{jj})$, was recommended for interactions not including helium.

Good and Hope (21) have suggested that the geometric mean is preferred to the arithmetic mean for σ_{ij} based on detailed analysis of various combining rules for ε_{ij} in conjunction with the arithmetic and geometirc mean rules respectively for σ_{ij}.

Geometric mean rules for both σ_{ij} and ε_{ij} have been proposed by Calvin and Reed (10). The 6, n Mie potential, with repulsive index n as an additional parameter, were employed for their analysis. More combining rules are listed elsewhere (46,21).

For three parameters corresponding states correlations, a third characteristic parameter is required. The combining rule for the third parameter usually assumed is an arithmetic average of the parameters for the pure components. If the parameter is an orientation factor γ, then the combining rule becomes:

$$\gamma_{ij} = (\gamma_{ii} + \gamma_{jj})/2 \tag{II-28}$$

2.3 Previous Work Related to Correlations for Binary Interaction Parameters

Various equations for correlating ζ_{ij} in Eq. (II-25) in terms of the characteristic parameters only of pure components have been proposed. Few correlations for η_{ij} in Eq. (II-24) have been developed since η_{ij} usually has been taken to be unity. Hudson and McCoubrey (31) suggested the following relationship for ζ_{ij}

$$\zeta_{ij} = \frac{2(I_i\ I_j)^{1/2}}{I_i + I_j} \left[\frac{2(\sigma_{ii}\ \sigma_{jj})^{1/2}}{\sigma_{ii} + \sigma_{jj}} \right]^6 \tag{II-29}$$

where I_i is the first ionization potential of component i. This equation can be obtained by equating the attractive part of the Lennard-Jones potential to the London's potential function. Chueh and Prausnitz (13) have investigated the correcting factor ζ_{ij} primarily for paraffin-paraffin hydrocarbon mixtures. The correlation developed for such systems is

$$\zeta_{ij} = \left[\frac{2(V_{c_i}\ V_{c_j})^{1/6}}{V_{c_i}^{\ 1/3} + V_{c_j}^{\ 1/3}} \right]^3 \tag{II-30}$$

Hiza and Duncan (30) found the following correlation from a purely empirical approach.

$$\zeta_{ij} = 1-0.17(I_i - I_j)^{1/2} \ln(I_i/I_j) \tag{II-31}$$

where i is the component with the larger ionization potential. This correlation is reasonable for binaries involving methane, ethane, ethylene, and inorganic gases. The harmonic mean for ε_{ij} proposed by Fender and Halsey (17) can provide the following equation (88):

$$\zeta_{ij} = \frac{2(T_{c_i} T_{c_j})^{1/2}}{T_{c_i} + T_{c_j}} \qquad \text{(II-32)}$$

This formula was found to be satisfactory for binaries of methane with hydrocarbons, argon, krypton, nitrogen and hydrogen sulfide (88). Teja (87) suggested the following correlation based on the carbon numbers of hydrocarbons:

$$\zeta_{ij} = 1 - m(n_{c_j} - n_{c_i} - 1) \qquad \text{(II-33)}$$

where n_{c_j} stands for the carbon number of component j with $n_{c_j} \geq n_{c_i}$; m=0.02 was proposed for n-paraffin binaries with methane; m=0.01 was recommended for binaries of ethane with paraffins greater than two carbon atoms; and m=0.04 was recommended for n-paraffin binaries with carbon dioxide. Tsonopoulos (88) also employed carbon number as a correlating parameter. The following equation has been proposed with m changing depending on the type of binary system;

$$\zeta_{ij} = 1 - m\left[\ln(n_{c_j} - n_{c_i} + 1)\right]^2 \qquad \text{(II-35)}$$

where m=0.0279 for hydrocarbon binaries with methane, m=0.0202 for hydrocarbon binaries with ethane and ethylene, and m=0.0364 for hydrocarbon binaries with nitrogen (note $n_{c_j} \geq n_{c_i}$).

CHAPTER III

THEORETICAL BASIS

3.1 Anisotropic Fluid Conformal Solution Theory

The method used here for considering conformal solution theories for fluids with molecular anisotropies is based on the method utilized by Smith (79) for treating isotropic one fluid conformal solution theories as a class of perturbation theories. The objective of the method is to closely approximate the properties of a mixture by calculating the properties of hypothetical pure reference fluid. The characterization parameters (in this case, intermolecular potential parameters) of the reference fluid are chosen to be functions of composition (i.e., mole fractions) and the characterization parameters for the various possible molecular pair interactions (like-like and unlike-unlike). In principle, all molecular anisotropies (dipole-dipole, quadrupole-quadrupole, dipole-quadrupole and higher multipole interactions, as well as overlap and dispersion interactions) can be included in the method. Here, the various molecular anisotropies are lumped into a single term, so that the intermolecular potential energy $u_{ij}(\underline{r}_{12}, \omega_1, \omega_2)$ between molecules 1 and 2 of species i and j can be written in the form

$$u_{ij}\left(\underline{r}_{12},\omega_1,\omega_2\right) = \varepsilon_{ij}\ \phi^{o}\left(\frac{r_{12}}{\sigma_{ij}}\right) + \delta_{ij}\varepsilon_{ij}\ \phi^{p}\left(\frac{\underline{r}_{12}}{\sigma_{ij}}\ ,\ \omega_1,\omega_2\right) \quad \text{(III-1)}$$

In Equation (III-1), $\underline{r}_{12}$ is the vector displacement of the molecular centers of molecules 1 and 2, r_{12} is the scaler separation, $r_{12} = |\underline{r}_{12}|$, and ω_1 and ω_2 are the Euler angles describing the orientations of molecules 1 and 2. The first term on the right hand side of Equation (III-1) involving ϕ^{o} is recognized as an isotropic potential form, so that the term involving ϕ^{p} describes anisotropic effects. The characterization parameters σ_{ij}, ε_{ij} and δ_{ij}, respectively, are characteristic distance, energy and anisotropic strength parameters for the interaction between molecules of species i and j.

The extension of the isotropic mixture conformal solution theory method of Smith (79) to the case of anisotropic molecular systems can be made easily in the following manner. Let the quantities a_{ij}, b_{ij}, and c_{ij} be defined by the relations $a_{ij} = \delta_{ij}^{k}\varepsilon_{ij}^{l}\sigma_{ij}^{m}$, $b_{ij} = \delta_{ij}^{p}\varepsilon_{ij}^{q}\sigma_{ij}^{r}$, $c_{ij} = \delta_{ij}^{u}\varepsilon_{ij}^{v}\sigma_{ij}^{w}$, where the exponents k, l, m, p, q, r, u, v, w are left unspecified at this point in the development. The configurational Helmholtz free energy A for an anisotropic mixture then can be expanded about the configurational Helmholtz free energy of a hypothetical pure reference fluid, A_x , with characterization parameters δ_x , ε_x , and σ_x (or a_x, b_x, c_x),

$$A = A_x + \frac{\partial A_x}{\partial a_x} \sum_{ij}\sum x_i x_j (a_{ij} - a_x) + \frac{\partial A_x}{\partial b_x} \sum_{ij}\sum x_i x_j (b_{ij} - b_x)$$

$$+ \frac{\partial A_x}{\partial c_x} \sum_{ij}\sum x_i x_j (c_{ij} - c_x) + \text{higher order terms} \qquad \text{(III-2)}$$

where x_i is the mole fraction of the ith component in the mixture. The following mixing rules annul the first order terms in the expansion in Equation (III-2),

$$\delta_x^k \varepsilon_x^l \sigma_x^m = \sum_{ij}\sum x_i x_j \delta_{ij}^k \varepsilon_{ij}^l \sigma_{ij}^m \qquad \text{(III-3)}$$

$$\delta_x^p \varepsilon_x^q \sigma_x^r = \sum_{ij}\sum x_i x_j \delta_{ij}^p \varepsilon_{ij}^q \sigma_{ij}^r \qquad \text{(III-4)}$$

$$\delta_x^u \varepsilon_x^v \sigma_x^w = \sum_{ij}\sum x_i x_j \delta_{ij}^u \varepsilon_{ij}^v \sigma_{ij}^w \qquad \text{(III-5)}$$

The application of conformal solution theory in industrial calculations suggests the use of the approximation $A = A_x$ to avoid the lengthy computation required to calculate the higher order terms in Equation (III-2).

Thus, a practical strategy for choosing the exponents k, l, m, p, q, r, u, v, w in Equations (III-3), (III-4), and (III-5) would be through minimization of the difference $A-A_x$ (actually, data for all available mixture thermodynamic properties can be used simultaneously to determine the exponents by regression). However, most applications of conformal solution theory have involved the use of exponents based on molecular theory and so this approach was utilized in the initial phase of the present work.

3.2 Modified van der Waals One-Fluid Mixing Rules

The well known van der Waals one-fluid mixing rules for the characterization parameters σ_x and ε_x for isotropic fluids are

$$\sigma_x^3 = \sum_{i}\sum_{j} x_i x_j \sigma_{ij}^3 \qquad \text{(III-6)}$$

$$\varepsilon_x \sigma_x^3 = \sum_{i}\sum_{j} x_i x_j \varepsilon_{ij} \sigma_{ij}^3 \qquad \text{(III-7)}$$

Thus, the van der Waals one-fluid rules correspond to the use of the following values of the exponents in Equations (III-3) and (III-4), k=0, l=0, m=3, p=0, q=1, r=3. Smith (80) has discussed the fact that for hard sphere mixtures, Equation (III-6) is the most reasonable theoretical choice for specifying σ_x (although other mixing rules have been used). Also, Smith (80) has shown for hard sphere binary mixtures that using the arithmetic mean rule, $\sigma_{12} = 1/2$ $(\sigma_{11} + \sigma_{22})$, the second order terms in Equation (III-2) for the Helmholtz free energy probably can be neglected only when σ_{11} and σ_{22} differ by less than about 10%. For isotropic fluids, the perturbation expansion of the Helmholtz free energy about that of a hard sphere system leads to Equation (III-7) when the mean density approximation is used for the hard sphere pair distribution function (80). Although the van der Waals one-fluid mixing rules yield reasonably accurate predictions of mixture behavior for molecules which are not greatly dissimilar, the cases of evaluation of the unlike interaction parameters, σ_{ij}, ε_{ij}, $i \neq j$, from the data may be compensatory in an empirical way.

For the derivation of a mixing rule for the anisotropic strength parameter, δ_x, consider the Pople expansion (53) of the Helmholtz free energy A about the free energy, A_o, of an isotropic fluid reference system,

$$A = A_o + A_1 + A_2 + \ldots \qquad \text{(III-8)}$$

where A_i are the ith order terms in the expansion. The isotropic reference system pair potential is defined to be the unweighted average of the anisotropic pair potential in Equation (1), that is,

$$\varepsilon_{ij} \; \phi^o\left(\frac{\underline{r}_{12}}{\sigma_{ij}}\right) = \left\langle u_{ij}\left(\underline{r}_{12}, \omega_1, \omega_2\right)\right\rangle_\omega \qquad \text{(III-9)}$$

where the brackets $\langle \; \rangle_\omega$ denote the angle average. Thus, $A_1 = 0$ and Equation (III-8) is a perturbation expansion for A provided higher order terms are small. For small anisotropies, truncation at A_2 is accurate, while for large anisotropies, the use of the Padé approximant used by Stell (85)

$$A = A_o + \frac{A_2}{(1 - A_3/A_2)}$$

yields good results. Herein the truncation at A_2 will be utilized. The second order term A_2 is given by the relation

$$A_2 = \frac{-\rho^2}{4kT} \sum_{ij}\sum x_i x_j \delta_{ij}^2 \varepsilon_{ij}^2 \int d\underline{r}_1 d\underline{r}_2 <(\phi_{ij}^P)^2>_\omega g_{ij}^o \qquad \text{(III-10)}$$

where ρ is the molecule number density, T is absolute temperature, k is Boltzman's constant, $\underline{r}_1$ and $\underline{r}_2$ are the position vectors of molecules 1 and 2, and g_{ij}^o is the isotropic pair distribution function. For the case in which ϕ_{ij}^P can be written as the product function

$$\phi_{ij}^P = F_{ij}\left(\frac{r_{12}}{\sigma_{ij}}\right) D\left(\omega_1, \omega_2\right) \qquad \text{(III-11)}$$

A_2 becomes

$$A_2 = \frac{-\pi\rho}{(kT)^2} \sum_{ij}\sum x_i x_j \delta_{ij}^2 \varepsilon_{ij}^2 \sigma_{ij}^3 \int dr_{12}^* r_{12}^{*2} F_{ij}^2 g_{ij}^o \langle D^2 \rangle_\omega \qquad \text{(III-12)}$$

where $r_{12}^* = r_{12}/\sigma_{12}$. For example, if the perturbation contribution to the pair potential were the overlap potential for linear molecules, the perturbation contribution could be approximated by the following expression, due to Pople (53),

$$\delta_{ij}\varepsilon_{ij}\phi_{ij}^p = \delta_{ij}\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r_{12}}\right)^{12}\left[3\cos^2\theta_1 + 3\cos^2\theta_2 - 2\right] \qquad \text{(III-13)}$$

so that $F_{ij} = \left(\frac{\sigma_{ij}}{r_{12}}\right)^{12}$ and $D = \left[3\cos^2\theta_1 + 3\cos^2\theta_2 - 2\right]$, where θ_1 and θ_2 are the polar angles of orientation of molecules 1 and 2. To obtain the expression for δ_x the following approximation is introduced,

$$g_{ij}^o\left(\frac{r_{12}}{\sigma_{ij}}, \frac{kT}{\varepsilon_{ij}}, \rho\sigma_{ij}^3, x_i, \ldots\right) = g_x^o(r^*, \rho^*, T^*) \qquad \text{(III-14)}$$

where $r^* = r/\sigma_x$, $\rho^* = \rho\sigma_x^3$, $T^* = kT/\varepsilon_x$. The approximation in Equation (III-14) is similar to, but more stringent than, the mean density approximation. With the assumption in Equation (III-14), A_2 becomes

$$A_2 = \frac{-\pi\rho\langle D^2\rangle}{(kT)^2}\omega\sum_{ij}\sum x_i x_j \delta_{ij}^2 \varepsilon_{ij}^2 \sigma_{ij}^3 \int dr^* \left(r^{*2} \quad F^2 g_x^o\right) \qquad \text{(III-15)}$$

It is then logical to choose the following mixing rule for the anisotropic strength parameter (overlap parameter in the specific example) δ_x,

$$\delta_x^2 \varepsilon_x^2 \sigma_x^3 = \sum_{ij}\sum x_i x_j \delta_{ij}^2 \varepsilon_{ij}^2 \sigma_{ij}^3 \qquad \text{(III-16)}$$

This mixing rule corresponds to the use of the following values of the exponents in Equation (III-5), u=2, v=2, w=3. The reduced Helmholtz free energy, $A^* = A/NkT$, where N is the number of molecules, then takes the form

$$A^* = A_o^* - \delta_x^2 \; \pi\langle D^2\rangle\rho^* J_x/(T^*)^2 \qquad \text{(III-17)}$$

where $\rho^* = \rho\sigma_x^3$, $T^* = kT/\varepsilon_x$ and J_x is the integral

$$J_x = \int dr^* \left(r^{*2} \; F^2 \; g_x^o\right) \qquad \text{(III-18)}$$

Note that A^* is of the form

$$A^* = A_o^* \quad + \delta_x^2 \; f^*(T^*, \rho^*) \qquad \text{(III-19)}$$

This result is identical to the expression which is obtained from the perturbation expansion of A for a pure fluid. Thus, referring to Equation (III-2), the first order conformal solution theory relation for anisotropic fluids is

$$A^*(T,\rho,\{\sigma_{ij}\}, \{\varepsilon_{ij}\},\{\delta_{ij}\}, \{x_k\})=A_x^*(T^*,\rho^*,\delta_x) \qquad \text{(III-20)}$$

where $\{\sigma_{ij}\}$, $\{\varepsilon_{ij}\}$ and $\{\delta_{ij}\}$ denote the sets of characterization parameters for the mixture constituent binary pairs; $\{x_k\}$ denotes the set of mole fractions of the mixture components, and

$$A_x^*(T^*, \rho^*, \delta_x) = A_o^*(T^*, \rho^*) + \delta_x^2 f^*(T^*, \rho^*) \qquad \text{(III-21)}$$

with the modified van der Waals mixing rules for σ_x, ε_x, and δ_x given in Equations (III-6), (III-7) and (III-16).

The equation of state expression for the absolute pressure P is obtained from Equation (III-19) using the thermodynamic relation

$$\frac{P}{\rho kT} = \rho^* \left(\frac{\partial A^*}{\partial \rho^*}\right)_{N,T} \qquad \text{(III-22)}$$

The resultant expression for the compressibility factor $Z = P/\rho kT$ is

$$Z = Z_o + \delta_x^2 Z_1 \qquad \text{(III-23)}$$

where

$$Z_o = \rho^* \left(\frac{\partial A_o^*}{\partial \rho^*}\right)_{N,T} \qquad \text{(III-24)}$$

$$Z_1 = \rho^*\left(\frac{\partial f^*}{\partial \rho^*}\right)_{N,T} = \rho^*\left[\frac{\partial}{\partial \rho^*}\left(\frac{-\pi \langle D^2 \rangle \rho^* J_x}{T^{*2}}\right)\right]_{N,T} \qquad \text{(III-25)}$$

3.3 Combining Rules

The combining rules considered for discussion here are the geometric mean rules, which are starting formulas for the development of unlike interaction characterization parameters in Chapter VI,

$$\varepsilon_{ij} = (\varepsilon_{ii}\ \varepsilon_{jj})^{1/2} \qquad \text{(III-26)}$$

$$\sigma_{ij} = (\sigma_{ii}\ \sigma_{jj})^{1/2} \qquad \text{(III-27)}$$

The following theoretical considerations for both ε_{ij} and σ_{ij} are based on the approaches utilized by Good and Hope (22). For the geometric mean rule for ε_{ij}, their theoretical basis is the London theory (47) of the dispersion forces. The attractive London forces between two simple, spherically symmetrical molecules at large distances are usually described by the potential function.

$$u_{ij} = -\frac{3}{2}\frac{\alpha_i \alpha_j}{r^6}\left(\frac{I_i\ I_j}{I_i + I_j}\right) \qquad \text{(III-28)}$$

Here I_i and I_j are the first ionization potentials of the molecules, and α_i and α_j indicate their polarizabilities. The above potential function is derived from certain simplifying assumptions on the dispersion forces in terms of the polarizabilities and the first ionization potentials of the individual molecules. If the molecules are alike, the above equation reduces to

$$u_{ii} = -\frac{3}{4}\frac{\alpha_i^2 I_i}{r^6} \tag{III-29}$$

The Lennard-Jones potential may be written as follows:

$$u=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right] \tag{III-30}$$

$$=\frac{C}{r^{12}}-\frac{A}{r^6} \tag{III-31}$$

where $C=4\sigma^{12}\varepsilon$, and $A=4\sigma^6\varepsilon$ (III-32)

If London's potential function is equated to the corresponding term in the Lennard-Jones potential, then

$$A_{ii}=\frac{3}{4}\alpha_i^2 I_i \tag{III-33}$$

$$A_{ij}=\frac{3}{4}\alpha_i\alpha_j\left\{(I_i\ I_j)/\left[1/2(I_i+I_j)\right]\right\} \tag{III-34}$$

$$A_{ij}/(A_{ii}A_{jj})^{1/2}=(I_iI_j)^{1/2}/\left[1/2(I_i+I_j)\right] \tag{III-35}$$

The preceding equation becomes with Equation (III-32)

$$\varepsilon_{ij}=\left[(\varepsilon_{ii}\varepsilon_{jj})^{1/2}(I_iI_j)^{1/2}\right]/\left[1/2(I_i+I_j)\right] \tag{III-36}$$

provided $\sigma_{ij}=\sigma_{ii}=\sigma_{jj}$. Since the ionization potentials of most substances are close to each other, the above equation simplifies to

$$\varepsilon_{ij} = (\varepsilon_{ii}\ \varepsilon_{jj})^{1/2} \tag{III-37}$$

For the case of geometric mean rule for σ_{ij}, the following relationships can be obtained from Equation (III-32):

$$A_{12}/(A_{11}A_{22})^{1/2} = \left[\varepsilon_{12}/(\varepsilon_{11}\varepsilon_{22})^{1/2}\right]\left[\sigma_{12}{}^{6}/(\sigma_{11}\sigma_{22})^{6/2}\right]. \tag{III-38}$$

$$A_{12}/(A_{11}A_{22})^{1/2} = \left[C_{12}/(C_{11}C_{22})^{1/2}\right]\left[\sigma_{12}{}^{-6}/(\sigma_{11}\sigma_{22})^{-6/2}\right] \tag{III-39}$$

$$C_{12}/(C_{11}C_{22})^{1/2} = \left[\varepsilon_{12}/(\varepsilon_{11}\varepsilon_{22})^{1/2}\right]\left[\sigma_{12}{}^{12}/(\sigma_{11}\sigma_{22})^{12/2}\right] \tag{III-40}$$

A geometric mean rule for each of A_{12} and ε_{12} is very reasonable. The above equations indicate that a geometric mean for σ_{12} would allow each of the equations to reduce to a single factor. This is one of the advantages of the choice of geometric mean rule for σ_{12}. Furthermore, a geometric mean rule for any two of the constants, A, C, ε and σ in Eqs. (III-38) - (III-40), leads to the same rule for the other two. A geometric mean rule for each of A_{12} and ε_{12} is very reasonable from observations of Eqs. (III-35) and (III-26).

Therefore, a geometric mean rule for σ_{12} is a logical choice.

CHAPTER IV

CALCULATION OF THERMODYNAMIC PROPERTIES

For the calculation of thermodynamic properties, Equation (III-23) was utilized in an empirical manner. Only data for nonpolar normal paraffin hydrocarbon systems were utilized in the correlation development, so that as an approximation, the Pitzer acentric factor, ω, could be taken as an estimate of the collective strength of molecular anisotropies (i.e., $\delta^2=\omega$). Because the use of the resultant correlation for fluids other than paraffin hydrocarbons (including polar systems) was anticipated, the parameter γ ($\gamma=\delta^2$), referred to herein as the orientation parameter, was utilized instead of the acentric factor ($\gamma\neq\omega$ for nonparaffin hydrocarbon fluids). The equation of state in Equation (III-23) then takes the form

$$Z(T^*, \rho^*, \gamma) = Z_o(T^*, \rho^*) + \gamma Z_1(T^*, \rho^*) \qquad \text{(IV-1)}$$

where Z is the compressibility factor and Z_o and Z_1 are functions of the reduced temperature $T^* = kT/\varepsilon$ and reduced density $\rho^*=\rho\sigma^3$. The equation of state form utilized herein is the modified Benedict-Webb-Rubin (MBWR) equation as given by Han and Starling (82). It is cast into the form of Equation(IV-1) by expressing the constants linearly in the equation into two parts, one isotropic part and one anisotropic part,

$$B_i = a_i + \gamma b_i \tag{IV-2}$$

a_i being the isotropic part and b_i being the anisotropic part, where as noted above, $\gamma \simeq \delta^2$ is an orientation parameter accounting for the nonsphericity of the molecule pair potentials under consideration. Therefore, the MBWR equation corresponding to Equation (IV-1) assumes the form

$$\begin{aligned} Z = 1 &+ \rho^* \left[B_1 - B_2 T^{*-1} - B_3 T^{*-3} + B_9 T^{*-4} - B_{11} T^{*-5}\right] \\ &+ \rho^{*2}\left[B_5 - B_6 T^{*-1} - B_{10} T^{*-2}\right] + \rho^{*5}\left[B_7 T^{*-1} + B_{12} T^{*-2}\right] \\ &+ B_8 \rho^{*2} T^{*-3}\left[(1 + B_4 \rho^{*2})\exp(-B_4 \rho^{*2})\right] \end{aligned} \tag{IV-3}$$

where b_4 in Equation (IV-2) is zero to insure linearity of Z in γ, ρ^* is the reduced density, $\rho^* = \rho\sigma^3$, and T^* is the reduced temperature, $T^* = kT/\varepsilon$. The characteristic molecular distance parameter σ, and energy parameter ε, were estimated from the critical constants using the relations:

$$\sigma^3 = \frac{0.3189}{\rho_c} \tag{IV-4}$$

$$\varepsilon = \frac{kT_c}{1.2593} \tag{IV-5}$$

where k is the Boltzmann constant. Pertinent relations for other thermodynamic properties have been presented elsewhere (41). Equations (IV-4) and (IV-5) are based on the relationships of the Lennard-Jones (12-6) potential parameters for argon to the argon critical constants. The use of Equations (IV-4) and (IV-5) in the MBWR equation of state given in Equations (IV-2) and (IV-3) has been shown to work well for pure normal paraffin hydrocarbons. The universal constants a_i and b_i, i=1,...12 (b_4=0) were determined by simultaneously using density, vapor pressure and enthalpy departure data for methane through normal decane in multiproperty analysis. Average absolute deviations of predicted from experimental properties were 1.00% for density, 1.13 Btu/lb for enthalpy and 0.85% for vapor pressure. Thus, the multiparameter corresponding states correlation framework provided by the perturbation equation form in Equation (IV-1) and the resultant generalized MBWR equation in Equation (IV-3) yields good results for the pure normal paraffin hydrocarbons. The values of the critical constants and orientation parameters given in Table IV-1 are recommended for use in the correlation to be consistent with thermodynamic property calculations. Table IV-2 lists the values of the constants a_i and b_i in Equation (IV-2).

TABLE IV-1

Generalization Parameters of Pure Materials to Be Used with Generalized Equation of State

	Critical Temp., °F	Critical Density, lb-mole/cu. ft.	Molecular Weight	Orientation Parameter, γ
Methane..................	-116.43	0.6274	16.042	0.01289
Ethane...................	90.03	0.4218	30.068	0.09623
Propane..................	206.13	0.3121	44.094	0.1538
i-Butane	274.96	0.2373	58.12	0.1812
n-Butane.................	305.67	0.2448	58.12	0.1991
i-Pentane................	369.	0.2027	72.146	0.2262
n-Pentane................	385.42	0.2007	72.146	0.2530
n-Hexane.................	453.45	0.1696	86.172	0.3054
n-Heptane................	512.85	0.1465	100.198	0.3499
n-Octane.................	563.79	0.1284	114.224	0.4004
n-Nonane.................	610.5	0.1150	128.24	0.4463
n-Decane.................	651.9	0.1037	142.276	0.4880
n-Undecane...............	692.31	0.0946	156.30	0.5219
Ethylene.................	49.82	0.5035	28.05	0.1007
Propylene................	197.4	0.3449	42.08	0.1486
Nitrogen.................	-232.6	0.6929	28.016	0.0263
Carbon Dioxide...........	87.8	0.6641	44.01	0.2093
Hydrogen Sulfide.........	212.7	0.6571	34.076	0.1092

TABLE IV-2

Generalized Parameters Used in the Modified Benedict-Webb-Rubin Equation

Parameter	$B_i = a_i + \gamma b_i$	
i	a_i	b_i
1	1.45907	0.32872
2	4.98813	-2.64399
3	2.20704	11.3293
4	4.86121	
5	4.59311	2.79979
6	5.06707	10.3901
7	11.4871	10.3730
8	9.22469	20.5388
9	0.094624	2.76010
10	1.48858	-3.11349
11	0.015273	0.18915
12	3.51486	0.94260

CHAPTER V

DEVELOPMENT OF MIXING RULES

5.1 Use of the Modified van der Waals One-Fluid Mixing Rules

The modified van der Waals one-fluid mixing rules for σ_x, ε_x and δ_x given in Equations (III-6), (III-7) and (III-16) were utilized to determine the ability of this formulation of conformal solution theory for prediction of mixture behavior. The following relations were used for σ_{ij}, ε_{ij}, and δ_{ij}, $i \neq j$,

$$\sigma_{ij} = \xi_{ij}(\sigma_{ii}\sigma_{jj})^{1/2} \tag{V-1}$$

$$\varepsilon_{ij} = \zeta_{ij}(\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{V-2}$$

$$\gamma_{ij} = \phi_{ij}(\gamma_{ii} + \gamma_{jj})/2 \tag{V-3}$$

where ξ_{ij}, ζ_{ij} and ϕ_{ij} are binary interaction parameters to be determined from binary mixture thermodynamic property data. It was found that there was little loss in accuracy of prediction when ϕ_{ij} was fixed at unity; therefore $\phi_{ij}=1$ was used for the calculations discussed herein. Values of the parameters ξ_{ij} and ζ_{ij} determined from available binary density, enthalpy and vapor-liquid equilibrium data for methane with heavier hydrocarbons are given in Table V-1. Table VII-1 presents binary interaction parameters for number of other fluid pairs. Conditions for all mixture data studied including the methane binaries are shown in Table VII-4. Table V-2 presents a summary of the deviations of predicted densities and methane K-values (equilibrium ratio of vapor to liquid mole fractions). A complete summary of deviations of predicted properites for the methane binaries as well as other mixtures is provided in Table VII-5. Deviations of predicted heavy component K-values from experimental data were not used to evaluate the accuracy of prediction because the vapor phase mole fraction of the heavy component often is so small that the measurement error is extremely large on a percentage basis. The trend which can be noted in Table V-2 is the fact that properties are predicted with reasonable accuracy for the methane-ethane and methane-propane systems but there is a decay in the accuracy of prediction for the mixtures of methane with normal butane and heavier components. This trend would be anticipated by virtue of the approximations made herein to develop the multiparameter corresponding states/conformal solution formulas. The major approximations of concern are (1) the second order truncation of the Pople expansion, (2)

TABLE V-1

Binary Interaction Parameters for Methane (First Component) with Heavier Hydrocarbons

Second Component	Modified VDW One-Fluid Mixing Rules		Semiempirical Exponent Mixing Rules	
	ξ_{12}	ζ_{12}	ξ_{12}	ζ_{12}
Ethane	0.999079	0.996810	1.00087	0.978262
Propane	1.02116	0.974404	1.01188	0.936840
n-Butane	1.03946	0.958079	1.02559	0.899345
n-Pentane	1.05214	0.936798	1.03220	0.860984
n-Hexane	1.07738	0.920368	1.04925	0.837207
n-Heptane	1.08744	0.921744	1.05967	0.818753
n-Nonane	1.09674	0.937876	1.07753	0.799090
n-Decane	1.11940	0.978290	1.08519	0.790355

TABLE V-2

Summary of Deviations of Predicted Binary Mixture Densities and Methane K-Values from Experimental Data

Second Component with Methane	Average Absolute Deviations, %*			
	Modified van der Waals one-Fluid Mixing Rules		Semiempirical Exponent Mixing Rules	
	Densities	K-Values	Densities	K-Values
Ethane	2.20	1.14	1.99	1.02
Propane	0.94	1.14	1.02	0.84
n-Butane	2.65	8.10	2.12	4.01
n-Pentane	2.12	9.61	1.49	4.58
n-Hexane	--	17.9	--	5.97
n-Heptane	3.57	13.6	3.07	8.77
n-Nonane	1.41	16.1	2.55	2.15
n-Decane	4.34	20.5	5.41	5.45

*Average Absolute Deviation, % (AAD %) = $\sum_{N} \left|(\text{Exp.-Calc.})/\text{Exp.}\right| \times 100/N$

the lumping of the collective effects of molecular anisotropies into a single term, characterized by a single orientation parameter, γ, (3) the first order truncation of the conformal solution expansion of the Helmholtz free energy, and (4) the choices made for the exponents in the mixing rules for the reference system characterization parameters σ_x, ε_x and δ_x. Because of the success of the formulation for predicting pure fluid properties, even as heavy as normal decane, the first two approximations appear adequate for practical industrially oriented correlations such as that utilized herein. Although the third approximation has been shown to be poor for binary mixtures of hard sphere molecules with large size differences, the use of second order conformal solution theory introduces additional computational requirements which would slow practical calculations, especially multicomponent vapor-liquid equilibrium predictions. For these reasons, the fourth approximation was focused on and a first alternative to the modified van der Waals one-fluid mixing rules used above was considered.

5.2 Semiempirical Exponent Mixing Rules

To determine if a significant level of improvement in predicted mixture properties over the van der Waals one-fluid mixing rules is possible, the nine exponents in the general mixing rules for σ_x, ε_x and δ_x in Equations (III-3), (III-4) and (III-5) could be determined empirically. However, all contact with the van der Waals one-fluid formulas might be lost by such an approach. Therefore, the exponents k, l and p were fixed at zero and nonlinear regression (20) was performed to determine the remaining exponents, starting the nonlinear regression with the van der Waals one-fluid values for the remaining exponents, i.e., m=3, q=1, r=3, u=2, v=2, and w=3. Since the resultant fugacity expression is different from that presented earlier (41), the component fugacity is given here,

$$\ell n\left(\frac{f_i}{x_i f_i^o}\right) = (1 + \bar V_i)\,\frac{H-H^o}{RT} - \frac{S-S^o}{R} + (\bar R_i - \bar V_i)(Z - 1)$$

$$+ \rho^*\left[\bar B_{1,i} - \bar B_{2,i} T^{*-1} - \bar B_{3,i} T^{*-3} + \bar B_{9,i} T^{*-4} - \bar B_{11,i} T^{*-5}\right]$$

$$+ \frac{\rho^{*2}}{2}\left[\bar B_{5,i} - \bar B_{6,i} T^{*-1} - \bar B_{10,i} T^{*-2}\right]$$

$$+ \frac{\rho^{*5}}{5}\left(\bar B_{7,i} T^{*-1} + \bar B_{12,i} T^{*-2}\right)$$

$$+ \bar B_{8,i} T^{*-3}\left[1 - e^{-B_4 \rho^{*2}} - \frac{1}{2} B_4 \rho^{*2} e^{-B_4 \rho^{*2}}\right]/B_4 \qquad \text{(V-4)}$$

where f_i^o is the standard-state fugacity, taken to be 1, and the derivatives are:

$$\bar B_{j,i} \equiv \left.\frac{\partial B_j}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= b_j \left.\frac{\partial \gamma_x}{\partial n_i}\right|_{T,V,n_{k\neq i}}$$

$$= b_j\,\gamma_x\left[\frac{4}{u}\left(\frac{\sum_\alpha x_\alpha \gamma_{\alpha i}^{u/2}\varepsilon_{\alpha i}^{v}\sigma_{\alpha i}^{w}}{\gamma_x^{u/2}\varepsilon_x^{v}\sigma_x^{w}} - 1\right) - \frac{2w}{3u}\bar R_i - \frac{2v}{u}\bar V_i\right] \qquad \text{(V-5)}$$

$$\overline{R}_i = \frac{1}{\rho^*}\frac{\partial \rho^*}{\partial n_i}\Bigg|_{T,V,n_{k\neq i}}$$

$$= \frac{6}{m}\left[\frac{\sum\limits_{\alpha} x_\alpha \sigma_{\alpha i}^m}{\sigma_x^m} - 1\right] \qquad \text{(V-6)}$$

$$\overline{V}_i = -\frac{1}{T^*}\frac{\partial T^*}{\partial n_i}\Bigg|_{T,V,n_{k\neq i}}$$

$$= \frac{2}{q}\left[\frac{\sum\limits_{\alpha} x_\alpha \varepsilon_{\alpha i}^q \sigma_{\alpha i}^r}{\varepsilon_x^q \sigma_x^r} - 1\right] - \frac{r}{3q}\overline{R}_i \qquad \text{(V-7)}$$

where m, q, r, u, v and w are the exponents in Eqs. (III-3) - (III-5). The above equations are on the basis of 1 mole of mixture. Available density, enthalpy and vapor-liquid equilibrium data for the eight binary systems in Table V-2 were used to determine the revised exponent values. The following scheme provided the present set of the optimum values:

1. Starting with the binary interaction parameters used with the modified VDW one-fluid mixing rules and using the same exponents set forth in Eqs. (III-6), (III-7) and (III-16) (m=3.0, q=1.0, r=3.0, u=2.0, v=2.0, w=3.0) as initial values, regression was done on ξ, v, and m.
2. Starting again with the same set of intial values employed in step 1, regress on ζ, w and r.
3. Taking each individual newly regressed parameter from step 1 and 2 and fixing q and u at 1.0 and 2.0 respectively, a new set of ξ, ζ, m, q, r, u, v, w was obtained.

4. Regress on v, w, m, and r, holding the other parameters at the values obtained in step 3. It was found in step 4 that the exponent v turned out to be zero for three binary systems (methane with n-pentane, n-heptane and n-decane). Therefore, for the remaining two systems (methane with n-hexane and n-nonane) v was set to zero and step 4 was omitted. The deviations for these two systems, at completion of step 5, were as small as when v was not fixed to zero and step 4 was carried out.
5. Regress w, m and r.
6. Start to include ξ or ζ one at a time with w, m, and r in regression.
7. Repeat the above six steps for each of the following binary mixtures: methane with n-pentane, n-hexane, n-heptane, n-nonane and n-decane. This step provides the best set of ξ, ζ, m, q, r, u, v, w for each methane binary system.
8. Regress w, m and r with u=2.0, q=1.0 and v=0.0 for the combined systems simultaneously. These systems consist of methane binaries with ethane through n-decane except n-octane. The initial values for the m, q, r, u, v, w were taken to be an average of the best exponents obtained in step 7 of the individual systems regressed for step 1 through step 6. They are m=3.12, q=1.0, r=3.98142, u=2.0, v=0.0 and w=3.12.

Values for ξ and ζ were already obtained in step 6. Step 8 supplies the optimum values of m, q, r, u, v and w applicable to all the eight binary systems (expressed as $\bar{m}$, $\bar{q}$, $\bar{r}$, $\bar{u}$, $\bar{v}$, $\bar{w}$): $\bar{m}=4.6917$, $\bar{q}=1.0$, $\bar{r}=4.5021$, $\bar{u}=2.0$, $\bar{v}=0.0$, $\bar{w}=3.79788$.

9. Regress ξ and ζ again for each individual binary system with the optimum set ($\bar{m}$, $\bar{q}$, $\bar{r}$, $\bar{u}$, $\bar{v}$, $\bar{w}$).
10. Repeat steps 8 and 9 with the latest parameter values until no significant improvements appear in the deviations for the thermodynamic properties. This step completes determination of optimum values for m, q, r, u, v, w for all the binary systems and also yields the optimum binary interaction parameters, ξ and ζ, for each individual binary system.

The optimum values of the exponents then are m=4.5255, q=1.0, r=4.44271, u=2.0, v=0.0, and w=3.4959. Rounding off these exponents yields the following semiempirical exponent mixing rules,

$$\sigma_x^{4.5} = \sum_{ij}\sum x_i x_j \sigma_{ij}^{4.5} \qquad \text{(V-8)}$$

$$\varepsilon_x \sigma_x^{4.5} = \sum_{ij}\sum x_i x_j \varepsilon_{ij} \sigma_{ij}^{4.5} \qquad \text{(V-9)}$$

$$\delta_x^{2} \sigma_x^{3.5} = \sum_{ij}\sum x_i x_j \delta_{ij}^{2} \sigma_{ij}^{3.5} \qquad \text{(V-10)}$$

The binary interaction parameters for use with the semi-empirical exponent mixing rules are given in Table V-1.

Table VII-2 shows binary parameters for additional fluid pairs. Summaries of deviations of predicted properties from experimental values using these semiempirical exponent mixing rules are given for binary systems in Table V-2. A complete summary of deviations of predicted properties for other mixtures in addition to the eight binary systems is presented in Table VII-5. The improvement in vapor-liquid equilibrium predictions is significant. The average absolute deviation of predicted methane K-values from experimental data for the semiempirical exponent mixing rules is 4.1% compared with 11.0% for the modified van der Waals one-fluid mixing rules.

5.3 Evaluation of Vapor-Liquid Equilibrium Predictions for Multicomponent Systems; Paraffin-Paraffin

Comparisons of predicted and experimental vapor-liquid equilibrium for ternary and quarternary systems are given in Tables V-3 and V-4, for both the semiempirical exponent and the modified van der Waals one-fluid mixing rules. The predicted results using the semiempirical exponent mixing rules with unlike interaction parameter correlations developed in Chapter VI are also given in these tables; analysis of the results will be made in Chapter VII. Vapor-liquid equilibrium predictions for additional multicomponent systems involving paraffin-paraffin interactions are treated in Chapter VII. For these systems, some of the binary interaction parameters are not available and thus the use of estimated

TABLE V-3

Summary of Deviations of Predicted Vapor-Liquid Phase Compositions for the System Methane-Ethane-Propane[1]

(Subscripts 1, 2, 3, Respectively)

No. Data Points: 33

Temperature Range: -176—-76°F

Pressure Range: 32-800 psia

Mixing Rules		x_1	x_2	x_3	y_1	y_2	y_3
*	AAD %	4.75	3.80	3.90	1.145	7.25	15.05
*	AAD[2]	0.00995	0.00687	0.00554	0.00786	0.00654	0.00138
**	AAD %	4.56	3.62	3.79	1.152	6.92	16.38
**	AAD	0.00956	0.00653	0.00570	0.00795	0.00650	0.00151
***	AAD %	8.14	6.01	5.59	1.43	9.02	17.67
***	AAD	0.01826	0.01144	0.00977	0.00979	0.00823	0.00163

* Modified van der Waals one-fluid mixing rules.

** Semiempirical exponent mixing rules.

*** Semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12).

[1] See Table VII-4 for data reference.

[2] Average Absolute Deviation, AAD = $\sum_{N} |\text{Exp.}-\text{Calc.}| / N$

TABLE V-4

Comparison of Predicted and Experimental *Vapor-Liquid Equilibrium for the Four-Component Systems of Methane-Ethane-Propane-n-Butane and Methane-Ethane-Propane-Isobutane

(Subscripts 1, 2, 3, 4, Respectively)

System	T(°F)	P(psia)		x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
Methane-Ethane-Propane-n-Butane	-60	204	Expt.	0.16	0.188	0.583	0.069	0.852	0.08	0.063	0.005
			Calc.[1]	0.184	0.186	0.562	0.0676	0.8869	0.0726	0.0396	0.00077
			Calc.[2]	0.144	0.188	0.596	0.0718	0.8809	0.0779	0.0402	0.00093
			Calc.[3]	0.134	0.194	0.600	0.0724	0.8860	0.0731	0.0401	0.00079
Methane-Ethane-Propane-n-Butane	-60	288	Expt.	0.234	0.178	0.527	0.061	0.874	0.060	0.059	0.007
			Calc.[1]	0.271	0.170	0.499	0.0601	0.915	0.054	0.030	0.00064
			Calc.[2]	0.212	0.177	0.545	0.0659	0.910	0.058	0.031	0.00078
			Calc.[3]	0.197	0.183	0.553	0.0670	0.914	0.054	0.031	0.00066
Methane-Ethane Propane-Isobutane	+20	200	Expt.	0.079	0.197	0.160	0.564	0.758	0.187	0.028	0.027
			Calc.[1]	0.0977	0.180	0.1488	0.573	0.677	0.201	0.050	0.0715
			Calc.[2]	0.0662	0.166	0.1558	0.612	0.663	0.210	0.051	0.075
			Calc.[3]	0.0703	0.163	0.1567	0.610	0.664	0.212	0.050	0.073

* See Table VII-4 for data reference.

[1] Modified van der Waals one-fluid mixing rules.

[2] Semiempirical exponent mixing rules.

[3] Semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12).

values is required for mixture property predictions (e.g., assume to be unity).

In the calculations of vapor-liquid equilibrium, the binary interaction parameters for each binary pair in the multicomponent systems considered herein were taken from Tables VII-1 amd VII-2. Direct comparisons with experimental data for the methane-ethane-propane system are presented in Appendix A. As shown in Tables V-3 and V-4, the semiempirical exponent mixing rules give better predictions of phase compositions for most components.

From inspection of Tables V-2, V-3, and V-4, it is obvious that for systems containing components heavier than propane, vapor-liquid equilibrium predictions are more accurate using the semiempirical exponent mixing rules rather than the van der Waals one-fluid mixing rules. Thus, from the point of view of practical industrial computations, the semiempirical mixing rules are recommended. It is difficult to ascertain the reasons for the magnitude of improvement in vapor-liquid predictions using the semiempirical exponent mixing rules instead of the modified van der Waals one-fluid mixing rules. It is probable that the semiempirical exponent mixing rules offset to some extent the truncation error in the approximation $A=A_x$.

CHAPTER VI

DEVELOPMENT OF UNLIKE INTERACTION PARAMETER CORRELATIONS

The mixing rules in Chapter V require two binary interaction parameters, ξ_{ij}, ζ_{ij}, to define the unlike interaction parameters, σ_{ij} and ε_{ij}. The binary interaction parameters were empirically determined by means of multiproperty regression anlysis (82) on binary mixture thermodynamic property data. For multicomponent mixtures, the only required information is the binary interaction parameters and the characterization parameters for the pure components. However, for mixtures lacking binary mixture data, methods must be devised to estimate the binary interaction parameters in order to predict mixture properties.

The simplest method for estimating the unlike interaction parameters is to assume binary interaction parameters to be unity. In fact, when components are very similar in size and chemical nature, binary interaction parameters become very close to unity (e.g., n-hexane - n-heptane). Unfortunately, small deviations from unity for the binary interaction parameters significantly affect the calculated properties, so that improvements are necessary over the unity assumption for mixtures of dissimilar molecules. Therefore, the approach taken herein was to correlate the binary interaction parameters ξ_{ij} and ζ_{ij} as functions of the pure fluid characterization parameters, σ_{ii}, σ_{jj}, ε_{ii}, ε_{jj}, γ_{ii}, γ_{jj} (or equivalently, V_{c_i}, V_{c_j}, T_{c_i}, T_{c_j}, γ_i, γ_j).

The geometric mean is employed herein as the base formula for both σ_{ij} and ε_{ij}, so that ξ_{ij} and ζ_{ij} are multipliers for $(\sigma_{ii}\ \sigma_{ij})^{1/2}$ and $(\varepsilon_{ii}\ \varepsilon_{jj})^{1/2}$, respectively, to obtain σ_{ij} and ε_{ij}. The reasons for adopting the geometric mean as the underlying unlike interaction parameter form are:

1. The geometric mean maintains consistency with the modified Berthelot rules used in the development of the semiempirical exponent mixing rules; 2. the modified Berthelot rules generally perform well for hydrocarbon mixtures. Two binary systems, methane with n-heptane and methane with n-decane, which are typical of highly dissimilar molecular sizes, were utilized in this investigation.

For the development of correlations for the unlike interaction parameters in the semiempirical exponent mixing rules, the binary mixtures in Table VII-4 are devided into five groups;

i. n-paraffins with n-paraffins;
ii. Hydrocarbons other than n-paraffins with n-paraffins;
iii. Carbon dioxide with hydrocarbons;
iv. Hydrogen sulfide with hydrocarbons and carbon dioxide;

v. Nitrogen with hydrocarbons, carbon dioxide and hydrogen sulfide.

6.1 Correlation for Hydrocarbons

6.1.1 n-Paraffins with n-Paraffins

Numerous types of formulas in terms of T_{c_i}, V_{c_i}, and γ_i have been attempted to find a best fit to a collection of binary mixture data for methane with n-paraffin hydrocarbons up to n-decane by multiproperty regression analysis (82). As a result of extensive comparisons of the formulas, it has been found that the following relationships provide low overall average absolute deviations for thermodynamic properties for the binaries of methane with n-paraffins and yet allow sensible values for the constants (a, b, c, d, e, and f).

$$\xi_{ij} = a\frac{(V_{c_i}^{1/3} + V_{c_j}^{1/3})^b}{(V_{c_i}^{1/3}V_{c_j}^{1/3})^c} \tag{VI-1}$$

$$\zeta_{ij} = d\frac{(V_{c_i}^{1/3} + V_{c_j}^{1/3})^e}{(V_{c_i}^{1/3}V_{c_j}^{1/3})^f} \tag{VI-2}$$

Eqs. (VI-1) and (VI-2) are the reciprocals of the forms found by Chueh and Prausnitz (13). The resulting equations for the unlike interaction parameters are

$$\sigma_{ij} = a \frac{(V_{c_i}^{1/3} + V_{c_j}^{1/3})^b}{(V_{c_i}^{1/3} V_{c_j}^{1/3})^c} \sqrt{\sigma_{ii}\sigma_{jj}} \qquad \text{(VI-3)}$$

$$\varepsilon_{ij} = d \frac{(V_{c_i}^{1/3} + V_{c_j}^{1/3})^e}{(V_{c_i}^{1/3} V_{c_j}^{1/3})^f} \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad \text{(VI-4)}$$

$$\gamma_{ij} = 1/2(\gamma_{ii} + \gamma_{jj}) \qquad \text{(VI-5)}$$

For the binaries of methane with n-paraffins, the constants are: $a = 0.433212$; $b = 1.1154$; $c = 0.5$; $d = 0.513663$; $e = 1.3203$; $f = 1.2659$. The overall average absolute deviation for the mole fraction of methane in the liquid phase in vapor-liquid equilibrium (VLE) predicted with Eqs. (VI-3) - (VI-5) is 7.64%, compared with 10.63% and 5.09% using the modified van der Waals (VDW) one-fluid rules and the semiempirical exponent rules respectively, with individual (not generalized) binary interaction parameters, for 120 representative VLE data points for the binaries of methane with n-paraffins.

It is reasonable to assume that Eqs. (VI-3) - (VI-5) developed for the binaries of methane with n-paraffins would work well for other paraffin binaries with adjustments of the six constants by means of multiproperty regression analysis. Indeed this is the case. For ethane binaries (ethane with propane and n-butane) the overall average absolute deviation of ethane mole fractions in the liquid phase in VLE using Eqs. (VI-3) - (VI-5) with optimum constants is 3.08%, versus 2.99% for the semiempirical exponent mixing rules using individual binary interaction parameters, for 30 VLE data points. For the binary of propane with n-butane, the overall average absolute deviation of propane mole fractions in the liquid phase in VLE using Eqs. (VI-3) - (VI-5) with optimum constants is 1.06%, versus 1.04% for the semiempirical exponent mixing rules using individual binary interaction parameters, for 19 VLE data points. As can be noted from the results, variations on the six constants for paraffin binaries provide accurate predictions. However, for reasons illustrated below, adjustment of two constants instead of all six constants in Eqs. (VI-3) - (VI-5) is desirable. When the two coefficients, a and d, are evaluated using multiproperty regression analysis employing the values of the four exponents for the methane binaries, there is little sacrifice in accuracy of predictions for the ethane binaries and an acceptable loss in accuracy for the propane-n-butane binary. These results for the ethane and propane binaries suggest that the exponents, b, c, e and f, can be fixed at the values determined for the methane binaries, while two coefficients (a and d) need further refinement. The binary interaction parameters for binaries of ethane and propane with n-paraffins for which binary mixture data are not available can thus be estimated through the use of Eqs. (VI-1) and (VI-2) with the coefficients a and d determined from the limited data for these systems and the fixed exponents.

For other paraffin binaries where experimental data are either sparse or unavailable, a similar procedure can be utilized. For instance, n-heptane data available include three binary systems, n-heptane with n-octane, n-nonane, and n-decane, respectively, from which three pairs of binary interaction parameters can be determined. Therefore, the two constants a and d can be evaluated by fitting the binary interaction parameters for these three binaries. When this procedure was carried out, it was possible to estimate a and d for systems lacking data by interpolation of the values of a and d. The results are given in Table VI-1.

Inspection of the coefficients a and d in Table VI-1 shows that the asymptotic behavior of a and d is apparent. The limiting values of a and d are 0.4 and 1.0 respectively, which make ξ_{ij} and ζ_{ij} unity for n-decane. With this fact taken into account, a and d for all normal paraffin binaries can be correlated in terms of the characteristic parameters for the pure components. The following correlations provide a satisfactory fit of the coefficients a and d:

$$a = 0.4\left\{1+\alpha_1\left[(T_{c_{10}}-T_{c_i})/T_{c_{10}}\right]^{\alpha_2}\right\} \tag{VI-6}$$

where $\alpha_1 = 0.12847$ and $\alpha_2 = 1.19103$ (VI-7)

$$d = 1 - \beta_1(\gamma_{10} - \gamma_i)^{\beta_2} \tag{VI-8}$$

TABLE VI-1

Optimum Values of the Constants in Eqs. (VI-3) - (VI-4) and Eqs. (VI-1) - (VI-2) for Paraffin Binaries

Binary System †	$\sigma_{ij} = (aX^b/Y^c)\sqrt{\sigma_{ii}\sigma_{jj}}$			$\varepsilon_{ij} = (dX^e/Y^f)\sqrt{\varepsilon_{ii}\varepsilon_{jj}}$		
	a	b	c	d	e	f
Methane	0.433212	1.154	0.5	0.513663	1.3203	1.2659
Ethane	0.423023	1.154	0.5	0.599219	1.3203	1.2659
Propane	0.416951	1.154	0.5	0.672510	1.3203	1.2659
	$\xi_{ij} = aX^b/Y^c$			$\zeta_{ij} = dX^e/Y^f$		
	a	b	c	d	e	f
n-Butane	0.412429	1.154	0.5	0.735506	1.3203	1.2659
n-Pentane	0.409344	1.154	0.5	0.791870	1.3203	1.2659
n-Hexane	0.406749	1.154	0.5	0.841150	1.3203	1.2659
n-Heptane	0.404521	1.154	0.5	0.886194	1.3203	1.2659
n-Octane	0.402722	1.154	0.5	0.927974	1.3203	1.2659

TABLE VI-1

(Continued)

	a	b	c	d	e	f
n-Nonane	0.401596	1.154	0.5	0.964576	1.3203	1.2659
n-Decane	0.4*	1.154	0.5	1.0**	1.3203	1.2659

$X = (V_{c_i}{}^{1/3} + V_{c_j}{}^{1/3})$

$Y = (V_{c_i}{}^{1/3} V_{c_j}{}^{1/3})$

*Calculated from Equation (VI-1) to make ξ_{ij} unity.

**Calculated form Equation (VI-2) to make ζ_{ij} unity.

†Second component is any normal paraffin hydrocarbon heavier than compound indicated, up to normal decane.

where $\beta_1 = 1.17365$ and $\beta_2 = 1.17384$ (VI-9)

and 10 refers to n-decane. With the above results, the equations for the unlike interaction parameters σ_{ij}, ε_{ij} and γ_{ij} for normal paraffin binary pairs become

$$\sigma_{ij}=0.4\left\{1+\alpha_1\left[(T_{c_{10}}-T_{c_i})/T_{c_{10}}\right]^{\alpha_2}\right\}\left\{\frac{(V_{c_i}^{1/3}+V_{c_j}^{1/3})^{1.1154}}{(V_{c_i}^{1/3}V_{c_j}^{1/3})^{0.5}}\right\}\sqrt{\sigma_{ii}\sigma_{jj}} \qquad \text{(VI-10)}$$

with $\alpha_1 = 0.12847$ and $\alpha_2 = 1.19103$

$$\varepsilon_{ij}=\left[1-\beta_1(\gamma_{10}-\gamma_i)^{\beta_2}\right]\frac{(V_{c_i}^{1/3}+V_{c_j}^{1/3})^{1.3203}}{(V_{c_i}^{1/3}V_{c_j}^{1/3})^{1.2659}}\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \qquad \text{(VI-11)}$$

with $\beta_1 = 1.17365$ and $\beta_2 = 1.17384$, and

$$\gamma_{ij} = 1/2(\gamma_{ii} + \gamma_{jj}) \qquad \text{(VI-12)}$$

where i refers to the component with the smaller carbon number for paraffin binaries and 10 indicates n-decane. For n-paraffin hydrocarbon pairs heavier than n-decane, values of unity are to be used for ξ_{ij} and ζ_{ij}. Since ξ_{ij} and ζ_{ij} are multipliers for $(\sigma_{ii}\sigma_{jj})^{1/2}$ and $(\varepsilon_{ii}\varepsilon_{jj})^{1/2}$, respectively, in Eqs. (VI-10) - and (VI-11), it follows that

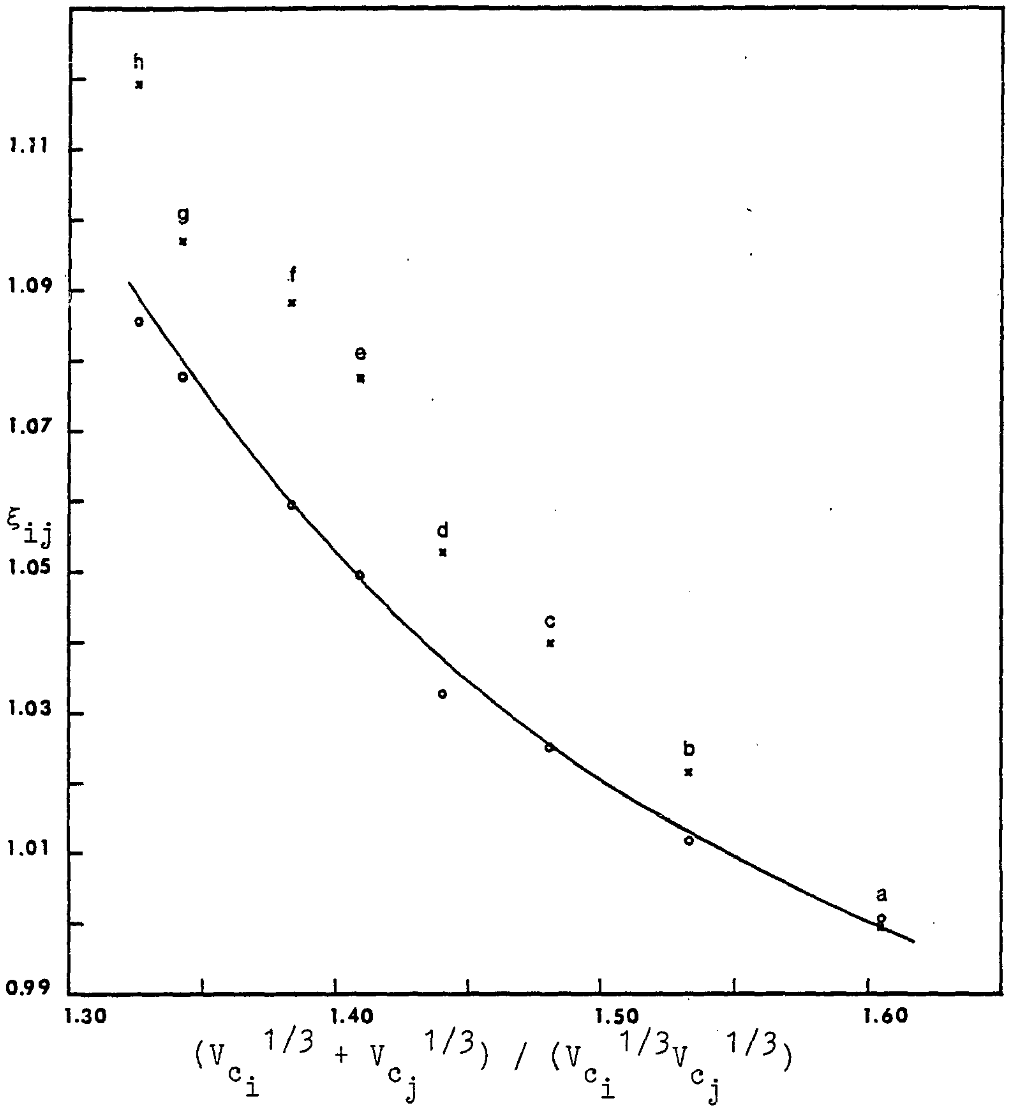
$$\xi_{ij}=0.4\left\{1.0+0.12847\left[(T_{c_{10}}-T_{c_i})/T_{c_{10}}\right]^{1.19103}\right\}\left\{\frac{(V_{c_i}^{1/3}+V_{c_j}^{1/3})^{1.1154}}{(V_{c_i}^{1/3}V_{c_j}^{1/3})^{0.5}}\right\} \qquad \text{(VI-13)}$$

$$\zeta_{ij}=\left[1.0-1.17365(\gamma_{10}-\gamma_i)^{1.17384}\right]\frac{(V_{c_i}^{\ 1/3}+V_{c_j}^{\ 1/3})^{1.3203}}{(V_{c_i}^{\ 1/3}V_{c_j}^{\ 1/3})^{1.2659}} \qquad \text{(VI-14)}$$

Generalized binary interaction parameters from Eqs. (VI-13) and (VI-14) for use with the semiempirical exponent mixing rules are included in Table VII-3 and also plotted versus $(V_{c_i}^{\ 1/3} + V_{c_j}^{\ 1/3}) / (V_{c_i}V_{c_j})^{1/3}$ in Figures (VI-1) - (VI-4) along with individual binary interaction parameters to be used with the modified VDW one-fluid and the semiempirical exponent mixing rules. As illustrated in Figs. (VI-1) and (VI-2), individual binary interaction parameters for use with the semiempirical exponent mixing rules are rather smooth functions, whereas those for use with the modified VDW one-fluid mixing rules show some scatter of the values.

6.1.2 Hydrocarbons Other Than n-Paraffin with n-Paraffins

The constants in Eqs. (VI-3) and (VI-4) were also determined for binaries of normal paraffins with hydrocarbons other than n-paraffins. The hydrocarbons other than n-paraffins include isobutane, isopentane, ethylene, and propylene. Isobutane binaries included isobutane with methane, ethane, and propane; isopentane binaries included isopentane with methane and propane; ethylene binaries included ethylene with methane and ethane; propylene binaries included propylene



a. CH_4-C_2H_6
b. CH_4-C_3H_8
c. CH_4-n-C_4H_{10}
d. CH_4-n-C_5H_{12}
e. CH_4-n-C_6H_{14}
f. CH_4-n-C_7H_{16}
g. CH_4-n-C_9H_{20}
h. CH_4-n-$C_{10}H_{22}$

x Individual values for modified VDW one-fluid rules.
o Individual values for semiempirical exponent rules.
— Calculated from Eq. (VI-13).

Fig. (VI -1) ξ_{ij} values for methane-n-paraffin binaries.

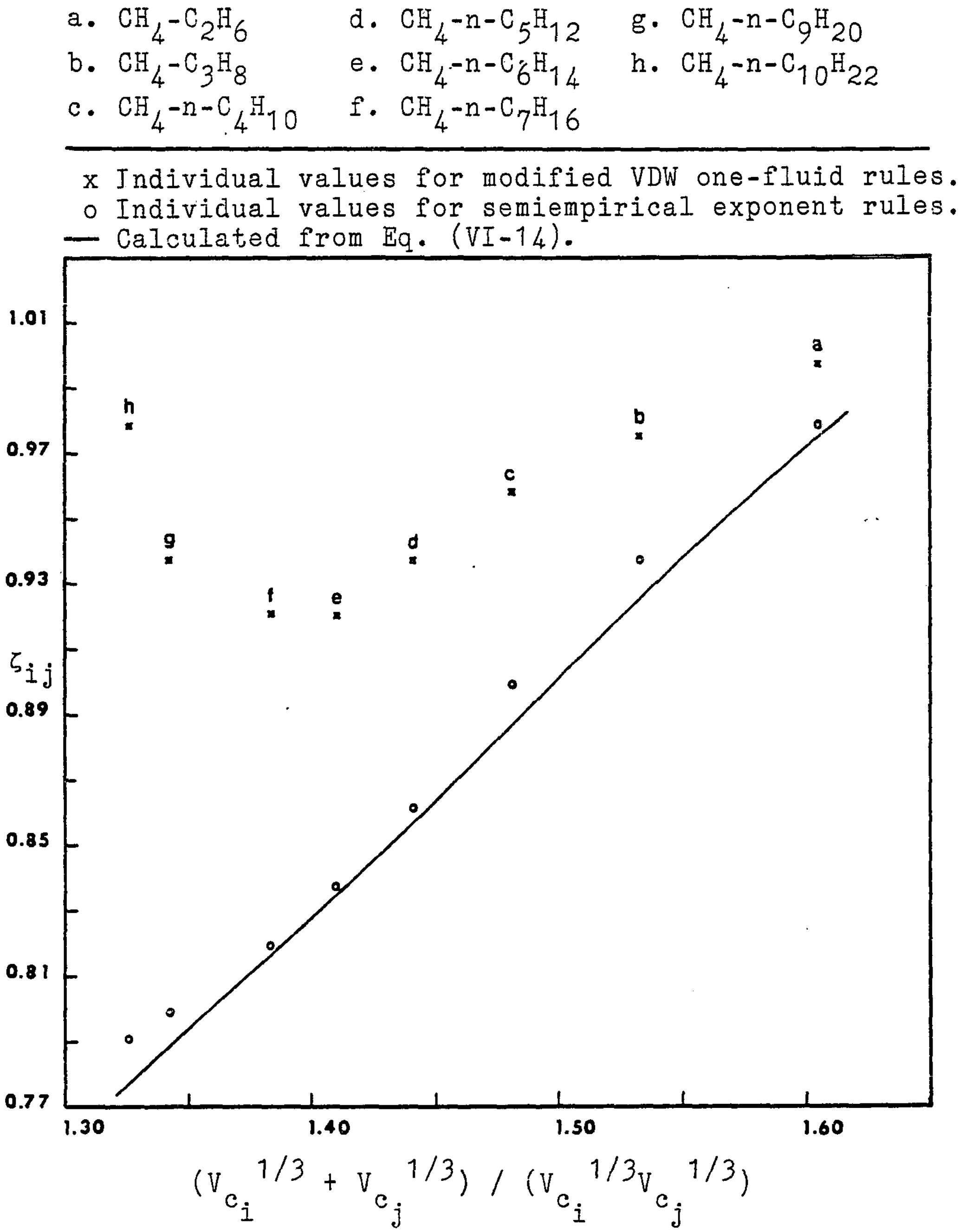


Fig. (VI -2) ζ_{ij} values for methane-n-paraffin binaries.

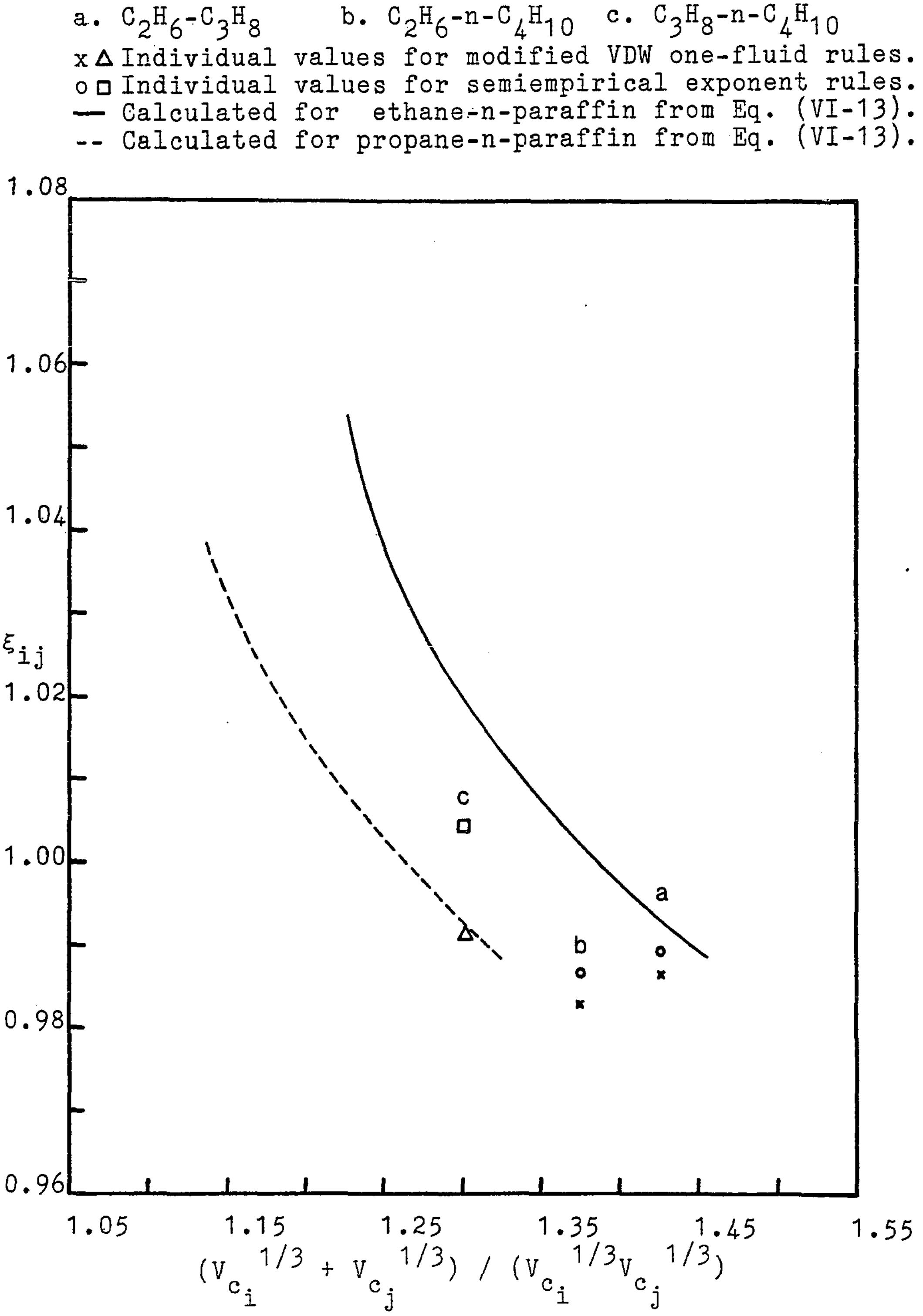


Fig. (VI -3) ξ_{ij} values for ethane- and propane-n-paraffin binaries.

a. C_2H_6-C_3H_8 b. C_2H_6-n-C_4H_{10} c. C_3H_8-n-C_4H_{10}

x △ Individual values for modified VDW one-fluid rules.

o □ Individual values for semiempirical exponent rules.

— Calculated for ethane-n-paraffin from Eq. (VI-14).

-- Calculated for propane-n-paraffin from Eq. (VI-14).

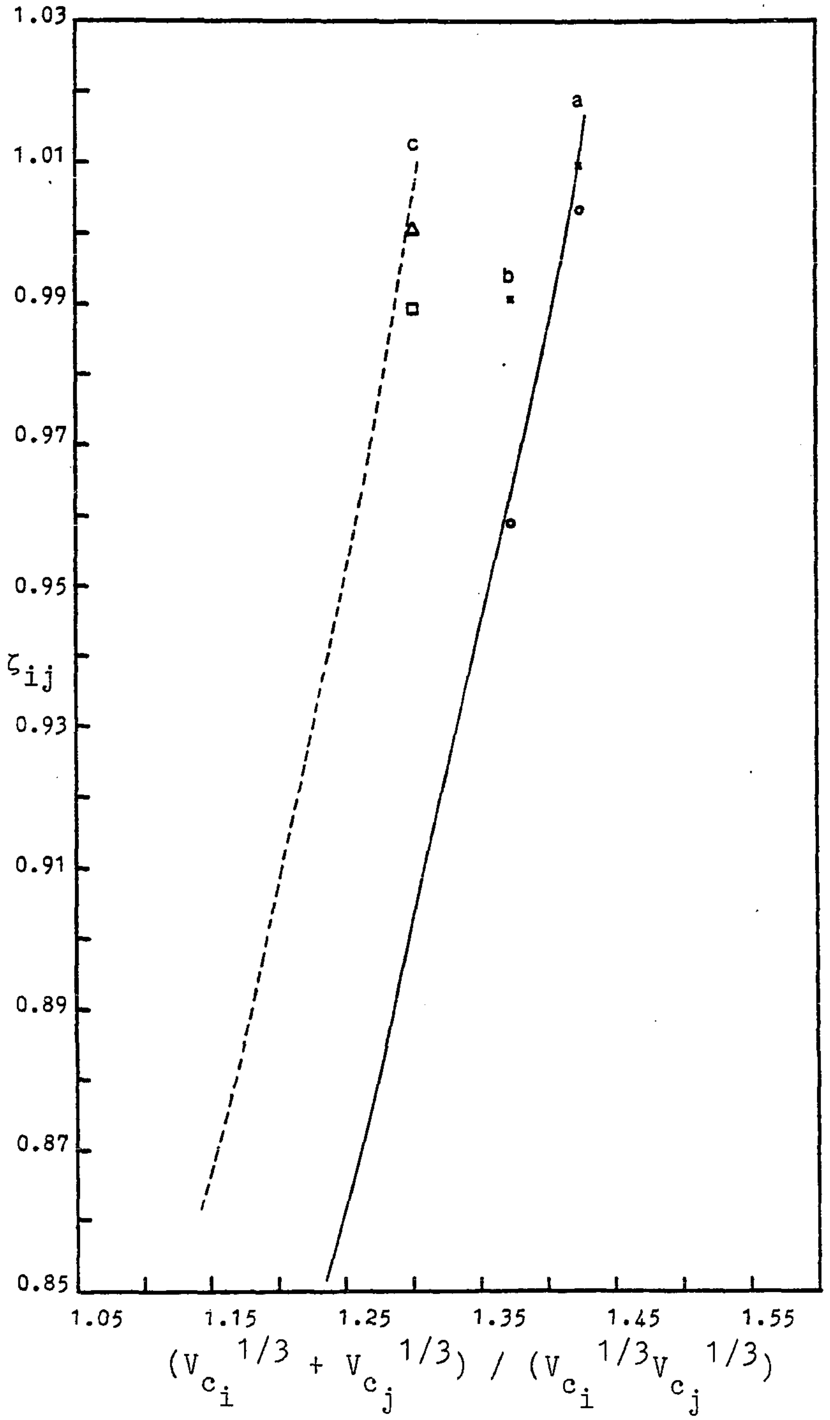


Fig. (VI-4) ζ_{ij} values for ethane- and propane-n-paraffin binaries.

with ethane, propane and isobutane. The optimum values of the constants in Eqs. (VI-3) and (VI-4) for these binaries are presented in Table VI-2. Since these systems are very similar to n-paraffin binaries in chemical nature and molecular size, Eqs. (VI-10) - (VI-12) can be expected to be fairly accurate. This expectation is borne out by the results. The subscripts i's in Eqs. (VI-10) and (VI-11) now refer to isobutane, isopentane and unsaturated hydrocarbon with the least carbon atom number. The overall average absolute deviation for isobutane liquid phase mole fractions predicted using Eqs. (VI-3) - (VI-5) is 5.54%, compared with 2.65% and 1.81%, using Eqs. (VI-10) - (VI-12) and individual binary interaction parameters, respectively (for 67 VLE data points). The isopentane liquid phase mole fraction average absolute deviation is 4.90%, versus 4.40% and 3.35% (for 57 VLE data points). The ethylene liquid phase mole fraction average absolute deviation is 7.52%, versus 28.9% and 7.54% (for 12 VLE data points). The propylene liquid phase mole fraction average absolute deviation is 7.04%, versus 12.10% and 3.48% (for 55 VLE data points). The binaries involving isobutane, isopentane, and propylene show satisfactory agreement for the predicted VLE results obtained using Eqs. (VI-3) - (VI-5) and Eqs. (VI-10) - (VI-12). For the ethylene binaries, only one system, ethane-ethylene, shows poor results for both K-values and phase compositions. The calculated values of binary interaction parameters from Eqs. (VI-13) and (VI-14)

TABLE VI-2

Optimum Values of the Constants in Eq. (VI-3) and (VI-4) for Hydrocarbon and Nonhydrocarbon Binaries

Binary System †	$\sigma_{ij} = (aX^b/Y^c)\sqrt{\sigma_{ii}\sigma_{jj}}$			$\varepsilon_{ij} = (dX^e/Y^f)\sqrt{\varepsilon_{ii}\varepsilon_{jj}}$		
	a	b	c	d	e	f
Isobutane	0.326879	1.465	0.564	0.119433	2.236	0.478
Isopentane	0.616126	1.307	1.148	0.176591	1.998	0.654
Ethylene	0.485957	1.429	1.211	0.328639	2.106	1.769
Propylene	0.333008	1.409	0.507	0.470313	1.40	1.054
CO_2 with Hydrocarbons	0.385675	1.304	0.522	0.446068	1.424	1.364
H_2S with Hydrocarbons and CO_2	0.257337	1.906	0.930	0.290325	1.894	1.270
N_2 with Hydrocarbons, CO_2 and H_2S	0.437184	1.119	0.416	0.352267	1.685	1.373

$X = (V_{c_i}^{1/3} + V_{c_j}^{1/3})$ $\quad$ $Y = (V_{c_i}^{1/3} V_{c_j}^{1/3})$

† Systems are defined in text.

are plotted versus $(V_{c_i}^{1/3} + V_{c_j}^{1/3}) / (V_{c_i} V_{c_j})^{1/3}$ in Figs. (VI-5) - (VI-8) along with individual binary interaction parameters.

6.2 Correlation for Carbon Dioxide with Hydrocarbons

Binaries of carbon dioxide with hydrocarbons studied include carbon dioxide with methane, ethane, propane, *n*-butane, and isobutane, respectively. The optimum constants for Eqs. (VI-3) and (VI-4) are listed in Table VI-2. The overall average absolute deviation for carbon dioxide K-values predicted using Eqs. (VI-3) - (VI-5) for the binaries is 6.91% compared with 6.50% using the individual binary interaction parameters (for 121 VLE data points). Thus, Eqs. (VI-3) - (VI-5) show accuracy of predictions similar to that obtained from the binary parameters. The calculated values of binary interaction parameters from Eqs. (VI-1) and (VI-2) are plotted versus $(V_{c_i}^{1/3} + V_{c_j}^{1/3}) / (V_{c_i} V_{c_j})^{1/3}$ in Figs. (VI-9) and (VI-10) along with individual binary interaction parameters.

6.3 Correlation for Hydrogen Sulfide with Hydrocarbons and Carbon Dioxide

Binaries of hydrogen sulfide with carbon dioxide and hydrocarbons studied include hydrogen sulfide with methane, ethane, propane, isobutane and carbon dioxide. Table VI-2 shows the optimum constants for Eqs. (VI-3) and (VI-4). The overall average absolute deviation for hydrogen sulfide

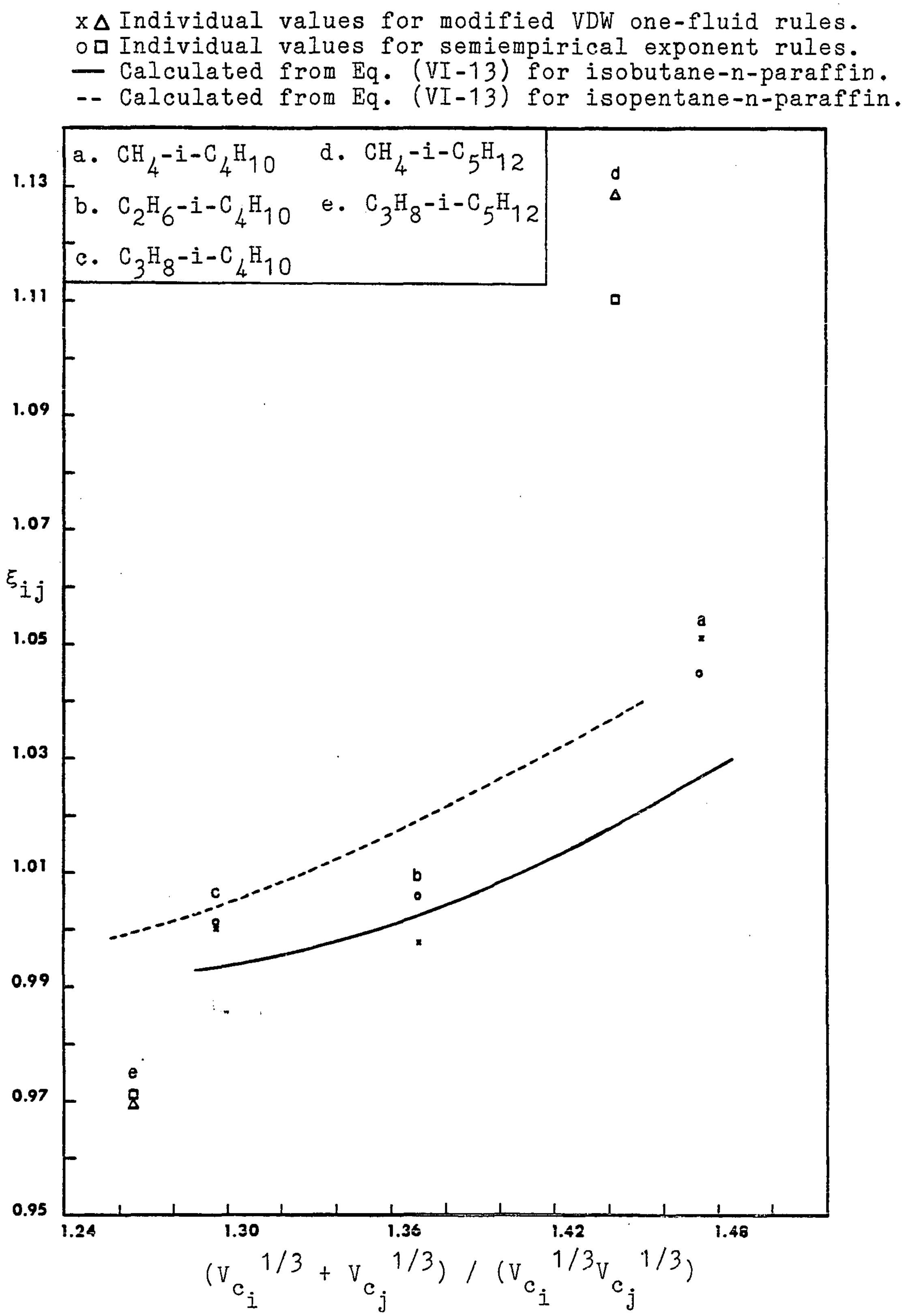


Fig. (VI-5) ξ_{ij} values for isobutane- and isopentane-n-paraffin binaries.

x△ Individual values for modified VDW one-fluid rules.
o□ Individual values for semiempirical exponent rules.
— Calculated from Eq. (VI-14) for isobutane-n-paraffin.
-- Calculated from Eq. (VI-14) for isopentane-n-paraffin.

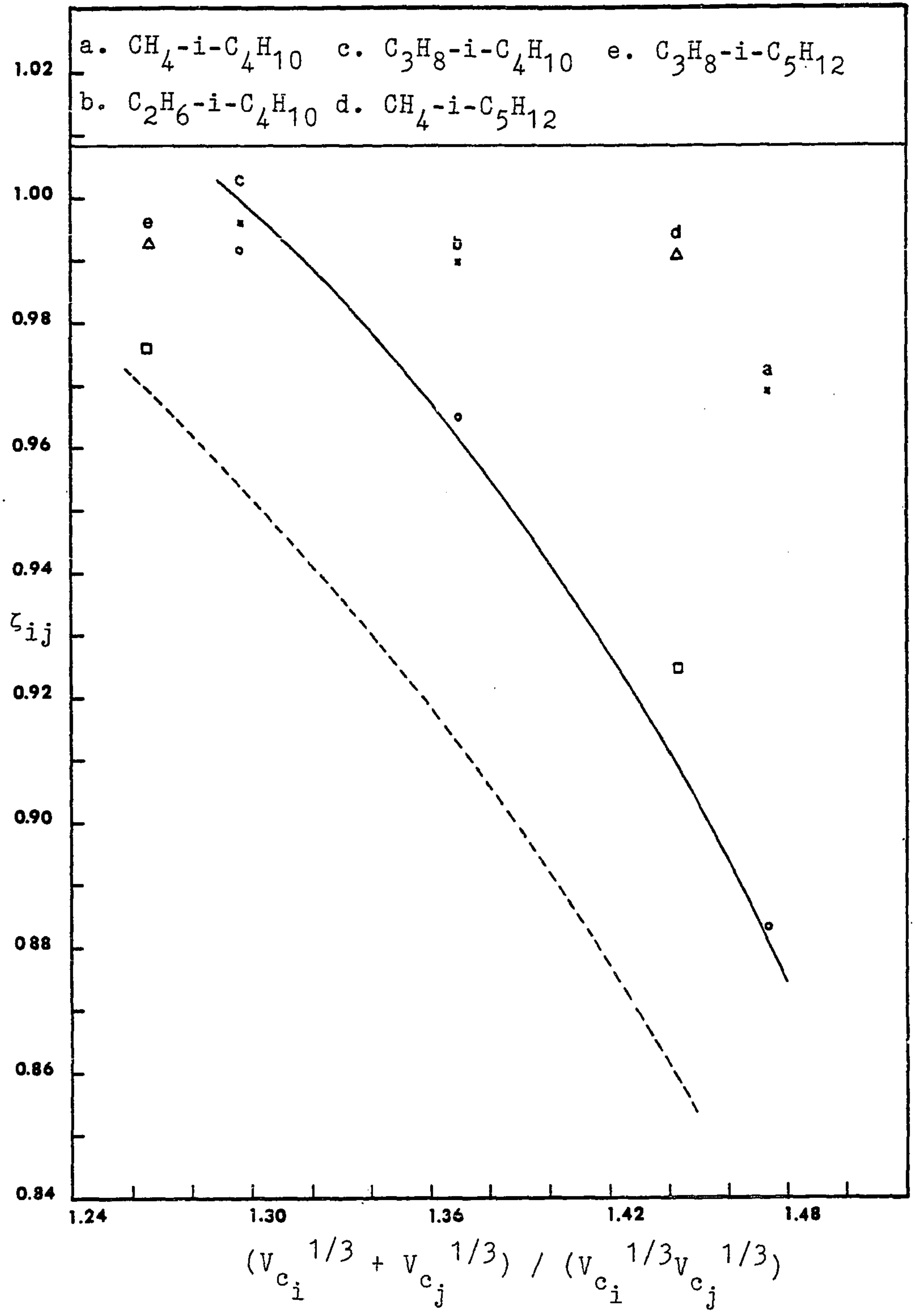


Fig. (VI-6) ζ_{ij} values for isobutane- and isopentane-n-paraffin binaries.

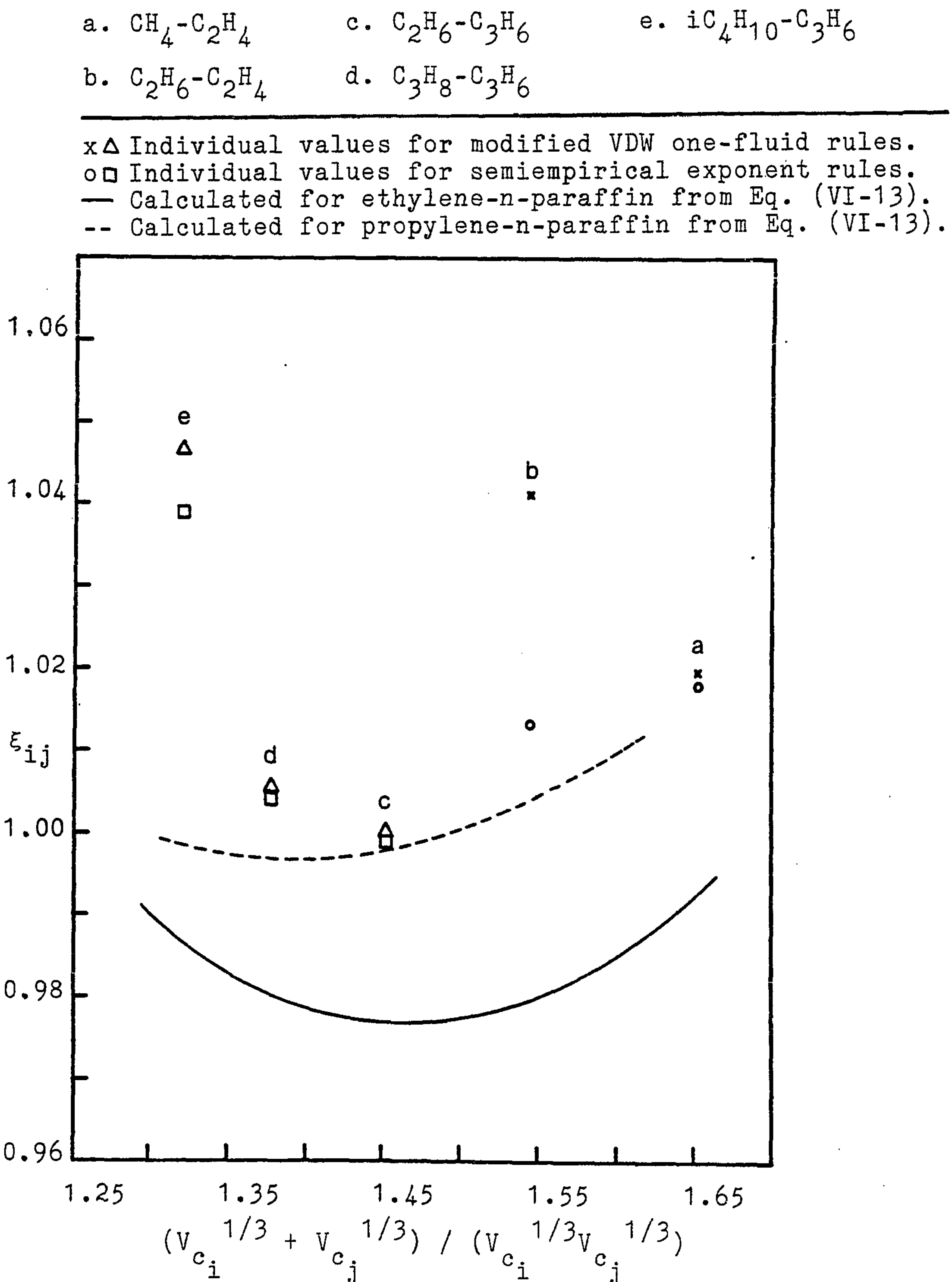


Fig. (VI-7) ξ_{ij} values for ethylene- and propylene-n-paraffin binaries.

a. CH_4-C_2H_4 c. C_2H_6-C_3H_6 e. iC_4H_{10}-C_3H_6

b. C_2H_6-C_2H_4 d. C_3H_8-C_3H_6

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x△ Individual values for modified VDW one-fluid rules.
o□ Individual values for semiempirical exponent rules.
— Calculated for ethylene-n-paraffin from Eq. (VI-14).
-- Calculated for propylene-n-paraffin from Eq. (VI-14).

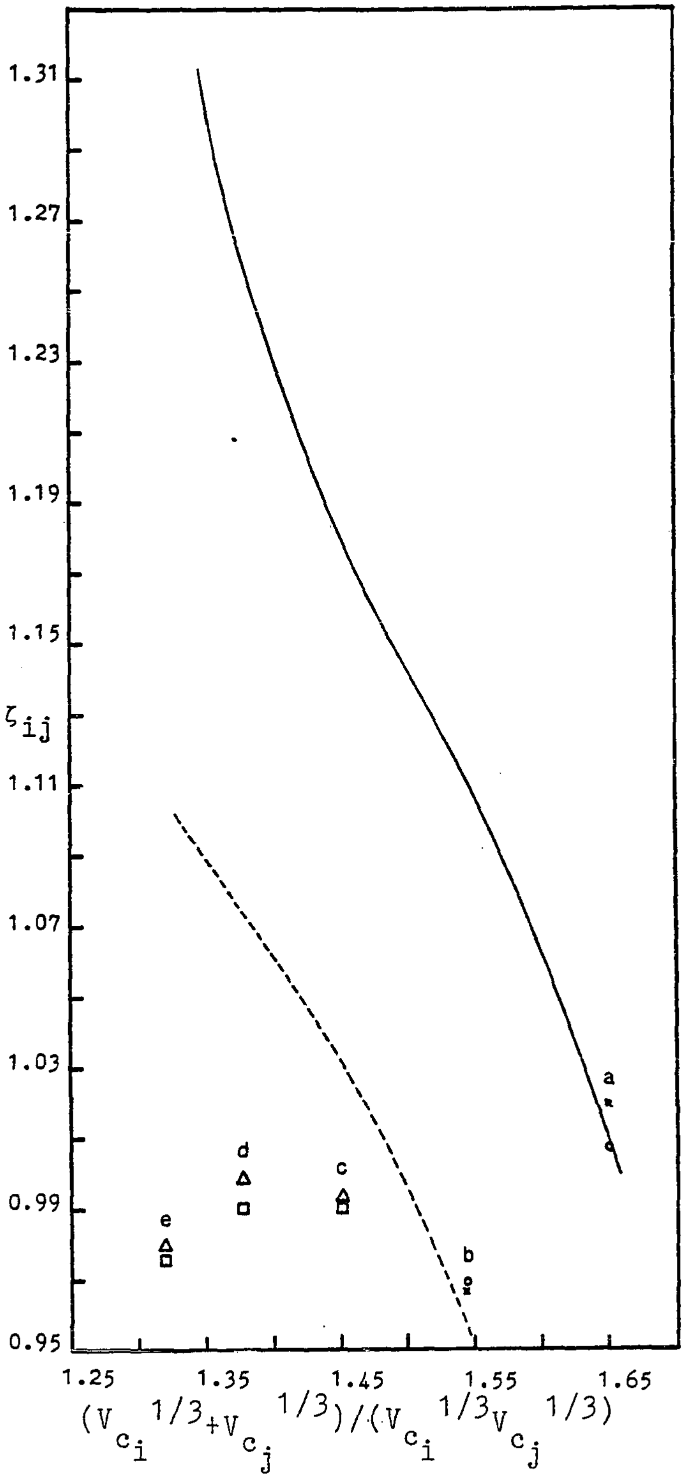

Fig. (VI-8) ζ_{ij} values for ethylene- and propylene-n-paraffin binaries.

a. CH_4-CO_2 c. C_3H_8-CO_2 e. iC_4H_{10}-CO_2

b. C_2H_6-CO_2 d. nC_4H_{10}-CO_2

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x Individual values for modified VDW one-fluid rules.
o Individual values for semiempirical exponent rules.
— Calculated from Eq. (VI-1).

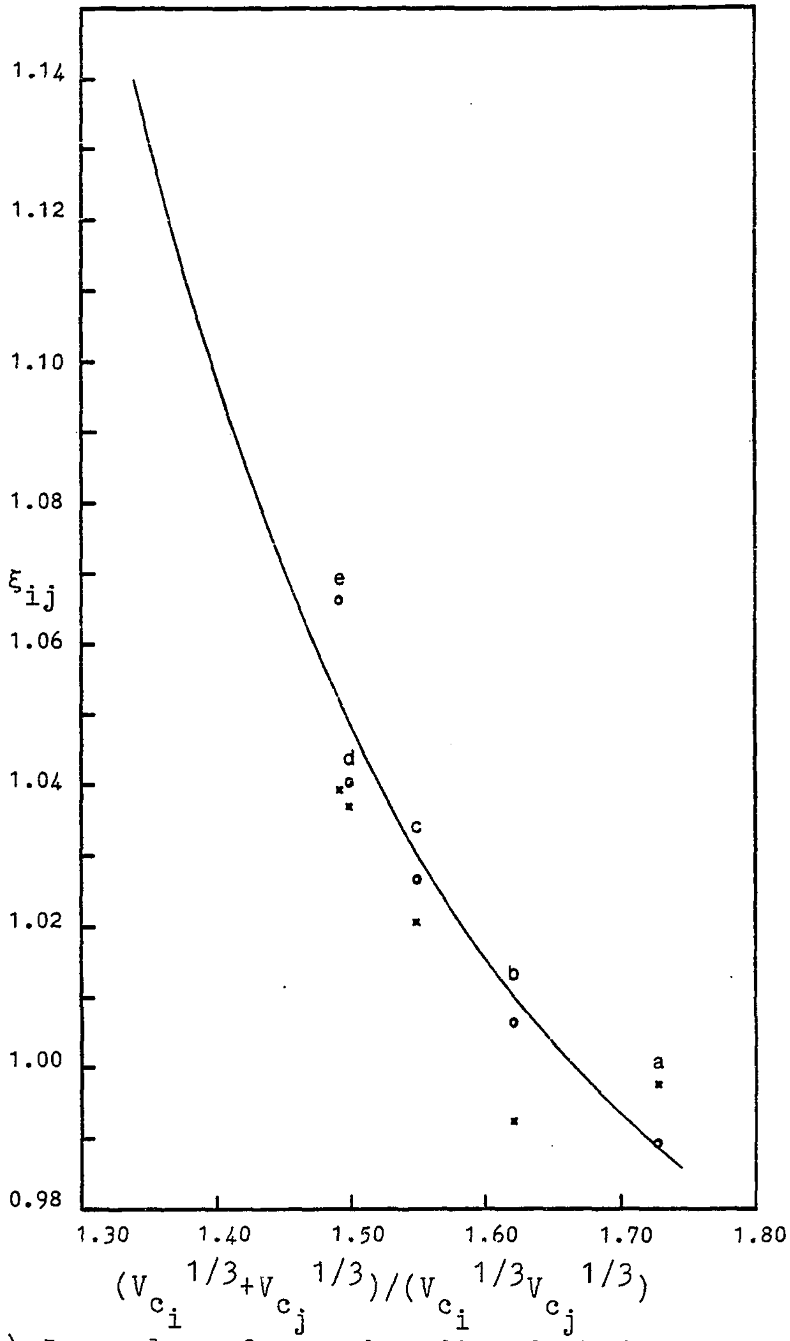

Fig. (VI-9) ξ_{ij} values for carbon dioxide-hydrocarbon binaries.

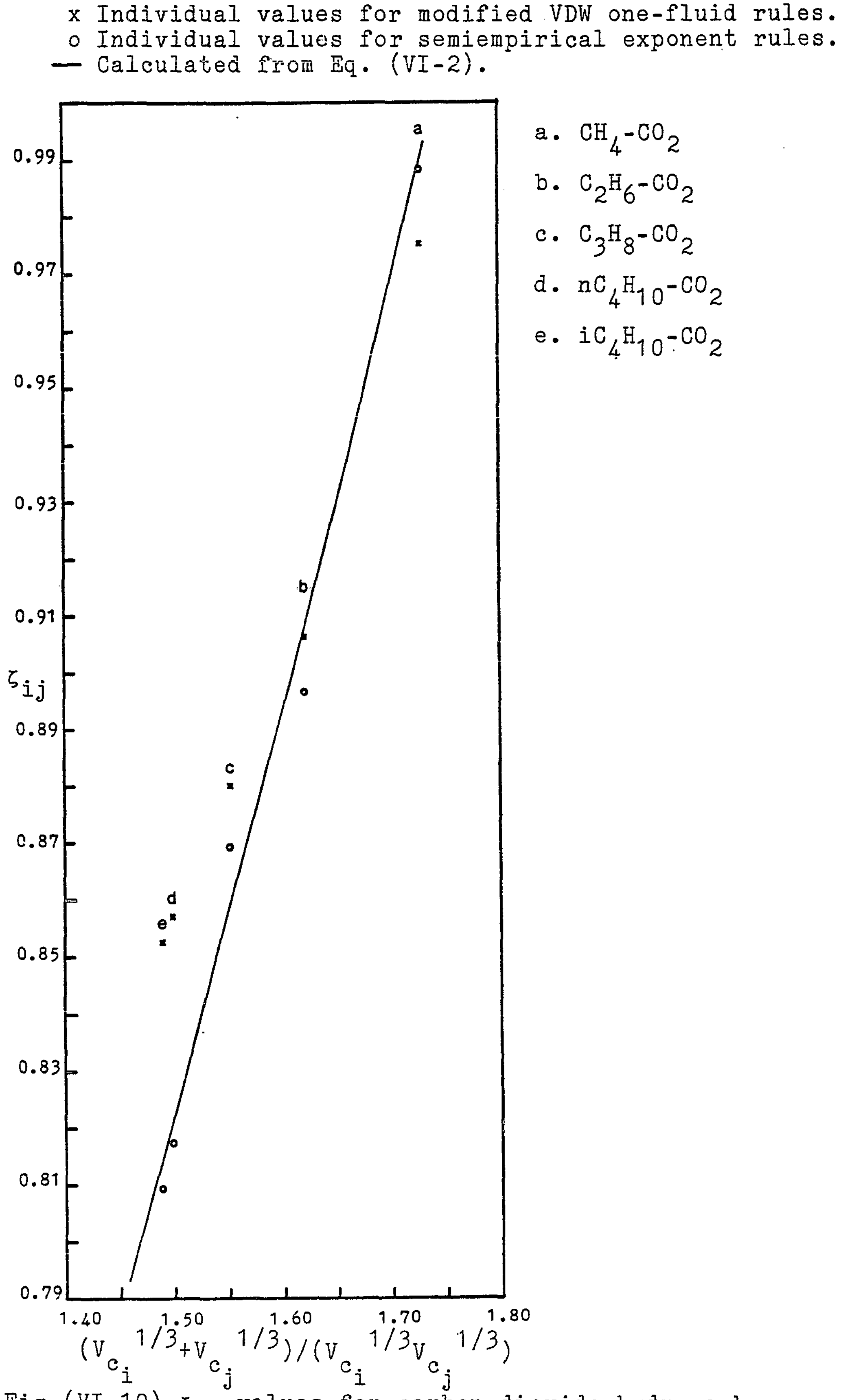

Fig.(VI-10) ζ_{ij} values for carbon dioxide-hydrocarbon binaries.

K-values predicted using Eqs. (VI-3) - (VI-5) for the binaries is 11.83% compared with 5.81% using the individual binary interaction parameters (for 147 VLE data points). Individual binary interaction parameters are plotted versus $(V_{c_i}^{1/3} + V_{c_j}^{1/3}) / (V_{c_i} V_{c_j})^{1/3}$ in Figs. (VI-11)and (VI-12) along with the calculated values of binary interaction parameters from Eqs. (VI-1) and (VI-2).

6.4 Correlation for Nitrogen with Hydrocarbons, Carbon Dioxide and Hydrogen Sulfide

Binaries of nitrogen with carbon dioxide, hydrogen sulfide and hydrocarbons studied include nitrogen with methane, ethane, propane, n-butane, isobutane, carbon dioxide and hydrogen sulfide. The optimum constants for Eqs. (VI-3) and (VI-4) are given in Table VI-2. The overall average absolute deviation of nitrogen K-values predicted using Eqs. (VI-3) - (VI-5) for the binaries is 10.84% compared with 7.69% using the individual binary interaction parameters (for 201 VLE data points). The individual binary interaction parameters are plotted against $(V_{c_i}^{1/3} + V_{c_j}^{1/3}) / (V_{c_i} V_{c_j})^{1/3}$ in Figs. (VI-13) and (VI-14) along with the calculated values of binary interaction parameters from Eqs. (VI-1) and (VI-2).

6.5 Summary

The correlations for the unlike interaction pair parameters σ_{ij}, ε_{ij} and γ_{ij} given in Eqs. (VI-3) - (VI-5)

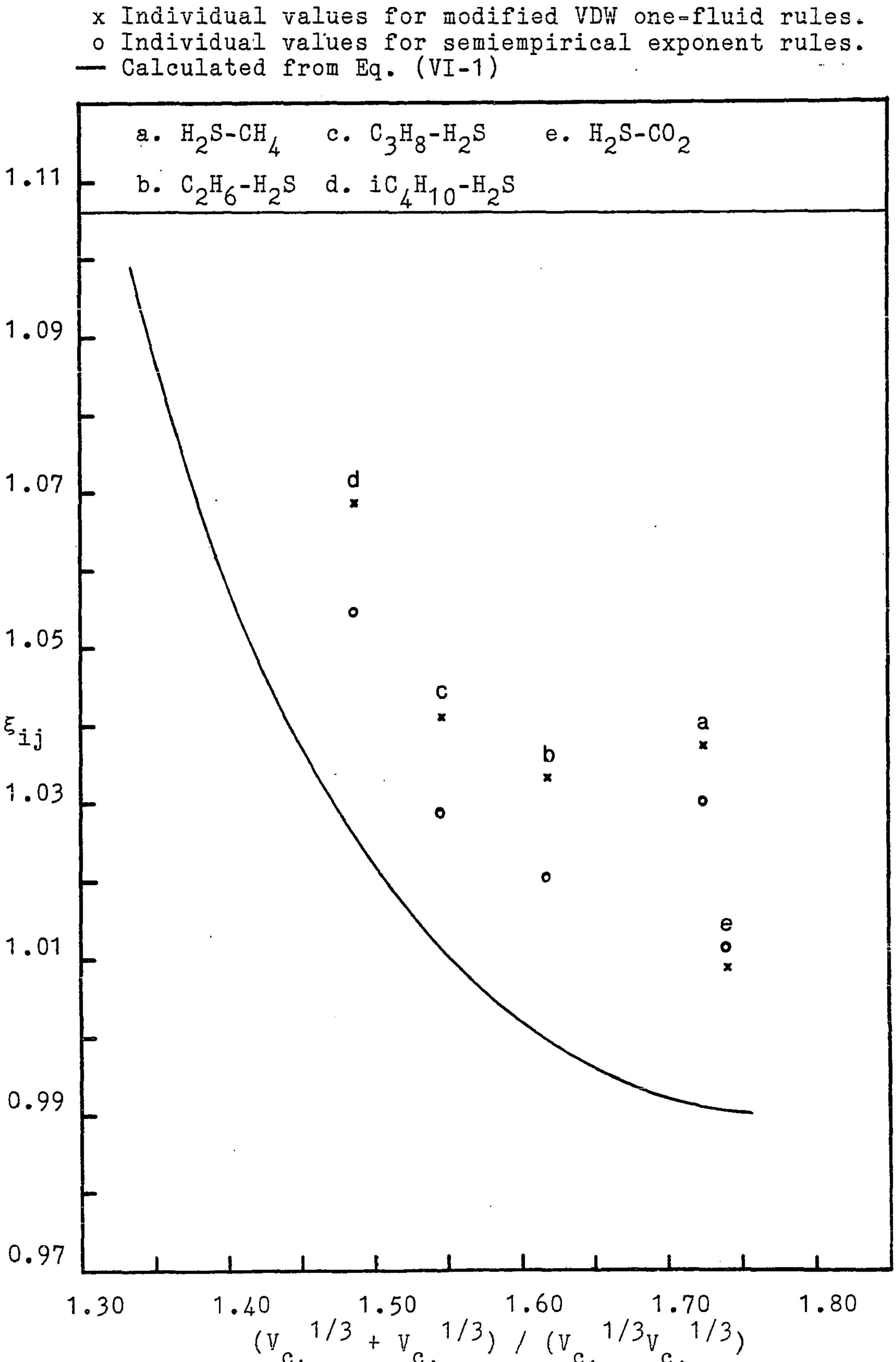

Fig.(VI-11) ξ_{ij} values for hydrogen sulfide-hydrocarbons and -carbon dioxide binaries.

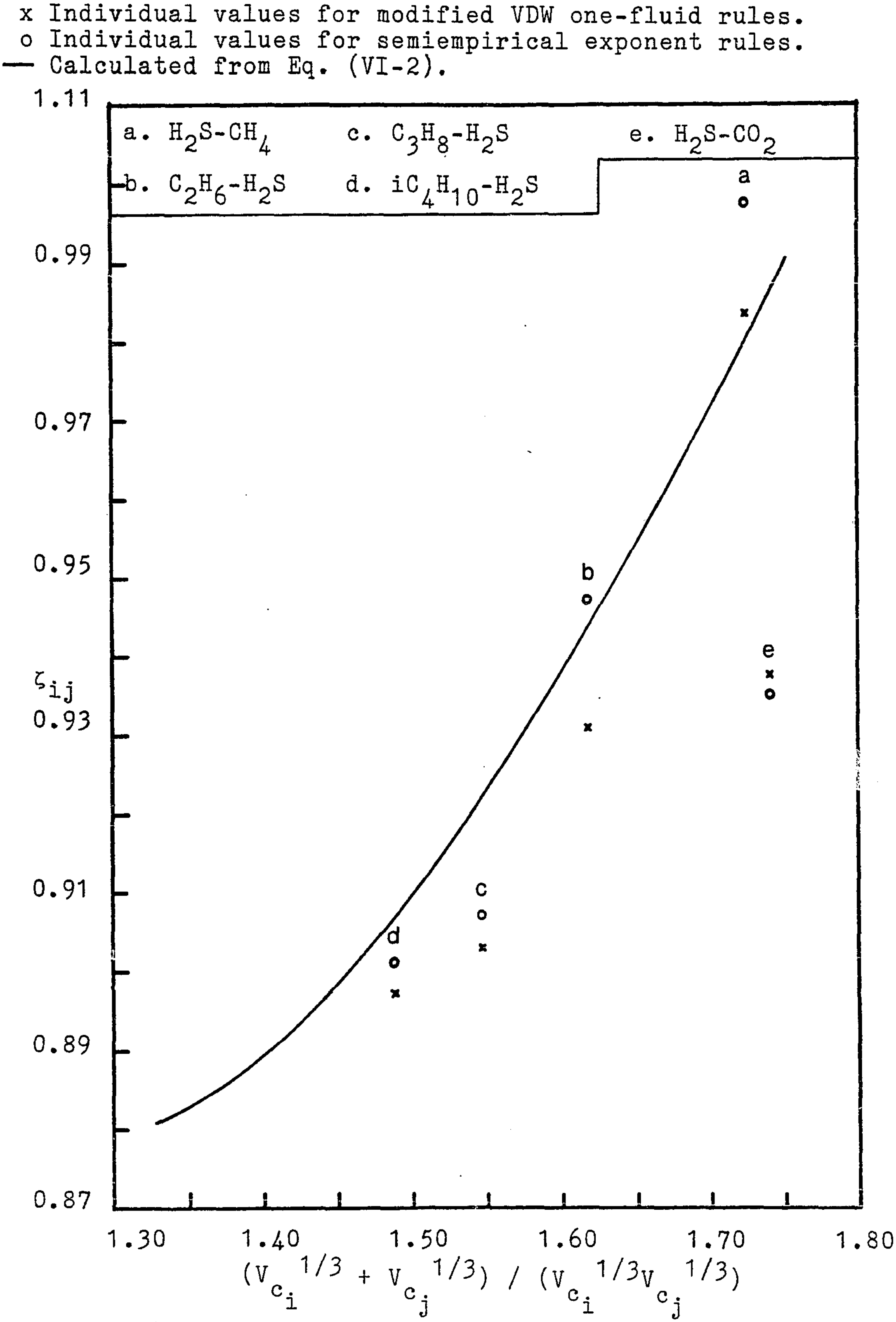

Fig.(VI-12) ζ_{ij} values for hydrogen sulfide-hydrocarbons and -carbon dioxide binaries.

x Individual values for modified VDW one-fluid rules.
o Individual values for semiempirical exponent rules.
— Calculated from Eq. (VI-1).

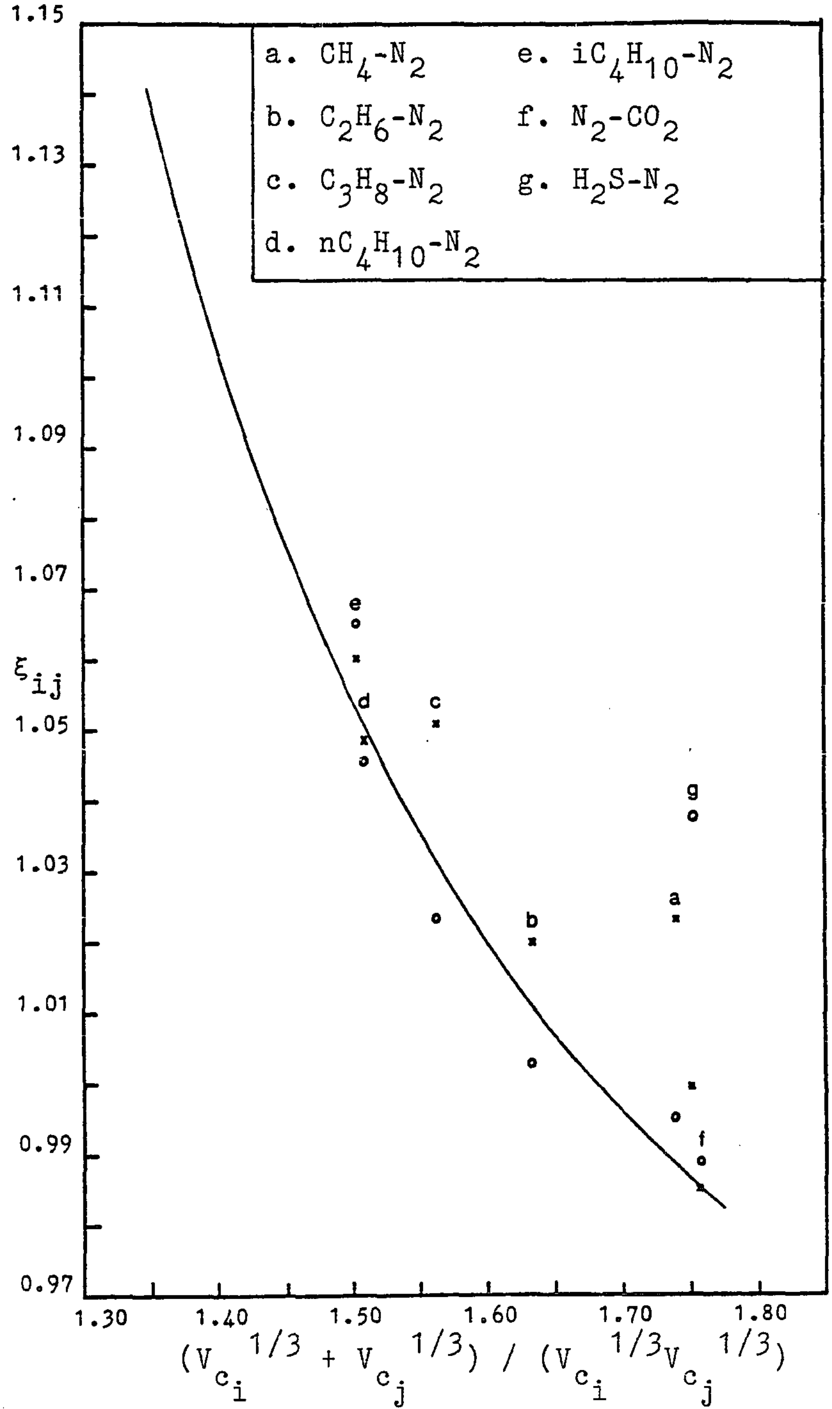

Fig.(VI-13) ξ_{ij} values for nitrogen-hydrocarbons, -carbon dioxide and -hydrogen sulfide binaries.

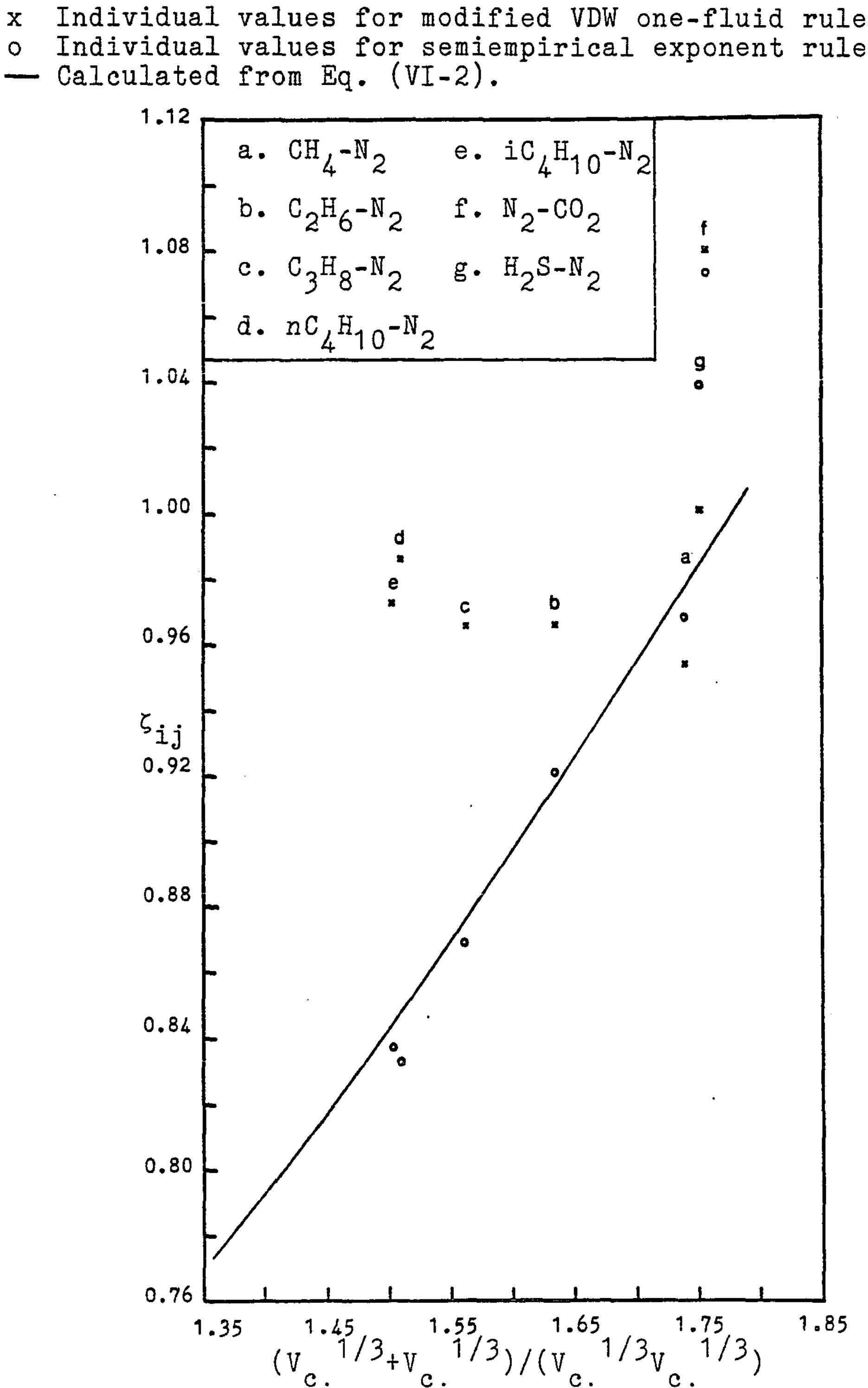

Fig.(VI-14) ζ_{ij} values for nitrogen-hydrocarbons, -carbon dioxide and -hydrogen sulfide binaries.

can be binary fluid pairs involving hydrocarbons, carbon dioxide, hydrogen sulfide and nitrogen. For the hydrocarbons, the six coefficients in Eqs. (VI-3) and (VI-4) have been correlated to yield the expressions for σ_{ij} and ε_{ij} in Eqs. (VI-12) and (VI-13) so that σ_{ij} and ε_{ij} can be estimated for hydrocarbon binary pairs for which there are no data available. For binary pairs involving the nonhydrocarbons, for which binary mixture data are not available, values of the constants in Eqs. (VI-3) and (VI-4) determined from the available data can be used. Predictions of thermodynamic behavior for each fluid studied in this chapter as well as multicomponent systems using the semiempirical exponent mixing rules with unlike interaction parameter correlations are summarized in Chapters VII and VIII along with those obtained using the modified VDW one-fluid and semiempirical exponent mixing rules (both using individual interaction parameters).

CHAPTER VII

COMPARISONS OF PREDICTED BINARY MIXTURE THERMODYNAMIC BEHAVIOR WITH EXPERIMENTAL DATA

Comparison calculations of predicted binary mixture properties and vapor-liquid equilibrium (VLE) with experimental values for 39 binary systems are given in this chapter using the modified VDW one-fluid and the semiempirical exponent mixing rules respectively. Deviations of equilibrium vapor compositions from the experimental values for heavy components are listed as average absolute deviation (AAD) in the mole fractions rather than average absolute percentage deviations because the vapor phase mole fractions of heavy components are so small that percentage uncertainties become very large. The binary interaction parameters used are given in Tables VII-1 and VII-2. For the case of the semiempirical exponent mixing rules, the binary interaction parameters for binary pairs for which data are lacking can be generated from the correlations presented herein for σ_{ij} and ε_{ij} using only the characteristic properties for the pure components with a satisfactory level of accuracy. Tables VII-2 and VII-3 show these generated binary interaction parameters. The systems studied, data types and data ranges utilized in the comparison studies are given in Table VII-4. The results are summarized in Table VII-5.

7.1 Hydrocarbons

7.1.1 n-Paraffins with Methane

Comparisons of predicted and experimental properties for binaries of methane with n-paraffins have already been summarized in Chapter V for both the modified VDW one-fluid and the semiempirical exponent mixing rules using individual values for the unlike interaction parameters, σ_{ij}, ε_{ij}, and γ_{ij}. In this section, the predicted results from both mixing rules using individual values for σ_{ij} and ε_{ij} are compared with results obtained from the semiempirical exponent mixing rules using the correlations developed herein for σ_{ij} and ε_{ij}. The relation for γ_{ij} stays the same as before, as given in Eq. (V-3) with ϕ_{ij} fixed at unity.

For mixtures of light hydrocarbons of similar sizes, such as methane with ethane and propane, both the modified VDW one-fluid and the semiempirical exponent mixing rules yield accurate predictions of bulk properties as well as phase compositions. The overall average absolute deviations of densities, enthalpy departures and methane K-values for the methane binaries using the semiempirical exponent mixing rules are 1.55%, 1.95 Btu/lb and 0.95%, respectively, compared with 1.63%, 2.50 Btu/lb, 1.14% for the modified VDW one-fluid mixing rules, and 1.63%, 2.49 Btu/lb, 3.21% for the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12) for σ_{ij}, ε_{ij} and γ_{ij}. These results exhibit close agreement with experimental data of the two methane binaries for all three formulations. The pressure-composition diagram for the methane-ethane system is shown in Fig. (VII-1) for graphicla comparisons.

As noted earlier in Chapter V, calculations for mixtures of hydrocarbons of dissimilar sizes (methane binaries with n-butane, n-pentane,..., n-decane) have shown significant improvement in VLE predictions using the semiempirical exponent mixing rules instead of the modified VDW one-fluid mixing rules. The overall average absolute deviations of densities and methane K-values for the binaries of methane with n-butane and heavier components up to n-decane using the semiempirical exponent mixing rules are 2.65% and 5.13%, respectively, compared with 2.65% and 13.61% for the modified VDW one-fluid rules, and 2.95% and 9.47% for the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12) for σ_{ij}, ε_{ij} and γ_{ij}. All three formulations predict densities accurately. The overall average absolute deviations of methane mole fractions in the liquid phase in VLE for the methane binaries with the heavy components show results very similar to K-values for each formulation. The average absolute deviations of methane K-values for individual binary systems

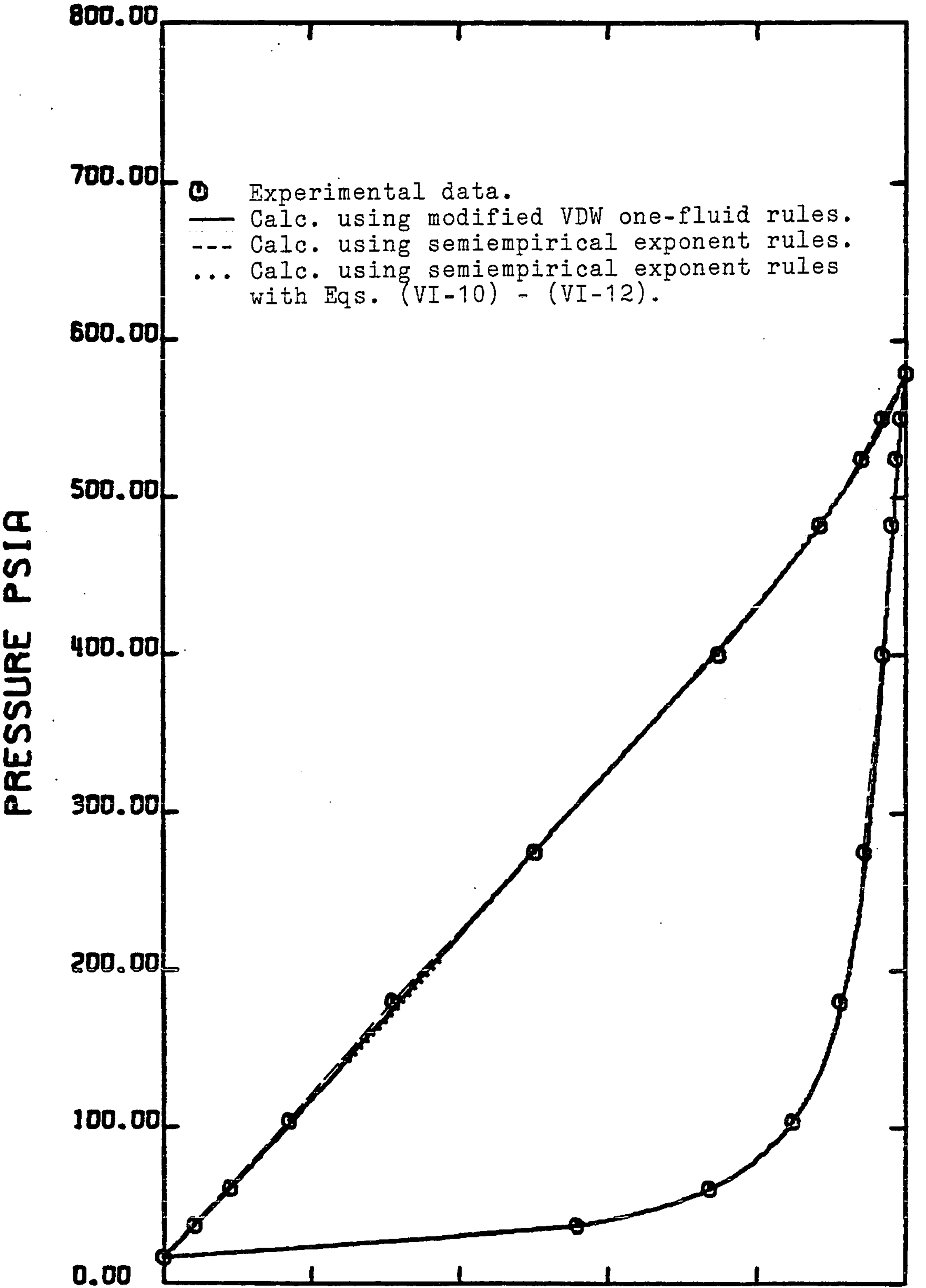

Fig. (VII-1) The P-X diagram of the methane-ethane system at 334.97°R.

range from 2.15% (methane-nonane) to 8.77% (methane-n-heptane) using the semiempirical exponent mixing rules; from 8.10% (methane-n-butane) to 20.5% (methane-n-decane) for the modified VDW one-fluid mixing rules; and from 5.83% (methane-n-hexane) to 11.7% (methane-n-decane) for the semiempirical exponent mixing rules with the correlations for σ_{ij}, ε_{ij} and γ_{ij} used. These results indicate that the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12) for σ_{ij}, ε_{ij} and γ_{ij} yield higher accuracy phase compositions than the modified VDW one-fluid mixing rules. The comparisons of predicted phase compositions for the methane-n-hexane system can be seen on pressure-composition diagram (Fig. VII-2).

7.1.2 Paraffins with Paraffins

The systems studied included ethane with propane and n-butane, propane-n-butane, n-butane-n-decane, isobutane with methane, ethane, and propane, and isopentane with methane and propane. The overall average absolute deviations of densities, enthalpy departures, and K-values of the light components for the ethane, propane, and n-butane binaries using the semiempirical exponent mixing rules are 1.74%, 2.58 Btu/lb and 2.99%, respectively, compared with 1.60%, 2.77 Btu/lb and 2.53% for the modified VDW one-fluid mixing rules, and 3.19%, 3.68 Btu/lb and 3.78% for the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12) for σ_{ij}, ε_{ij}, γ_{ij}. The overall average

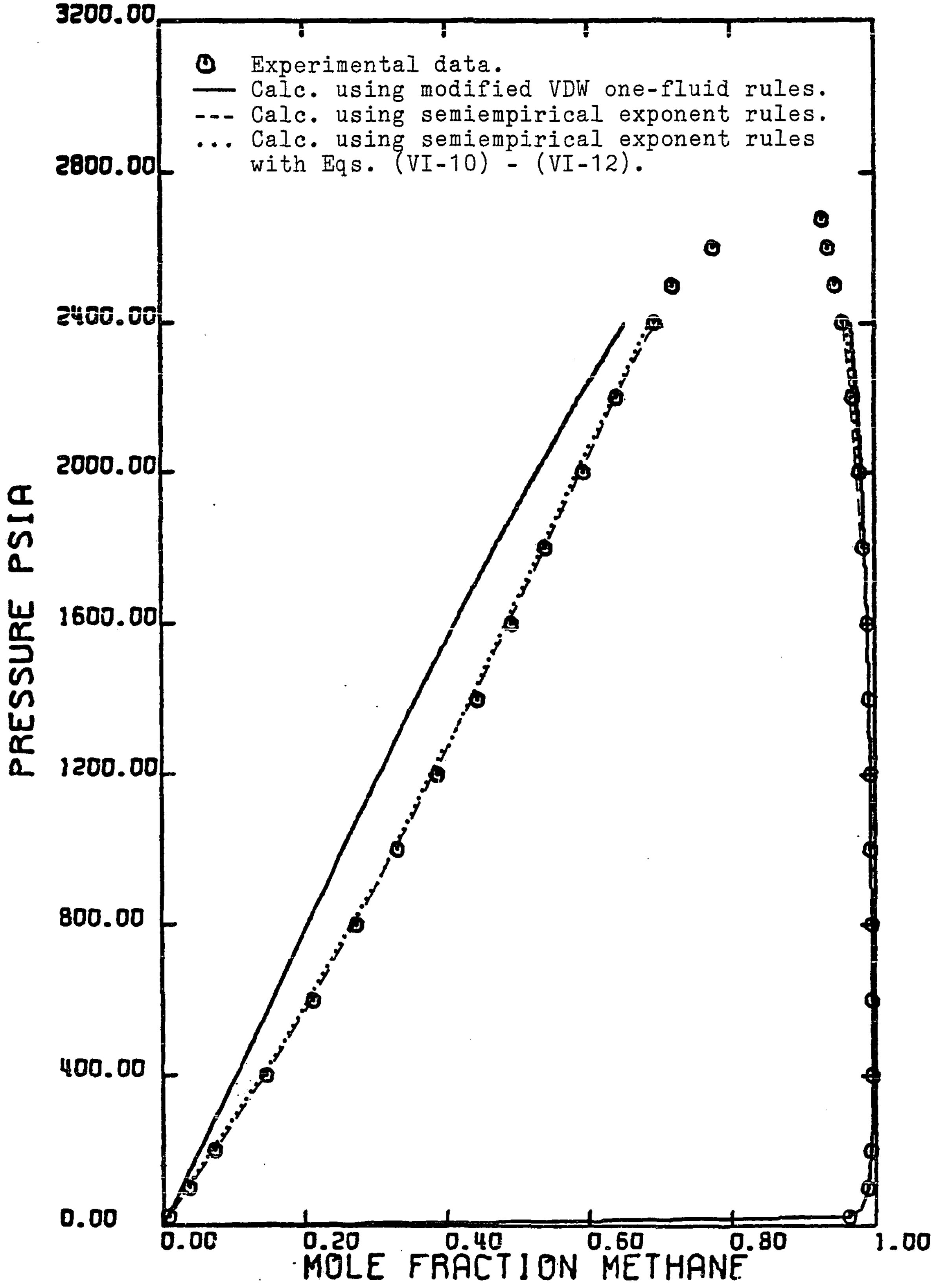

Fig. (VII-2) The P-X diagram of the methane-n-hexane system at 491.69°R.

absolute deviations of densities and K-values (of isobutane and isopentane) for the isobutane and isopentane binaries using the semiempirical exponent mixing rules are 2.78% and 4.27%, respectively, compared with 2.41% and 4.29% for the modified VDW one-fluid mixing rules, and 2.32% and 6.00% for the semiempirical exponent mixing rules with the correlations for σ_{ij}, ε_{ij} and γ_{ij}. Thus, each of the three formulations shows accurate predictions of densities, enthalpy departures, and VLE data.

7.1.3 Paraffins with Unsaturated Hydrocarbons

Ethylene with methane and ethane and propylene with ethane, propane, and isobutane were examined. The overall average absolute deviations of densities and mole fractions of paraffin hydrocarbons in the liquid phase for these five binaries using the semiempirical exponent mixing rules are 0.85% and 1.95%, respectively, compared with 0.84% and 2.06% for the modified VDW one-fluid mixing rules, and 2.12% and 13.2% for the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12) for σ_{ij}, ε_{ij} and γ_{ij}. The overall average absolute deviations of K-values for ethylene and propylene using the semiempirical exponent mixing rules are 2.02%, compared with 2.20% for the modified VDW one-fluid mixing rules, and 10.99% for the semiempirical exponent mixing rules with the correlations for σ_{ij}, ε_{ij} and γ_{ij}. Both the semiempirical exponent and the modified VDW one-fluid mixing rules accurately predict densities as well as VLE. Using the correlations for σ_{ij}, ε_{ij} and γ_{ij} appearing in the semiempirical exponent mixing rules, the overall deviation of the predicted K-values is higher but acceptable for engineering calculations. Poor predictions of ethylene K-values for the ethane-ethylene system increase the overall deviation of the K-values for the five binary systems.

7.2 Nonhydrocarbons with Paraffin Hydrocarbons

For binaries of carbon dioxide with methane, ethane, propane, n-butane and isobutane, the overall average absolute deviations of densities and carbon dioxide K-values using the semiempirical exponent mixing rules are 1.65% and 6.50% respectively compared with 1.22% and 3.06% for the modified VDW one-fluid mixing rules and 1.51% and 6.91% for the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-3) - (VI-5) for σ_{ij}, ε_{ij} and γ_{ij}. The results indicate accurate predictions of densities using all three formulations. For predicted phase compositions, the modified VDW one-fluid mixing rules show better predictions than other two formulations. The average absolute deviations of carbon dioxide K-values range from 3.01% (methane-carbon dioxide) to 9.80% (n-butane-carbon dioxide) using the semiempirical exponent mixing rules; from 1.78% (isobutane-carbon dioxide) to 7.33% (ethane-carbon dioxide) using the modified VDW one-fluid rules; from 3.04% to 10.1% (n-butane-carbon dioxide) using the correlations for σ_{ij} and ε_{ij} in the semiempirical exponent mixing rules. Table VII-5 shows that both the semiempirical exponent mixing rules with the correlations given in Eqs. (VI-3) - (VI-5) for σ_{ij}, ε_{ij} and γ_{ij} and the semiempirical mixing rules with individual σ_{ij}, ε_{ij} and γ_{ij} are satisfactory for prediction of phase compositions for individual binaries of the carbon dioxide systems.

Hydrogen sulfide binaries used in comparison calculations include methane, ethane, propane, and isobutane. The overall average absolute deviations of densities and hydrogen sulfide K-values using the semiempirical exponent mixing rules are 1.87% and 7.23%, respectively, compared with 1.86% and 4.28% for the modified VDW one-fluid mixing rules, and 2.96% and 12.01% for the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-3) - (VI-5), for σ_{ij}, ε_{ij} and γ_{ij}. Densities are accurately predicted using all three formulations. The average absolute deviations of hydrogen sulfide K-values range from 2.23% (hydrogen sulfide-methane) to 11.9% (isobutane-hydrogen sulfide) using the semiempirical exponent mixing rules; from 1.61% (hydrogen sulfide-methane) to 6.94% (propane-hydrogen sulfide) for the modified VDW one-fluid mixing rules; from 2.85% (ethane-hydrogen sulfide) to 16.6% (propane-hydrogen sulfide) for the semiempirical exponent mixing rules using the correlations for σ_{ij}, ε_{ij} and γ_{ij}. Table VII-5 shows that both the modified VDW one-fluid and the semiempirical exponent mixing rules provide reasonably good descriptions of phase compositions for individual binaries involving hydrogen sulfide. On the other hand, the semiempirical exponent mixing rules using the correlations for σ_{ij}, ε_{ij} and γ_{ij} show somewhat poor predictions of phase compositions. Since the K-value deviations for the paraffin hydrocarbons for the hydrogen sulfide binaries range from 4.05% to 9.65%, they are predicted with reasonable accuracy for engineering practice using the semiempirical exponent mixing rules with the correlations for σ_{ij}, ε_{ij} and γ_{ij}.

For binaries of nitrogen with methane, ethane, propane, n-butane and isobutane, the overall average absolute deviations of densities and nitrogen K-values using the semiempirical exponent mixing rules is 2.16% and 7.69%, respectively, compared with 2.23% and 10.99% for the modified VDW one-fluid mixing rules, and 2.25% and 10.84% for the semiempirical exponent mixing rules using the correlations for σ_{ij}, ε_{ij} and γ_{ij}. Density predictions are accurate for all three formulations. For predicted phase compositions, the semiempirical exponent mixing rules show the best predictions. The average absolute deviations of nitrogen K-values range from 3.28% (methane-nitrogen) to 13.6% (n-butane-nitrogen) using the semiempirical exponent mixing rules; from 4.50% (ethane-nitrogen) to 17.7% (propane-nitrogen) for the modified VDW one-fluid mixing rules; from 5.21% (methane-nitrogen) to 14.4% (propane-nitrogen) for the semiempirical mixing rules using the correlations for σ_{ij}, ε_{ij} and γ_{ij}. The results show that the semiempirical exponent mixing rules are satisfactory to predict phase compositions of individual binaries for the nitrogen systems. Both the modified VDW one-fluid mixing rules and the semiempirical exponent mixing rules with the correlations for σ_{ij}, ε_{ij} and γ_{ij} show somewhat poor predictions of phase compositions. However, the semiempirical exponent mixing rules using the correlations for σ_{ij}, ε_{ij} and γ_{ij} can be used for the nitrogen binaries since the accuracy is adequate for engineering calculations.

7.3 Nonhydrocarbons with Nonhydrocarbons

The systems studied involve nonhydrocarbon-nonhydrocarbon binary interactions among nitrogen, carbon dioxide, and hydrogen sulfide. Phase composition predictions in Table VII-5 were analyzed for the hydrogen sulfide-carbon dioxide and hydrogen sulfide-nitrogen systems while density predictions were examined for these systems and the nitrogen-carbon dioxide systems.

Both the semiempirical exponent and modified VDW one-fluid mixing rules show accurate density predictions. The former indicates 1.38 AAD% (nitrogen-carbon dioxide) to 3.04 AAD% (hydrogen sulfide-carbon dioxide) and the latter exhibits 1.23 AAD% (nitrogen-carbon dioxide) to 3.23 AAD% (hydrogen sulfide-carbon dioxide). The semiempirical exponent mixing rules using the correlations given in Eqs. (VI-3) - (VI-5) for σ_{ij}, ε_{ij} and γ_{ij} show less accurate densities for the mixtures containing carbon dioxide, with 11.2 AAD% for the hydrogen sulfide-carbon dioxide system and 5.61 AAD% for the nitrogen-carbon dioxide system.

For vapor-liquid equilibrium predictions, the semiempirical exponent mixing rules show deviations ranging from 1.58 AAD% for hydrogen sulfide K-values in the hydrogen sulfide-carbon dioxide system to 14.0 AAD% for hydrogen sulfide K-values in the hydrogen sulfide-nitrogen system; the modified VDW one-fluid mixing rules exhibit from 1.55 AAD% for hydrogen sulfide K-values in the hydrogen sulfide-carbon dioxide system to 24.90 AAD% for nitrogen K-values in the hydrogen sulfide-nitrogen system; the semiempirical exponent mixing rules with the correlations used for σ_{ij}, ε_{ij} and γ_{ij} yield deviations from 4.20 AAD% for hydrogen sulfide K-values in the hydrogen sulfide-carbon dioxide system to 24.6 AAD% for carbon dioxide K-values in the hydrogen sulfide-carbon dioxide system. Both the semiempirical exponent and modified VDW one-fluid mixing rules show similar accuracy for VLE predictions for the hydrogen sulfide-carbon dioxide system. For the hydrogen sulfide-nitrogen system, the semiempirical exponent mixing rules predict more accurate nitrogen K-values (12.3 AAD%) than the modified VDW one-fluid mixing rules (24.9 AAD%) but yield poorer predictions for hydrogen sulfide K-values (14.0 AAD% compared with 4.64 AAD%).

Using the semiempirical exponent mixing rules with the correlations for σ_{ij}, ε_{ij} and γ_{ij} employed, carbon dioxide K-values and nitrogen K-values are poorly predicted (24.6 AAD%

and 23.3 AAD%, respectively) while the hydrogen sulfide K-values of 4.20 AAD% to 5.43 AAD% are acceptable. These results suggest that the correlations for σ_{ij} and ε_{ij} developed herein should be used only as rough guides for the values of the unlike interaction parameters for nonhydrocarbon-nonhydrocarbon pairs.

TABLE VII-1

Binary Interaction Parameters*(84) for Use with the Modified VDW One-Fluid Mixing Rules

		C_2	C_3	nC_4	iC_4	nC_5	iC_5	nC_6	nC_7	nC_8	nC_9	nC_{10}	CO_2	H_2S	N_2	$C_2=$	$C_3=$
C_1	ξ	0.999079	1.02116	1.03946	1.05117	1.05214	1.1285	1.07738	1.08744	(1.094)	1.09674	1.11940	0.997963	1.01746	1.02347	1.01959	(0.990)
	ζ	0.996010	0.974404	0.958079	0.968823	0.936798	0.9907	0.920368	0.921744	(0.933)	0.937876	0.978290	0.974942	0.983624	0.955616	1.01923	(0.97)
C_2	ξ		0.986756	0.982901	0.997931	(1.000)	(1.001)	(1.0055)	(1.011)	(1.015)	(1.0175)	(1.0205)	0.992456	1.01379	1.02059	1.04127	1.00025
	ζ		1.00960	0.990839	0.989809	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	0.906294	0.931330	0.967085	0.969139	0.993943
C_3	ξ			0.991834	1.00074	[1.0]	0.969682	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	1.02162	1.02112	1.05083	[1.0]	1.00561
	ζ			1.00073	0.995525	[1.0]	0.992158	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	0.880238	0.903190	0.965661	[1.0]	0.998592
nC_4	ξ				[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	1.01605	1.03705	(1.048)	1.04839	[1.0]	[1.0]
	ζ				[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	0.93770	0.857607	(0.885)	0.985565	[1.0]	[1.0]
iC_4	ξ					[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	1.03987	1.04838	1.06007	[1.0]	1.04661
	ζ					[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	0.852854	0.897313	0.973348	[1.0]	0.979696
nC_5	ξ						[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	(1.050)	(1.076)	(1.069)	[1.0]	[1.0]
	ζ						[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	(0.841)	(0.855)	(0.991)	[1.0]	[1.0]
iC_5	ξ							[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	(1.051)	(1.080)	(1.071)	[1.0]	[1.0]
	ζ							[1.0]	[1.0]	[1.0]	[1.0]	[1.0]	(0.857)	(0.883)	(0.981)	[1.0]	[1.0]
nC_6	ξ								[1.0]	[1.0]	[1.0]	[1.0]	(1.061)	(1.105)	(1.084)	[1.0]	[1.0]
	ζ								[1.0]	[1.0]	[1.0]	[1.0]	(0.827)	(0.856)	(1.004)	[1.0]	[1.0]
nC_7	ξ									[1.0]	[1.0]	[1.0]	(1.075)	(1.126)	(1.097)	[1.0]	[1.0]
	ζ									[1.0]	[1.0]	[1.0]	(0.817)	(0.848)	(1.011)	[1.0]	[1.0]
nC_8	ξ										[1.0]	[1.0]	(1.086)	(1.147)	(1.108)	[1.0]	[1.0]
	ζ										[1.0]	[1.0]	(0.808)	(0.840)	(1.018)	[1.0]	[1.0]
nC_9	ξ											[1.0]	(1.096)	(1.162)	(1.118)	[1.0]	[1.0]
	ζ											[1.0]	(0.801)	(0.834)	(1.024)	[1.0]	[1.0]
nC_{10}	ξ												(1.104)	(1.176)	[1.0]	[1.0]	[1.0]
	ζ												(0.786)	(0.830)	[1.0]	[1.0]	[1.0]
CO_2	ξ													0.988689	0.985340	[1.0]	[1.0]
	ζ													0.937529	1.08098	[1.0]	[1.0]
H_2S	ξ														0.99919	[1.0]	[1.0]
	ζ														1.00111	[1.0]	[1.0]
N_2	ξ															[1.0]	[1.0]
	ζ															[1.0]	[1.0]
$C_2=$	ξ																[1.0]
	ζ																[1.0]
$C_3=$	ξ																
	ζ																

*The numbers in ( ) are estimated values.

Those in [ ] are suggested values to be used with caution.

TABLE VII-2

Binary Interaction Parameters* for Use with the Semiempirical Exponent Mixing Rules

		C_2	C_3	nC_4	nC_5	nC_6	nC_7	nC_8	nC_9	nC_{10}	iC_4	iC_5	$C_2^=$	$C_3^=$	CO_2	H_2S	N_2
C_1	ξ	1.00087	1.01188	1.02559	1.03220	1.04925	1.05967	(1.06997)	1.07753	1.08519	1.04495	1.11080	1.01803	(1.00816)	0.989815	1.01068	0.995042
	ζ	0.978262	0.936840	0.899345	0.860984	0.837207	0.819753	(0.801687)	0.79909	0.790355	0.883598	0.924655	1.00865	(0.941209)	0.988937	0.997639	0.968058
C_2	ξ		0.989889	0.986861	(1.01130)	(1.02019)	(1.02873)	(1.03707)	(1.04453)	(1.05193)	1.00600	(1.0108)	1.01373	0.998941	1.00646	1.00002	1.00370
	ζ		1.00348	0.958857	(0.933581)	(0.906967)	(0.885169)	(0.866552)	(0.851695)	(0.838307)	0.964358	(0.935202)	0.978118	0.990189	0.89641	0.947827	0.92058
C_3	ξ			1.00465	(1.00019)	(1.00736)	(1.01439)	(1.02135)	(1.02764)	(1.03393)	1.00170	0.971767	(0.977379)	1.00524	1.02608	1.00862	1.02381
	ζ			0.989819	(0.968026)	(0.938706)	(0.914695)	(0.894187)	(0.877819)	(0.863075)	0.991294	0.975854	(1.16630)	0.990497	0.86959	0.906652	0.869638
C_4	ξ				(0.993117)	(0.998941)	(1.00477)	(1.01064)	(1.01601)	1.00066	(0.988247)	(0.992803)	(0.977427)	(0.980636)	1.04024	[1.00348]	1.04581
	ζ				(0.988370)	(0.957002)	(0.931318)	(0.909382)	(0.891879)	0.901652	(1.02165)	(0.990281)	(1.20058)	(1.10413)	0.817053	[0.909249]	0.833806
nC_5	ξ					(0.994097)	(0.998881)	(1.00388)	(1.00850)	(1.01322)	(0.985469)	(0.989021)	(0.979328)	(0.980206)	[1.06030]	[1.01643]	[1.06853]
	ζ					(0.991847)	(0.964202)	(0.940595)	(0.921756)	(0.904786)	(1.06144)	(1.02767)	(1.25415)	(1.15026)	[0.794459]	[0.900065]	[0.828121]
nC_6	ξ						(0.995164)	(0.999433)	(1.00344)	(1.00758)	(0.984361)	(0.987067)	(0.982156)	(0.981069)	[1.08240]	[1.02996]	[1.08454]
	ζ						(0.995760)	(0.970591)	(0.950508)	(0.932416)	(1.09945)	(1.06343)	(1.30503)	(1.19418)	[0.772375]	[0.893749]	[0.812121]
nC_7	ξ							(0.996615)	(1.00010)	(1.00373)	(0.984412)	(0.986394)	(0.985620)	(0.981828)	[1.09748]	[1.04157]	[1.09940]
	ζ							(0.991201)	(0.970117)	(0.951125)	(1.12650)	(1.08868)	(1.34246)	(1.22600)	[0.754324]	[0.889317]	[0.799273]
nC_8	ξ								(0.998248)	(1.00144)	(0.985599)	(0.986928)	(0.989873)	(0.985547)	[1.11193]	[1.05384]	[1.11355]
	ζ								(0.994531)	(0.974575)	(1.15889)	(1.11914)	(1.38597)	(1.26350)	[0.738932]	[0.886150]	[0.788511]
nC_9	ξ									(1.00000)	(0.987057)	(0.987843)	(0.993895)	(0.980282)	[1.12465]	[1.06490]	[1.12595]
	ζ									(0.992505)	(1.18416)	(1.14281)	(1.42037)	(1.29296)	[0.726663]	[0.884096]	[0.780076]
nC_{10}	ξ										(0.984544)	(0.985328)	(0.991364)	(0.985766)	[1.13715]	[1.07596]	[1.13807]
	ζ										(1.21848)	(1.175941)	(1.46154)	(1.33044)	[0.715625]	[0.882628]	[0.772609]
iC_4	ξ											(0.996709)	(0.982160)	1.03957	1.06617	1.03452	1.06542
	ζ											(0.956837)	(1.16126)	0.977922	0.809988	0.901115	0.83894
iC_5	ξ												(0.980451)	(0.981447)	[1.06539]	[1.01573]	[1.06763]
	ζ												(1.20991)	(1.10183)	[0.795805]	[0.900478]	[0.829107]
$C_2^=$	ξ													(0.990924)	[0.999962]	[0.974458]	[1.00019]
	ζ													(1.08050)	[0.944769]	[0.959678]	[0.942479]
$C_3^=$	ξ														[1.02299]	[0.986223]	[1.02454]
	ζ														[0.876269]	[0.929741]	[0.889440]
CO_2	ξ															0.991906	0.988814
	ζ															0.934872	1.07311
H_2S	ξ																1.03781
	ζ																1.03972
N_2	ξ																
	ζ																

*The values in ( ) are generated from the unlike interaction parameter correlations given in Eqs. (VI-10) - (VI-12).

Those in [ ] are generated from the unlike interaction parameter correlations given in Eqs. (VI-3) - (VI-5).

TABLE VII-3*

Estimated Binary Interaction Parameters**

Components (1) (2)	ξ_{12}	ζ_{12}
$CH_4-C_2H_6$	0.999753	0.976663
$CH_4-C_3H_8$	1.01284	0.924594
CH_4-n-C_4H_{10}	1.02565	0.886754
CH_4-n-C_5H_{12}	1.03768	0.858308
CH_4-n-C_6H_{14}	1.04899	0.835827
CH_4-n-C_7H_{16}	1.05967	0.817415
CH_4-n-C_9H_{20}	1.07909	0.789136
CH_4-n-$C_{10}H_{22}$	1.08808	0.777827
$C_2H_6-C_3H_8$	0.992562	1.01207
C_2H_6-n-C_4H_{10}	1.00206	0.967259
C_3H_8-n-C_4H_{10}	0.992936	1.00513
n-C_4H_{10}-n-$C_{10}H_{22}$	1.02142	0.876107
CH_4-i-C_4H_{10}	1.02745	0.882154
C_2H_6-i-C_4H_{10}	1.00341	0.961811
C_3H_8-i-C_4H_{10}	0.993986	0.999134
CH_4-i-C_5H_{12}	1.03705	0.859679
C_3H_8-i-C_5H_{12}	0.999792	0.969813
$CH_4-C_2H_4$	0.993481	1.01019

TABLE VII-3*

(Continued)

Components (1) (2)	ξ_{12}	ζ_{12}
C_2H_6-C_2H_4	0.979521	1.11346
C_2H_6-C_3H_6	0.989223	1.03174
C_3H_8-C_3H_6	0.983465	1.07621
iC_4H_{10}-C_3H_6	0.985016	1.06749
CH_4-CO_2	0.989159	0.989601
C_2H_6-CO_2	1.01002	0.911431
C_3H_8-CO_2	1.03004	0.859826
n-C_4H_{10}-CO_2	1.04894	0.822463
i-C_4H_{10}-CO_2	1.05154	0.817930
H_2S-CH_4	0.971047	0.980905
C_2H_6-H_2S	0.979027	0.944669
C_3H_8-H_2S	0.990596	0.923143
i-C_4H_{10}-H_2S	1.00536	0.907684
H_2S-CO_2	0.970572	0.986874
CH_4-N_2	0.988300	0.977760
C_2H_6-N_2	1.01095	0.916516
C_3H_8-N_2	1.03183	0.876907
n-C_4H_{10}-N_2	1.05110	0.848793
i-C_4H_{10}-N_2	1.05373	0.845421

TABLE VII-3*

(Continued)

Components (1) (2)	ξ_{12}	ζ_{12}
N_2-CO_2	0.985493	0.987451
H_2S-N_2	0.986008	0.985627

*This table lists only the binary mixtures whose predicted properties have been compared herein in Chapter VII.

**The estimated values are obtained from the correlations in Chapter VI (the corresponding individual values are shown in Table VII-2).

TABLE VII-4

Data Used for Comparison of Predicted Properties for Study of Mixing Rules and Unlike Interaction Parameter Correlations

(ρ=Density, H-H^{o}=Enthalpy Departure, VLE=Vapor-Liquid Equilibrium)

System Components	Property	Data Points	Temperature Range (°F)	Pressure Range psia	Ref.
CH_4-C_2H_6	ρ	92	70~ 250	200~ 3000	75
	VLE	73	-225~-100	28~ 719	92
CH_4-C_2H_4	ρ	90	77~ 167	153~11998	43
CH_4-C_3H_8	ρ	76	-238~ 32	500~ 5000	75
	H-H^{o}	84	-250~ 250	500~ 2000	83
	VLE	51	-175~ -75	26~ 708	92
CH_4-nC_4H_{10}	ρ	55	70~ 130	40~10000	75
	VLE	67	-160~ 50	20~ 1597	33
CH_4-iC_4H_{10}	ρ	67	100~ 220	80~ 1600	52
	VLE	31	100~ 220	200~ 1600	52
CH_4-nC_5H_{12}	ρ	64	100~ 400	200~ 5000	74
	VLE	39	-142~ 32	50~ 2000	74
CH_4-iC_5H_{12}	ρ	41	126~ 329	200~ 1400	2
	VLE	19	160~ 280	400~ 1000	2

TABLE VII-4

(Continued)

System Components	Property	Data Points	Temperature Range (°F)	Pressure Range psia	Ref.
CH_4-nC_6H_{14}	VLE	33	-117~ 32	25~ 2550	12
CH_4-nC_7H_{16}	ρ	40	40~ 460	304~ 9984	60
	VLE	41	-100~ 0	100~ 2250	11
CH_4-nC_9H_{20}	ρ	62	-58~ 302	147~ 2646	78
	VLE	32	32 302	294 1764	78
CH_4-n$C_{10}H_{22}$	ρ	43	100~ 460	1000~ 9000	58
	VLE	44	100~ 460	100~ 4000	58
C_2H_6-C_2H_4	VLE	12	-424~-211	36~ 249	26
C_2H_6-C_3H_8	$H-H^o$	46	-240~ 240	250~ 2000	54
	VLE	11	-40~ -40	20~ 101	24
C_2H_6-C_3H_6	ρ	50	10~ 400	600~ 9000	49
	VLE	23	10~ 160	100~ 722	49
C_2H_6-nC_4H_{10}	ρ	49	62~ 272	75~ 625	36
	VLE	19	150~ 250	470~ 805	50
C_2H_6-iC_4H_{10}	ρ	65	100~ 249	155~ 779	6
	VLE	25	100~ 220	155~ 693	6

TABLE VII-4

(Continued)

System Components	Property	Data Points	Temperature Range (°F)	Pressure Range psia	Ref.
C_3H_8-C_3H_6	ρ	50	10~ 400	150~5000	59
	VLE	17	10~ 100	52~ 206	59
C_3H_8-nC_4H_{10}	ρ	80	163~ 289	225~ 600	35
	VLE	19	194~ 248	300~ 550	35
C_3H_8-iC_4H_{10}	ρ	10	60~ 130	48~ 242	34
	VLE	11	152~ 152	176~ 332	29
C_3H_8-iC_5H_{12}	ρ	50	77~ 572	73~1176	90
	VLE	38	32~ 338	15~ 588	90
nC_4H_{10}-$nC_{10}H_{22}$	ρ	100	100~ 460	400~9000	62
iC_4H_{10}-C_3H_6	VLE	15	124~ 217	197~399	18
CH_4-N_2	ρ	45	-283~ 392	11~4813	39,32
	$H-H^o$	50	-250~ 250	250~2000	83
	VLE	34	-255~-130	50~ 676	86
C_2H_6-N_2	ρ	50	40~ 460	200~8000	63
	VLE	34	-210~-110	50~1415	86

TABLE VII-4

(Continued)

System Components	Property	Data Points	Temperature Range (°F)	Pressure Range psia	Ref.
C_3H_8-N_2	ρ	50	257~ 300	92~ 3792	76
	VLE	41	-202~ 176	200~ 2000	91
nC_4H_{10}-N_2	ρ	50	310~ 400	484~ 9997	16
	VLE	23	100~ 280	236~ 2594	1,66
iC_4H_{10}-N_2	VLE	22	50~ 250	82~ 2462	70
N_2-CO_2	ρ	97	32~ 59	351~ 2105	4
CH_4-CO_2	ρ	66	32~ 59	351~ 2106	3
	VLE	22	-65~ 29	215~ 1108	15
C_2H_6-CO_2	ρ	128	-25~ 460	15~10000	57,25
	VLE	14	-60~ 20	102~ 409	19
C_3H_8-CO_2	ρ	116	40~ 460	200~10000	61
	VLE	28	40~ 160	200~ 800	61
nC_4H_{10}-CO_2	ρ	123	100~ 460	200~10000	4
	VLE	40	100~ 280	60~ 1000	51
iC_4H_{10}-CO_2	VLE	17	100~ 220	105~ 908	6

TABLE VII-4

(Continued)

System Components	Property	Data Points	Temperature Range (°F)	Pressure Range psia	Ref.
H_2S-CH_4	ρ	82	40~ 340	200~10000	73
	VLE	41	40~ 160	200~ 1750	73
$C_2H_6-H_2S$	ρ	49	39~ 181	250~ 1100	37
	VLE	11	-100~ 50	14~ 300	71
$C_3H_8-H_2S$	ρ	36	70~ 160	218~ 779	38
	VLE	36	-68~ 160	20~ 400	8
$iC_4H_{10}-H_2S$	ρ	50	40~ 160	30~ 742	68
	VLE	22	40~ 220	57~ 701	68
H_2S-CO_2	ρ	76	33~ 192	294~ 1176	7
	VLE	37	-40~ 190	100~ 1200	81
H_2S-N_2	ρ	50	2~ 160	495~ 3003	68
	VLE	47	2~ 120	495~ 3003	68
$CH_4-C_2H_6-C_3H_8$	VLE	33	-176~ -76	32~ 800	92
$CH_4-CO_2-H_2S$	VLE	12	-59~ 100	300~ 1200	67, 28
$CH_4-C_2H_6-C_3H_8-nC_4H_{10}$	VLE	2	-60~ -60	204~ 288	14

TABLE VII-4

(Continued)

System Components	Property	Data Points	Temperature Range (^oF)	Pressure Range psia	Ref.
CH_4-C_2H_6-C_3H_8-iC_4H_{10}	VLE	1	20~ 20	200~ 200	14
CH_4-C_2H_6-C_3H_8-nC_5H_{12}-nC_6H_{14}-$nC_{10}H_{22}$	VLE	5	150~ 250	100~3000	89
N_2-CH_4-CO_2-C_2H_6-H_2S-C_3H_8	VLE	7	-125~ -50	398~ 999	69

TABLE VII-5

Summary of Comparisons of Predicted and Experimental Thermodynamic Behavior for Binary Mixtures Using Different Mixing Rules

(Mixing Rules Indices:
1=Modified VDW One-Fluid Rules with Individual Binary Interaction Parameters
2=Semiempirical Exponent Rules with Individual Binary Interaction Parameters
3=Semiempirical Exponent Rules Using the Correlations in Eqs. (VI-10)-(VI-12)
4=Semiempirical Exponent Rules Using the Correlations in Eqs. (VI-3)-(VI-5))

Components (1) (2)	Mixing Rules Index	Density AAD%	Enthalpy AAD Btu/lb	K Values		Equilibrium Compositions			
				K_1 AAD%	K_2 AAD%	x_1 AAD%	x_2 AAD%	y_1 AAD%	y_2 AAD
CH_4-C_2H_6	1	2.20		1.14	8.60	1.06	3.45	0.28	0.0026
	2	1.99		1.02	8.50	0.95	3.17	0.28	0.0026
	3	2.03		1.37	8.29	1.19	3.51	0.26	0.0024
CH_4-C_2H_4	1	0.80							
	2	0.83							
	3	0.95							
CH_4-C_3H_8	1	0.94	2.50	1.14	19.5	1.44	4.17	0.18	0.0018
	2	1.02	1.95	0.84	19.8	0.93	3.19	0.18	0.0018
	3	1.15	2.49	5.84	19.2	5.17	5.85	0.17	0.0016
CH_4-nC_4H_{10}	1	2.65		8.10	10.5	7.89	5.88	0.16	0.0013
	2	2.12		4.01	10.4	3.99	4.48	1.19	0.0016
	3	2.42		10.6	11.6	8.98	6.83	0.19	0.0016

TABLE VII-5

(Continued)

Components (1) (2)	Mixing Rules Index	Density AAD%	Enthalpy AAD Btu/lb	K Values K_1 AAD%	K_2 AAD%	Equilibrium Compositions x_1 AAD%	x_2 AAD%	y_1 AAD%	y_2 AAD
CH_4-iC_4H_{10}	1	1.85		3.12	4.48	1.77	0.57	3.19	0.0153
	2	2.08		2.95	4.51	2.15	0.50	3.39	0.0157
	3	1.24		5.38	10.9	5.96	1.78	5.70	0.0307
CH_4-nC_5H_{12}	1	2.12		9.61	29.4	9.23	5.78	0.20	0.0019
	2	1.49		4.58	31.8	4.64	2.82	0.28	0.0027
	3	1.76		9.02	24.7	8.35	5.35	0.21	0.0019
CH_4-iC_5H_{12}	1	2.61		15.6	8.25	16.3	2.56	3.52	0.0233
	2	3.16		17.0	8.78	17.4	2.76	3.26	0.0228
	3	1.70		20.1	7.69	26.3	2.87	2.49	0.0173
CH_4-nC_6H_{14}	1			17.9	20.7	16.0	6.95	0.15	0.0014
	2			5.97	19.5	6.91	3.44	0.20	0.0018
	3			5.83	20.6	6.59	2.93	0.20	0.0019
CH_4-nC_7H_{16}	1	3.57		13.6	75.8	17.4	6.05	0.06	0.0006
	2	3.07		8.77	61.5	10.1	4.84	0.06	0.0006
	3	3.09		9.09	60.5	10.2	4.89	0.06	0.0006
CH_4-nC_9H_{20}	1	1.41		16.1	*	14.8	4.36	0.18	*
	2	2.55		2.15	*	2.19	0.66	0.21	*
	3	2.87		8.81	*	8.05	2.78	0.21	*

TABLE VII-5

(Continued)

Components (1) (2)	Mixing Rules Index	Density AAD%	Enthalpy AAD Btu/lb	K Values		Equilibrium Compositions			
				K_1 AAD%	K_2 AAD%	x_1 AAD%	x_2 AAD%	y_1 AAD%	y_2 AAD
CH_4-$nC_{10}H_{22}$	1	4.34		20.5	18.9	17.2	10.9	1.40	0.0108
	2	5.41		5.45	19.0	4.17	4.74	1.57	0.0123
	3	5.97		11.7	17.6	9.36	7.24	1.57	0.0123
C_2H_6-C_2H_4	1			0.74	3.05	1.37	8.26	1.41	0.0098
	2			0.57	2.32	1.34	7.54	1.65	0.0104
	3			10.8	29.9	7.20	28.9	16.9	0.0857
C_2H_6-C_3H_8	1		2.77	2.55	3.08	2.62	2.43	2.60	0.0109
	2		2.58	2.85	3.35	2.37	2.24	2.52	0.0104
	3		3.68	5.90	6.10	5.95	2.76	2.64	0.0128
C_2H_6-C_3H_6	1	1.04		2.13	1.38	1.37	1.35	2.50	0.0069
	2	1.06		2.20	1.34	1.36	1.22	2.41	0.0065
	3	2.44		10.2	6.25	23.6	10.7	10.1	0.0428
C_2H_6-nC_4H_{10}	1	1.88		3.37	6.06	2.07	1.50	3.05	0.0174
	2	1.40		3.95	5.87	2.97	2.49	2.66	0.0150
	3	0.80		3.38	1.63	7.11	5.47	3.68	0.0206
C_2H_6-iC_4H_{10}	1	3.44		2.37	2.00	3.53	2.65	1.74	0.0064
	2	4.16		2.73	1.67	4.31	2.27	2.02	0.0077
	3	4.44		2.79	1.79	4.26	3.19	2.02	0.0082

TABLE VII-5

(Continued)

Components (1) (2)	Mixing Rules Index	Density AAD%	Enthalpy AAD Btu/lb	K Values		Equilibrium Compositions			
				K_1 AAD%	K_2 AAD%	x_1 AAD%	x_2 AAD%	y_1 AAD%	y_2 AAD
C_3H_8-C_3H_6	1	0.70		0.38	0.69	1.67	2.13	1.43	0.0070
	2	0.70		0.40	0.65	1.40	1.78	1.21	0.0056
	3	3.92		15.5	7.02	3.96	5.80	13.3	0.0624
C_3H_8-nC_4H_{10}	1	2.54		1.68	1.13	1.19	1.31	1.86	0.0076
	2	3.20		2.12	1.88	1.04	1.32	2.40	0.0101
	3	5.03		2.95	1.32	7.18	3.66	3.73	0.0152
C_3H_8-iC_4H_{10}	1	0.84		3.15	4.14	1.95	4.44	3.28	0.0156
	2	1.01		3.11	4.15	1.95	4.47	3.28	0.0156
	3	0.72		2.28	4.08	3.38	3.85	5.07	0.0223
C_3H_8-iC_5H_{12}	1	1.91		3.17	3.71	2.73	2.94	1.00	0.0057
	2	1.95		4.14	3.58	4.31	5.22	1.41	0.0073
	3	1.83		5.17	4.48	5.75	3.59	2.31	0.0113
nC_4H_{10}-$nC_{10}H_{22}$	1	0.70							
		0.75							
		2.90							
iC_4H_{10}-C_3H_6	1			4.63	4.48	4.13	9.19	6.03	0.0237
	2			4.65	4.37	3.95	8.87	5.85	0.0231
	3			7.38	15.6	12.5	21.4	12.8	0.0395

TABLE VII-5

(Continued)

Components (1) (2)	Mixing Rules Index	Density AAD%	Enthalpy AAD Btu/lb	K Values		Equilibrium Compositions			
				K_1 AAD%	K_2 AAD%	x_1 AAD%	x_2 AAD%	y_1 AAD%	y_2 AAD
CH_4-N_2	1	3.25	0.76	2.00	5.77	4.57	6.41	5.31	0.0048
	2	3.69	0.92	4.49	3.28	3.12	6.06	6.44	0.0117
	4	3.87	1.06	5.72	5.21	3.52	10.5	8.10	0.0519
C_2H_6-N_2	1	2.39		17.6	4.50	0.60	3.91	18.1	0.0078
	2	1.85		22.8	7.45	0.87	8.90	23.5	0.0103
	4	2.06		21.2	9.77	1.09	8.13	20.7	0.0090
C_3H_8-N_2	1	2.29		14.2	17.7	1.59	12.9	19.7	0.0157
	2	2.31		13.8	7.56	0.74	6.45	20.9	0.0215
	4	2.31		11.7	14.4	1.14	9.67	18.7	0.0176
nC_4H_{10}-N_2	1	1.09		18.7	15.0	2.24	13.8	19.5	0.0459
	2	0.95		18.0	13.6	1.83	12.1	18.7	0.0444
	4	0.93		15.8	13.5	1.92	12.6	16.6	0.0408
iC_4H_{10}-N_2	1			4.55	12.4	1.24	11.4	3.85	0.0118
	2			5.47	8.94	0.82	6.69	5.05	0.0110
	4			5.90	11.8	1.72	18.7	5.48	0.0212
N_2-CO_2	1	1.23							
	2	1.38							
	4	5.61							

TABLE VII-5

(Continued)

Components (1) (2)	Mixing Rules Index	Density AAD%	Enthalpy AAD Btu/lb	K Values		Equilibrium Compositions			
				K_1 AAD%	K_2 AAD%	x_1 AAD%	x_2 AAD%	y_1 AAD%	y_2 AAD
CH_4-CO_2	1	1.18		7.67	2.79	6.31	1.51	1.98	0.0082
	2	1.24		7.12	3.01	5.29	1.29	2.77	0.0107
	4	1.26		7.01	3.04	5.37	1.31	2.86	0.0110
C_2H_6-CO_2	1	1.86		3.87	7.33	3.14	14.5	6.37	0.0426
	2	2.65		4.24	6.08	3.80	18.8	7.27	0.0489
	4	1.53		4.32	8.24	7.43	33.1	10.10	0.0667
C_3H_8-CO_2	1	0.99		1.78	1.98	0.95	2.06	1.44	0.0036
	2	0.78		5.08	6.69	3.63	11.7	6.63	0.0239
	4	0.97		4.30	5.07	4.21	8.72	5.92	0.0188
nC_4H_{10}-CO_2	1	0.78		1.47	3.02	0.47	3.35	1.72	0.0059
	2	1.66		2.49	9.80	2.30	13.6	3.56	0.0114
	4	2.12		3.20	10.1	2.85	14.4	4.83	0.0155
iC_4H_{10}-CO_2	1			3.34	1.78	0.85	3.05	3.19	0.0116
	2			7.43	3.28	2.86	7.34	8.75	0.0308
	4			6.69	6.36	3.66	12.8	7.81	0.0307
H_2S-CH_4	1	0.97		1.61	7.46	0.78	6.99	1.20	0.0066
	2	1.04		2.23	10.2	1.06	8.25	1.48	0.0078
	4	2.35		9.65	15.3	2.11	10.2	8.45	0.0321

TABLE VII-5

(Continued)

Components (1) (2)	Mixing Rules Index	Density AAD%	Enthalpy AAD Btu/lb	K Values		Equilibrium Compositions			
				K_1 AAD%	K_2 AAD%	x_1 AAD%	x_2 AAD%	y_1 AAD%	y_2 AAD
C_2H_6-H_2S	1	2.10		2.35	3.19	5.28	0.36	5.03	0.0163
	2	2.67		2.45	3.23	4.80	0.31	5.01	0.0163
	4	4.43		7.40	2.85	7.33	0.74	5.01	0.0157
C_3H_8-H_2S	1	2.24		3.41	6.94	3.42	13.4	6.01	0.0257
	2	1.93		4.07	11.3	5.35	26.3	7.57	0.0351
	4	2.47		4.05	16.6	9.39	42.4	10.8	0.0511
iC_4H_{10}-H_2S	1	2.81		4.75	5.47	2.57	5.76	5.04	0.0120
	2	2.41		7.54	11.9	6.41	19.8	8.21	0.0190
	4	2.86		7.66	13.5	7.26	23.5	9.59	0.0233
H_2S-CO_2	1	3.23		1.55	7.57	1.70	13.5	2.33	0.0119
	2	3.04		1.58	8.35	1.84	15.3	2.53	0.0129
	4	11.20		4.20	24.6	11.3	70.6	13.9	0.0646
H_2S-N_2	1	3.22		4.64	24.9	1.41	34.9	4.75	0.0165
	2	2.69		14.0	12.3	0.58	12.2	14.2	0.0258
	4	3.53		5.43	23.3	1.46	36.2	6.02	0.0218

* Vapor compositions not measured for a number of points

CHAPTER VIII

COMPARISONS OF PREDICTED MULTICOMPONENT MIXTURE THERMODYNAMIC BEHAVIOR WITH EXPERIMENTAL DATA

The different mixing rules also were applied to calculate the thermodynamic properties of multicomponent systems. Predicted results are given in Tables V-3, V-4 and VIII-1 - VIII-3. The results for one ternary system (methane-ethane-propane) and two quarternary systems (methane-ethane-propane-n-butane and methane-ethane-propane-isobutane) have already been shown in Tables V-3 and V-4 in Chapter V. The individual binary interaction parameters were available for each binary pair of components in the three multicomponent systems. Therefore, comparisons of predicted vapor-liquid equilibrium for these multicomponent systems can be made on an equal basis among the different mixing rules. Tables V-3 and V-4 show clearly that the semiempirical exponent mixing rules give better accuracy of predictions for most phase compositions than either the modified VDW one-fluid mixing rules or the semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12) for σ_{ij}, ε_{ij} and γ_{ij}.

Although the semiempirical exponent mixing rules using the correlations for σ_{ij}, ε_{ij} and γ_{ij} are inferior to the modified VDW one-fluid mixing rules for the predicted phase compositions of the ternary and quarternary systems, their predicted results are reasonably accurate.

Tables VIII-1 through VIII-3 summarize results for one ternery system (methane-carbon dioxide-hydrogen sulfide) and two 6-component systems (methane-ethane-propane-n-pentane-n-hexane-n-decane and nitrogen-methane-carbon dioxide-ethane-hydrogen sulfide-propane). For the systems in Table VIII-2 and VIII-3, individual values of σ_{ij} and ε_{ij} have not been determined for some of the binary pairs. The binary interaction parameters for these pairs are taken to be unity for use with the modified van der Waals one-fluid mixing rules, unless otherwise indicated in Table VII-1. The binary interaction parameters estimated from the correlations for σ_{ij} and ε_{ij} developed herein were used with the semiempirical exponent mixing rules (see Table VII-2).

Predictions for the methane-carbon dioxide-hydrogen sulfide system show large deviations from the experimental data using all three formulations (see Table VIII-1). Direct comparisons with experimental data for this system are presented in Appendix B. The modified VDW one-fluid mixing rules are slightly better than the semiempirical exponent mixing rules, but both rules are close to each other in predicted results. The semiempirical exponent mixing rules using the correlations given in Eqs. (VI-3) - (VI-5) for σ_{ij}, ε_{ij} and γ_{ij}, even though the least accurate, provide comparable predictions to the other formulations.

In Table VIII-2, predicted phase compositions for the 6-component system involving paraffin-paraffin interactions are reasonably accurate using both formulations of the semiempirical exponent mixing rules. The modified VDW one-fluid mixing rules yield poorer predictions especially for the liquid compositions of lighter components.

For the nitrogen-methane-carbon dioxide-ethane-hydrogen sulfide-propane system, both the semiempirical exponent and the modified VDW one-fluid mixing rules provide reasonably accurate predictions of phase compositions (see Table VIII-3). The semiempirical exponent mixing rules using the correlations developed herein for σ_{ij}, ε_{ij} and γ_{ij} show poorer predictions for liquid phase compositions but comparable representation of vapor phase compositions. The fact that this system contains three nonhydrocarbons probably leads to the lower accuracy using the correlations for the unlike interaction parameters.

TABLE VIII-1

Summary of Deviations of Predicted Vapor-Liquid Phase Compositions for the System Methane-Carbon Dioxide-Hydrogen Sulfide[1]

(Subscripts 1, 2, 3, Respectively)

Mixing Rules		x_1	x_2	x_3	y_1	y_2	y_3
*	AAD%	16.52	10.35	3.45	5.35	21.57	20.98
*	AAD	0.0213	0.0168	0.0179	0.0326	0.0146	0.0287
**	AAD%	18.37	9.99	3.57	5.59	20.66	21.48
**	AAD	0.0219	0.0153	0.0189	0.0342	0.0144	0.0293
***	AAD%	22.89	15.45	4.50	8.80	24.04	33.66
***	AAD	0.0268	0.0159	0.0212	0.0561	0.0218	0.0434

* Modified van der Waals one-fluid mixing rules.
** Semiempirical exponent mixing rules.
*** Semiempirical exponent mixing rules using the correlations given in Eqs. (VI-3) - (VI-5).

[1] See Table VII-4 for data reference.

TABLE VIII-2

Comparison of Predicted and Experimental* Vapor-Liquid Equilibrium Mole Fractions for the System Methane-Ethane-Propane-n-Pentane-n-Hexane-n-Decane (Subscripts 1, 2, 3, 4, 5, 6, Respectively)

	x_1	x_2	x_3	x_4	x_5	x_6	y_1	y_2	y_3	y_4	y_5	y_6
T=609.67°R, P=100 psia												
Expt.	0.0266	0.0025	0.0019	0.2023	0.2004	0.5703	0.8712	0.0216	0.0062	0.0701	0.0269	0.0040
Calc.^{1}	0.0206	0.0059	0.0032	0.2040	0.1983	0.5680	0.8804	0.0182	0.0049	0.0670	0.0276	0.0019
Calc.^{2}	0.0277	0.0025	0.0015	0.1570	0.1895	0.6218	0.8039	0.0201	0.0062	0.1181	0.0490	0.0027
Calc.^{3}	0.0246	0.0025	0.0015	0.1570	0.1901	0.6245	0.8038	0.0201	0.0062	0.1183	0.0490	0.0027
T=609.67°R, P=3000 psia												
Expt.	0.5753	0.0409	0.0272	0.0509	0.0616	0.2441	0.8585	0.0414	0.0183	0.0179	0.0172	0.0466
Calc.^{1}	0.5536	0.0492	0.0298	0.0528	0.0628	0.2519	0.9150	0.0314	0.0142	0.0121	0.0110	0.0162
Calc.^{2}	0.6337	0.0424	0.0248	0.0422	0.0505	0.2063	0.8731	0.0388	0.0188	0.0197	0.0186	0.0310
Calc.^{3}	0.6070	0.0428	0.0253	0.0436	0.0538	0.2274	0.8661	0.0389	0.0192	0.0219	0.0199	0.0340
T=709.67°R, P=100 psia												
Expt.	0.0177	0.0016	0.0014	0.1694	0.1785	0.6314	0.5986	0.0231	0.0090	0.2103	0.1207	0.0382
Calc.^{1}	0.0123	0.0034	0.0023	0.1800	0.1869	0.6152	0.6376	0.0224	0.0085	0.2008	0.1081	0.0227
Calc.^{2}	0.0166	0.0016	0.0011	0.1103	0.1477	0.7227	0.5372	0.0208	0.0084	0.2523	0.1511	0.0302
Calc.^{3}	0.0150	0.0016	0.0011	0.1102	0.1478	0.7243	0.5375	0.0207	0.0084	0.2522	0.1511	0.0301
T=709.67°R, P=1000 psia												
Expt.	0.2157	0.0232	0.0182	0.1265	0.1428	0.4737	0.8797	0.0383	0.0165	0.0337	0.0211	0.0105
Calc.^{1}	0.1600	0.0303	0.0214	0.1361	0.1511	0.5012	0.9014	0.0312	0.0135	0.0291	0.0189	0.0060
Calc.^{2}	0.2321	0.0229	0.0165	0.1156	0.1361	0.4768	0.8622	0.0385	0.0180	0.0447	0.0280	0.0084
Calc.^{3}	0.2177	0.0230	0.0165	0.1166	0.1385	0.4877	0.8619	0.0382	0.0179	0.0454	0.0281	0.0084

TABLE VIII-2

(Continued)

	x_1	x_2	x_3	x_4	x_5	x_6	y_1	y_2	y_3	y_4	y_5	y_6
T=709.67°R, P=2000 psia												
Expt.	0.4122	0.0342	0.0235	0.0947	0.0993	0.3362	0.8510	0.0415	0.0192	0.0363	0.0261	0.0259
Calc.[1]	0.3114	0.0429	0.0287	0.1140	0.1171	0.3858	0.9014	0.0336	0.0151	0.0246	0.0168	0.0085
Calc.[2]	0.4197	0.0357	0.0234	0.0929	0.0978	0.3306	0.8694	0.0403	0.0191	0.0347	0.0233	0.0132
Calc.[3]	0.4015	0.0359	0.0236	0.0944	1.0077	0.3438	0.8688	0.0399	0.0190	0.0357	0.0234	0.0132
AAD%[1]	21.49	64.41	35.60	7.76	6.30	5.34	4.51	16.10	17.75	17.40	18.96	53.67
AAD [1]	0.0380	0.0058	0.0026	0.0086	0.0076	0.0207	0.0354	0.0058	0.0026	0.0069	0.0062	0.0140
AAD%[2]	5.99	2.53	12.43	16.96	9.39	8.26	4.77	5.37	3.84	27.17	31.83	31.28
AAD [2]	0.0169	0.0006	0.0009	0.0251	0.0122	0.0378	0.0358	0.0015	0.0005	0.0209	0.0127	0.0079
AAD%[3]	6.34	2.79	11.98	15.95	7.91	7.25	4.59	5.54	4.355	29.48	33.32	29.97
AAD [3]	0.0098	0.0007	0.0008	0.0244	0.0109	0.0370	0.0343	0.0016	0.0006	0.0212	0.0129	0.0073

*See Table VII-4 for data reference.

[1] Modified van der Waals one-fluid mixing rules.

[2] Semiempirical exponent mixing rules.

[3] Semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12).

TABLE VIII-3

Comparison of Predicted and Experimental* Vapor-Liquid Equilibrium Mole Fractions for the System Nitrogen-Methane-Carbon Dioxide-Ethane-Hydrogen Sulfide-Propane (Subscripts 1, 2, 3, 4, 5, 6, Respectively)

	x_1	x_2	x_3	x_4	x_5	x_6	y_1	y_2	y_3	y_4	y_5	y_6
T=-50°F, P=900 psia												
Expt.	0.0239	0.4779	0.0299	0.1306	0.2518	0.0859	0.0904	0.7712	0.0171	0.0508	0.0594	0.0111
Calc.^{1}	0.0248	0.5039	0.0295	0.1283	0.2343	0.0792	0.0980	0.7771	0.0160	0.0432	0.0561	0.0096
Calc.^{2}	0.0275	0.5140	0.0293	0.1254	0.2269	0.0768	0.0983	0.7780	0.0154	0.0425	0.0566	0.0092
Calc.^{3}	0.1704	0.4125	0.0346	0.1484	0.2905	0.0971	0.0868	0.7814	0.0153	0.0480	0.0558	0.0125
T=-50°F, P=999 psia												
Expt.	0.0334	0.5532	0.0284	0.1143	0.2055	0.0652	0.0989	0.7579	0.0168	0.0497	0.0629	0.0138
Calc.^{1}	0.0330	0.5533	0.0284	0.1162	0.2032	0.0658	0.1023	0.7673	0.0162	0.0446	0.0587	0.0108
Calc.^{2}	0.0372	0.5676	0.0280	0.1121	0.1930	0.0621	0.1038	0.7699	0.0156	0.0429	0.0577	0.0101
Calc.^{3}	0.0220	0.4454	0.0349	0.1382	0.2752	0.0841	0.0876	0.7577	0.0165	0.0546	0.0655	0.0178
T=-74.9°F, P=714 psia												
Expt.	0.0203	0.4766	0.0329	0.1375	0.2512	0.0815	0.0996	0.8106	0.0133	0.0356	0.0349	0.0060
Calc.^{1}	0.0221	0.5188	0.0308	0.1293	0.2253	0.0734	0.1095	0.8071	0.0128	0.0304	0.0358	0.0047
Calc.^{2}	0.0250	0.5285	0.0306	0.1262	0.2182	0.0712	0.1096	0.8075	0.0123	0.0299	0.0358	0.0045
Calc.^{3}	0.0154	0.4281	0.0366	0.1512	0.2766	0.0918	0.0960	0.8183	0.0121	0.0340	0.0346	0.0047

TABLE VIII-3

(Continued)

	x_1	x_2	x_3	x_4	x_5	x_6	y_1	y_2	y_3	y_4	y_5	y_6
T=-75°F, P=799 psia												
Expt.	0.0284	0.5623	0.0299	0.1181	0.1994	0.0619	0.1100	0.7973	0.0135	0.0350	0.0379	0.00634
Calc.[1]	0.0301	0.5794	0.0291	0.1151	0.1878	0.0582	0.1165	0.8016	0.0127	0.0296	0.0346	0.00477
Calc.[2]	0.0348	0.5911	0.0285	0.1109	0.1794	0.0554	0.1171	0.8020	0.0122	0.0290	0.0348	0.00458
Calc.[3]	0.0221	0.4956	0.0350	0.1379	0.2367	0.0724	0.1019	0.8080	0.0124	0.0337	0.0363	0.00741
T=-99.9°F, P=601 psia												
Expt.	0.0123	0.5521	0.0315	0.1233	0.2089	0.0629	0.1136	0.8253	0.0113	0.0237	0.0234	0.00277
Calc.[1]	0.0256	0.5955	0.0230	0.1118	0.1831	0.0543	0.1275	0.8225	0.0094	0.0185	0.0200	0.00206
Calc.[2]	0.0299	0.6062	0.0290	0.1076	0.1752	0.0518	0.1282	0.8221	0.0090	0.0182	0.0204	0.00200
Calc.[3]	0.0189	0.5144	0.0360	0.1353	0.2272	0.0678	0.1087	0.8370	0.0088	0.0207	0.0215	0.00298
T=-100°F, P=553 psia												
Expt.	0.0161	0.5004	0.0345	0.1384	0.2382	0.0724	0.1108	0.8308	0.0099	0.0246	0.0207	0.00324
Calc.[1]	0.0206	0.5474	0.0314	0.1268	0.2097	0.0641	0.1217	0.8260	0.0097	0.0201	0.0206	0.00213
Calc.[2]	0.0238	0.5568	0.0309	0.1233	0.2028	0.0620	0.1218	0.8258	0.0092	0.0197	0.0212	0.00207
Calc.[3]	0.0141	0.4511	0.0382	0.1532	0.2616	0.0814	0.1037	0.8409	0.0090	0.0227	0.0213	0.00211
T=-125°F, P=398 psia												
Expt.	0.0167	0.4969	0.0378	0.1449	0.2314	0.0723	0.1334	0.8285	0.0083	0.0166	0.0166	0.00165
Calc.[1]	0.0194	0.5466	0.0348	0.1314	0.2038	0.0639	0.1495	0.8182	0.0073	0.0129	0.0113	0.00092
Calc.[2]	0.0229	0.5541	0.0342	0.1282	0.1981	0.0621	0.1495	0.8179	0.0070	0.0127	0.0118	0.00091
Calc.[3]	0.0128	0.4407	0.0433	0.1628	0.2581	0.0819	0.1248	0.8404	0.0067	0.0149	0.0120	0.00092

TABLE VIII-3

(Continued)

	x_1	x_2	x_3	x_4	x_5	x_6	y_1	y_2	y_3	y_4	y_5	y_6
AAD%[1]	12.00	6.37	4.64	5.56	8.64	8.72	8.85	0.738	7.24	16.82	5.62	26.34
AAD [1]	0.0023	0.0322	0.0016	0.0074	0.0199	0.0063	0.0098	0.0059	0.0009	0.0052	0.0021	0.0014
AAD%[2]	28.23	8.40	6.03	7.87	12.05	12.00	9.31	0.811	10.77	18.42	5.84	29.05
AAD [2]	0.0058	0.0427	0.0020	0.0104	0.0275	0.0086	0.0102	0.0064	0.0013	0.0058	0.0022	0.0016
AAD%[3]	22.10	11.88	15.37	13.47	15.48	15.09	6.18	1.10	11.04	7.51	4.21	23.90
AAD [3]	0.0053	0.0616	0.0048	0.0171	0.0342	0.0106	0.0067	0.0089	0.0013	0.0024	0.0015	0.0014

*See Table VII-4 for data reference.

[1] Modified van der Waals one-fluid mixing rules.

[2] Semiempirical exponent mixing rules.

[3] Semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12) and Eqs. (VI-3) - (VI-5).

CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

In this study it has been determined that the modified VDW conformal solution method based on the three-parameter, corresponding-states correlation of pure fluid thermodynamic properties yields accurate mixture property predictions if the components are not greatly dissimilar. However, there is a progressive decay in prediction accuracy as molecular dissimilarities increase. This study indicates that if the VDW one-fluid mixing rule exponents are modified empirically (i.e., to noninteger values), the resulting semiempirical exponent mixing rules yield significant improvements in vapor-liquid equilibrium predictions for mixtures of molecules as dissimilar as methane and normal decane. Both mixing rules exhibit reasonably accurate predictions of bulk properties.

Correlations were developed herein for the unlike interaction parameters appearing in the semiempirical exponent mixing rules as functions of the characteristic parameters, T_{c_i}, V_{c_i}, γ_i of the pure components alone. The correlations given in Eqs. (VI-10) - (VI-12) are suitable for hydrocarbon-

hydrocarbon interactions. The correlations in Eqs. (VI-3) - (VI-5) are applicable to nonhydrocarbon-hydrocarbon interactions with reasonable predicted results and can be used as a rough guide for nonhydrocarbon-nonhydrocarbon interaction predictions.

The study presented herein has a number of implications. First, this study implies that it is possible to obtain accurate predictions of the thermodynamic behavior of mixtures within a multiparameter, corresponding-states framework using empirically determined exponents in mixing rules. This result is important to the continuing effort to develop a highly accurate multiparameter, corresponding-states framework for correlation of fluid properties, including mixtures, and to the industrial use of such a correlation. Second, this study demonstrates that there is a need to study separately rather than collectively (as herein) the errors introduced by the various major approximations introduced into the correlation methodology. These approximations include: (1) the choice for the form of the pair potential; (2) the method for estimation of the pure-fluid pair potential parameters; (3) the order and method (e.g., use of the Padé approximant) of truncation of the Pople expansion of the thermodynamic properties; (4) the order of truncation of the expansion of mixture properties about the properties of the pure-fluid reference system in the conformal solution methodology; (5) the method for choosing the mixing rules for the reference system characterization parameters as functions of composition and the pair parameters for the molecular interactions of the components; and (6) the method for determination of the unlike interaction pair parameters. With a better understanding of the errors introduced by these approximations, the development of a more truly comprehensive correlation, capable of describing fluid systems with wide ranges of characteristics over wide ranges of conditions, should be possible.

From the point of view of further improvement of the first order conformal solution method for practical industrial calculations, the following considerations seem warranted, (1) the empirical determination of all nine exponents in the conformal solution mixing rules (2) the determination of the binary interaction parameter ϕ_{ij} in the relation $\gamma_{ij} = \phi_{ij}(\gamma_{ii} + \gamma_{jj})/2$ and (3) the modification of the formulas for estimation of the pure-fluid pair potential parameters using data for both pure components and mixtures.

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NOMENCLATURE

A = Helmholtz free energy

A_o = reference system Helmholtz free energy

A_i = the ith order term in perturbation of A

A_x = Helmholtz free energy of a hypothetical pure reference fluid

A^* = reduced Helmholtz free energy, A/NkT

a_i = constant in expression for B_i, $i=1,\ldots 12$

a_x, b_x, c_x = parameters in Equation (III-2)

a_{ij} = $\delta_{ij}{}^{k}\varepsilon_{ij}{}^{l}\sigma_{ij}{}^{m}$

B_i = coefficients of MBWR equation, $B_i \equiv a_i + \gamma b_i$,

$i = 1,\ldots 12$

b_i = constant in expression for B_i, $i=1,\ldots 12$

b_{ij} = $\delta_{ij}{}^{p}\varepsilon_{ij}{}^{q}\sigma_{ij}{}^{r}$

c_{ij} = $\delta_{ij}{}^{u}\varepsilon_{ij}{}^{v}\sigma_{ij}{}^{w}$

D = angle dependent part of an isotropic potential in Equation (III-11)

F_{ij} = distance dependent part of an isotropic potential in Equation (III-11)

f^* = function, see Equation (III-21)

$g_{ij}{}^{o}$ = radial distribution function of the reference system with pair potential $U_{ij}{}^{o}$

$g_x{}^{o}$ = radial distribution function of a hypothetical pure reference fluid with pair potential $U_{ij}{}^{o}$

J_x = integral defined in Equation (III-8)

K = Boltzman constant

k,l,m,p,q,r,u,v,w = exponent in Equations (III-3) - (III-5)

P = pressure

p_c = critical pressure

p_r = reduced pressure, p/p_c

p_{c_m} = pseudocritical mixture pressure

$\underline{r}_1$ = position vector of molecule 1

r_{12} = distance between molecular centers

r^* = reduced distance, r/σ_x

T = absolute temperature

T_c = critical temperature

T_r = reduced temperature, T/T_c

T_{c_m} = pseudocritical mixture temperature

T^* = reduced temperature, kT/ε_x

U_{ij} = intermolecular pair potential

U_{ij}^o = spherically symmetric part of the interaction potential

V = volume

V_c = critical volume

V_r = reduced volume, V/V_c

V_{c_m} = pseudocritical mixture volume

x_i = mole fraction of component i

Z = compressibility factor of fluid

Z_o = reference fluid compressibility factor

Z_1 = pertubation contribution to compressibility factor

$Z^{(o)}$ = simple fluid compressibility factor, see Eq. (II-9)

Greek Symbols

γ = orientation parameter

γ_{ii} = orientation parameter for component i

γ_{ij} = interaction orientation parameter species for i and j

γ_x = orientation parameter obtained from conformal solution theory mixing rule

δ = overlap potential parameter

δ_{ij} = unlike interaction overlap poteneial parameter

δ_x = mixture reference overlap parameter

ε = characteristic molecular energy parameter

ε_{ii} = ε for component i

ε_{ij} = interaction parameter for characteristic molecular energy parameter ε between species i and j

ε_x = mixture reference systems energy parameter

ζ_{ij} = unlike-pair separation parameter coefficient for species i and j

η, η' = unlike-pair separation parameter coefficient for species i and j

θ_1 = polar angles of orientation for molecule 1

ξ_{ij} = unlike-pair energy parameter coefficient for i and j species

ρ = molecule number density

ρ^* = reduced number density, $\rho\sigma_x^3$

ρ_c = critical density

σ = characteristic molecular distance parameter

σ_{ii} = σ for component i

σ_{ij} = interaction parameter for characteristic molecular distance parameter, σ between substance i and j

σ_x = mixture reference system molecular distance parameter

ϕ^o = isotropic part of potential

ϕ^p = anisotropic part of potential

ω = acentric factor

ω_i = orientation of molecule i

Superscripts

* = reduced form

R = reference fluid

Subscript

m = mixture

APPENDIX A

Comparison of Vapor-Liquid Equilibrium Calculations for the System Methane-Ethane-Propane (Subscripts 1, 2, 3, Respectively)

Pressure (psia)	Temp. (^{o}R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
100	384.67	Expt.	0.0533	0.9008	0.0459	0.44814	0.54755	0.00431
		Calc.^{1}	0.0521	0.9023	0.0456	0.45794	0.53833	0.00373
		Calc.^{2}	0.0524	0.9020	0.0456	0.45793	0.53837	0.00371
		Calc.^{3}	0.0516	0.9023	0.0460	0.45904	0.53776	0.00320
200	384.67	Expt.	0.1777	0.1834	0.6389	0.90348	0.06461	0.03191
		Calc.^{1}	0.1631	0.19074	0.64614	0.91036	0.05863	0.03101
		Calc.^{2}	0.1698	0.18934	0.64078	0.91074	0.05877	0.03049
		Calc.^{3}	0.1560	0.19514	0.64882	0.91457	0.05482	0.03061
100	384.67	Expt.	0.0813	0.2052	0.7135	0.81743	0.12625	0.05632
		Calc.^{1}	0.0730	0.21533	0.71159	0.82907	0.11567	0.05526
		Calc.^{2}	0.0767	0.21482	0.70843	0.82958	0.11563	0.05479
		Calc.^{3}	0.0703	0.22142	0.70823	0.83681	0.10879	0.05441
100	384.67	Expt.	0.0580	0.7770	0.1650	0.50037	0.48624	0.01339
		Calc.^{1}	0.0554	0.78463	0.15996	0.52143	0.46598	0.01259
		Calc.^{2}	0.0557	0.78428	0.15997	0.52135	0.46616	0.01249
		Calc.^{3}	0.0542	0.78555	0.16021	0.52613	0.46264	0.01124

APPENDIX A

(Continued)

Pressure (psia)	Temp. ($^\circ$R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
		Expt.	0.1667	0.6943	0.1390	0.74702	0.24446	0.00852
200	384.67	Calc.^{1}	0.1584	0.70107	0.14045	0.75486	0.23798	0.00716
		Calc.^{2}	0.1604	0.69945	0.14009	0.75485	0.23807	0.00708
		Calc.^{3}	0.1552	0.70343	0.14137	0.75716	0.23638	0.00646
		Expt.	0.1624	0.7963	0.0413	0.71442	0.28343	0.00215
200	384.67	Calc.^{1}	0.1597	0.79941	0.04085	0.72336	0.27446	0.00218
		Calc.^{2}	0.1618	0.79743	0.04071	0.72346	0.27438	0.00217
		Calc.^{3}	0.1590	0.79980	0.04113	0.72393	0.27417	0.00190
		Expt.	0.3725	0.51930	0.10820	0.86716	0.12712	0.00572
400	384.67	Calc.^{1}	0.3612	0.52859	0.11015	0.87256	0.12245	0.00498
		Calc.^{2}	0.3677	0.52345	0.10882	0.87297	0.12213	0.00489
		Calc.^{3}	0.3563	0.53242	0.11128	0.87381	0.12158	0.00462
		Expt.	0.5453	0.09710	0.35760	0.95770	0.02335	0.01895
600	384.67	Calc.^{1}	0.5458	0.09887	0.35528	0.96157	0.02075	0.01767
		Calc.^{2}	0.5511	0.09767	0.35116	0.96224	0.02084	0.01692
		Calc.^{3}	0.5253	0.10349	0.37112	0.96257	0.01984	0.01759
		Expt.	0.7796	0.1795	0.0409	0.91765	0.07395	0.00840
800	384.67	Calc.^{1}	0.7544	0.10879	0.04672	0.92586	0.06759	0.00654
		Calc.^{2}	0.7594	0.19514	0.04546	0.92726	0.06643	0.00631
		Calc.^{3}	0.7510	0.20150	0.04741	0.92678	0.06680	0.00642

APPENDIX A

(Continued)

Pressure (psia)	Temp. (^{o}R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
		Expt.	0.7840	0.2037	0.0123	0.90632	0.09115	0.00253
800	384.67	Calc.^{1}	0.7589	0.2272	0.01383	0.91521	0.08258	0.00221
		Calc.^{2}	0.7644	0.22217	0.01336	0.91689	0.08098	0.00214
		Calc.^{3}	0.7593	0.22688	0.01378	0.91621	0.08163	0.00215
		Expt.	0.0390	0.1999	0.7611	0.77157	0.16379	0.06464
40.00	359.67	Calc.^{1}	0.0349	0.21275	0.75232	0.79052	0.14790	0.05978
		Calc.^{2}	0.0359	0.21250	0.75152	0.79053	0.14987	0.05960
		Calc.^{3}	0.0325	0.22043	0.74700	0.80013	0.14098	0.05889
		Expt.	0.0255	0.67710	0.29740	0.43703	0.53611	0.02686
40.00	359.67	Calc.^{1}	0.0222	0.67779	0.30000	0.44247	0.53469	0.02284
		Calc.^{2}	0.0219	0.67756	0.30047	0.44204	0.53515	0.02281
		Calc.^{3}	0.0212	0.68275	0.29600	0.45291	0.52624	0.02086
		Expt.	0.1058	0.5843	0.3099	0.78184	0.20508	0.01308
100	359.67	Calc.^{1}	0.0973	0.58948	0.31315	0.78692	0.20179	0.01129
		Calc.^{2}	0.0970	0.58936	0.31362	0.78635	0.20242	0.01123
		Calc.^{3}	0.0916	0.59431	0.31406	0.79217	0.19725	0.01058
		Expt.	0.1037	0.8045	0.0918	0.71928	0.27656	0.00416
100	359.67	Calc.^{1}	0.09965	0.80680	0.09355	0.71562	0.28086	0.00352
		Calc.^{2}	0.09914	0.80717	0.09369	0.71515	0.28132	0.00353
		Calc.^{3}	0.09646	0.80922	0.09433	0.71658	0.28035	0.00308

APPENDIX A

(Continued)

Pressure (psia)	Temp. (°R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
200	359.67	Expt.	0.2332	0.05280	0.7140	0.96902	0.01232	0.01866
		Calc.[1]	0.22683	0.05553	0.71765	0.97311	0.00973	0.01716
		Calc.[2]	0.23233	0.05506	0.71261	0.97327	0.00985	0.01687
		Calc.[3]	0.20946	0.05742	0.73312	0.97381	0.00890	0.01724
200	359.67	Expt.	0.2366	0.4960	0.2674	0.89046	0.10178	0.00776
		Calc.[1]	0.22488	0.50292	0.27220	0.89294	0.10043	0.00644
		Calc.[2]	0.22572	0.50215	0.27213	0.89247	0.10096	0.00657
		Calc.[3]	0.21266	0.51086	0.27648	0.89516	0.09854	0.00630
400	359.67	Expt.	0.4877	0.03730	0.4750	0.98122	0.00627	0.01251
		Calc.[1]	0.48228	0.03846	0.47926	0.98370	0.00530	0.01100
		Calc.[2]	0.48498	0.03818	0.47684	0.98393	0.00539	0.01067
		Calc.[3]	0.45281	0.04078	0.50640	0.98383	0.00497	0.01121
400	359.67	Expt.	0.5206	0.3083	0.1711	0.94363	0.05125	0.00512
		Calc.[1]	0.49401	0.32516	0.18083	0.94654	0.04884	0.00461
		Calc.[2]	0.49898	0.32204	0.17898	0.94654	0.04893	0.00453
		Calc.[3]	0.47725	0.33559	0.18716	0.94718	0.04829	0.00453
600	359.67	Expt.	0.7668	0.0179	0.2153	0.98420	0.00355	0.01225
		Calc.[1]	0.75208	0.01890	0.22902	0.98696	0.00335	0.00969
		Calc.[2]	0.74904	0.01905	0.23191	0.98727	0.00337	0.00936
		Calc.[3]	0.73228	0.02035	0.24737	0.98660	0.00326	0.01014

APPENDIX A

(Continued)

Pressure (psia)	Temp. (^{o}R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
600	359.67	Expt.	0.7795	0.1364	0.0841	0.96332	0.03113	0.00555
		Calc.^{1}	0.76482	0.14552	0.08966	0.96701	0.02838	0.00461
		Calc.^{2}	0.76772	0.14391	0.08837	0.96742	0.02808	0.00450
		Calc.^{3}	0.75648	0.15055	0.09297	0.96708	0.02818	0.00474
725	359.67	Expt.	0.9194	0.0056	0.0750	0.98562	0.00184	0.01254
		Calc.^{1}	0.90633	0.00615	0.08753	0.98808	0.00185	0.01007
		Calc.^{2}	0.90399	0.00626	0.08974	0.98839	0.00183	0.00977
		Calc.^{3}	0.90264	0.00639	0.09097	0.98746	0.00184	0.01070
32.00	334.67	Expt.	0.04510	0.2274	0.7275	0.83393	0.13182	0.03425
		Calc.^{1}	0.04034	0.24471	0.71495	0.86140	0.11082	0.02778
		Calc.^{2}	0.04012	0.24425	0.71563	0.86081	0.11144	0.02775
		Calc.^{3}	0.03591	0.25128	0.71281	0.86926	0.10332	0.02743
32.00	334.67	Expt.	0.0304	0.8378	0.1318	0.51306	0.48024	0.00670
		Calc.^{1}	0.03347	0.84449	0.12203	0.56377	0.43169	0.00454
		Calc.^{2}	0.03233	0.84528	0.12239	0.56302	0.43243	0.00458
		Calc.^{3}	0.03136	0.84604	0.12260	0.56599	0.43009	0.00392
725	359.67	Expt.	0.9291	0.0501	0.0298	0.97067	0.02209	0.00724
		Calc.^{1}	0.91131	0.05507	0.03362	0.97553	0.01931	0.00517
		Calc.^{2}	0.91160	0.05499	0.03341	0.97600	0.01898	0.00502
		Calc.^{3}	0.91004	0.05594	0.03402	0.97532	0.01929	0.00539

APPENDIX A

(Continued)

Pressure (psia)	Temp. (°R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
100	334.67	Expt.	0.1479	0.7354	0.1167	0.84909	0.14858	0.00233
		Calc.[1]	0.15888	0.72790	0.11322	0.86371	0.13453	0.00176
		Calc.[2]	0.15623	0.73004	0.11373	0.86295	0.13526	0.00179
		Calc.[3]	0.15044	0.73483	0.11472	0.86383	0.13460	0.00157
200	334.67	Expt.	0.3142	0.1579	0.5279	0.07149	0.02149	0.00702
		Calc.[1]	0.31598	0.16102	0.52300	0.97772	0.01662	0.00566
		Calc.[2]	0.31298	0.16137	0.52565	0.97739	0.01700	0.00561
		Calc.[3]	0.28299	0.16910	0.54791	0.97864	0.01559	0.00577
400	334.67	Expt.	0.6828	0.0729	0.2443	0.98718	0.00785	0.00497
		Calc.[1]	0.72162	0.06500	0.21338	0.98982	0.00674	0.00344
		Calc.[2]	0.71915	0.06547	0.21537	0.98975	0.00684	0.00341
		Calc.[3]	0.69663	0.07057	0.23281	0.98963	0.00663	0.00373
32.00	309.67	Expt.	0.0715	0.7701	0.1584	0.81724	0.18068	0.00208
		Calc.[1]	0.06677	0.77358	0.15965	0.81666	0.18139	0.00195
		Calc.[2]	0.06296	0.77641	0.16063	0.81562	0.18239	0.00199
		Calc.[3]	0.06004	0.77888	0.16108	0.81767	0.18061	0.00172
100	309.67	Expt.	0.2541	0.6805	0.0654	0.93931	0.06034	0.00035
		Calc.[1]	0.25508	0.67967	0.06525	0.93957	0.06005	0.00038
		Calc.[2]	0.24992	0.68429	0.06579	0.93883	0.06077	0.00040
		Calc.[3]	0.24173	0.69166	0.06662	0.93891	0.06075	0.00034

APPENDIX A

(Continued)

Pressure (psia)	Temp. (^{o}R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
		Expt.	0.5487	0.3826	0.0687	0.97513	0.02460	0.00027
200	309.67	Calc.[1]	0.54457	0.38634	0.06910	0.97609	0.02354	0.00038
		Calc.[2]	0.54673	0.38449	0.06878	0.97577	0.02384	0.00040
		Calc.[3]	0.52950	0.39894	0.07156	0.97563	0.02399	0.00039
		Expt.	0.8565	0.0462	0.0973	0.99553	0.00351	0.00096
300	309.67	Calc.[1]	0.85031	0.04815	0.10154	0.99574	0.00340	0.00086
		Calc.[2]	0.84942	0.04841	0.10217	0.99567	0.00344	0.00090
		Calc.[3]	0.84123	0.05097	0.10780	0.99553	0.00344	0.00103
		Expt.	0.4190	0.3783	0.2027	0.98520	0.01449	0.00031
100	284.67	Calc.[1]	0.40218	0.38936	0.20846	0.98571	0.01393	0.00036
		Calc.[2]	0.38582	0.39968	0.21450	0.98514	0.01448	0.00038
		Calc.[3]	0.35317	0.42077	0.22606	0.98541	0.01422	0.00037
		Expt.	0.1174	0.3770	0.5056	0.96179	0.03639	0.00182
32.00	284.67	Calc.[1]	0.10185	0.38550	0.51265	0.96557	0.03270	0.00173
		Calc.[2]	0.09192	0.38904	0.51904	0.96471	0.03354	0.00175
		Calc.[3]	0.08113	0.39512	0.52375	0.96743	0.03086	0.00172

[1] Modified van der Waals one-fluid mixing rules.

[2] Semiempirical exponent mixing rules.

[3] Semiempirical exponent mixing rules using the correlations given in Eqs. (VI-10) - (VI-12).

APPENDIX B

Comparison of Vapor-Liquid Equilibrium Calculations for the System

Methane-Carbon Dioxide-Hydrogen Sulfide

(Subscripts 1, 2, 3, Respectively)

Pressure (psia)	Temp. (°R)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
600.00	559.83	Expt.	0.0280	0.0200	0.9520	0.2509	0.0628	0.6863
		Calc.[1]	0.0223	0.0219	0.9558	0.2287	0.0562	0.7151
		Calc.[2]	0.0219	0.0224	0.9558	0.2304	0.0561	0.7135
		Calc.[3]	0.0262	0.0294	0.9444	0.2449	0.0525	0.7026
1200.00	559.83	Expt.	0.1120	0.0460	0.8420	0.4267	0.1049	0.4684
		Calc.[1]	0.1093	0.0629	0.8279	0.4443	0.0892	0.4665
		Calc.[2]	0.1098	0.0638	0.8264	0.4488	0.0885	0.4627
		Calc.[3]	0.1058	0.0711	0.8231	0.4905	0.0814	0.4282
300.00	429.91	Expt.	0.0480	0.1270	0.8250	0.6528	0.1397	0.2075
		Calc.[1]	0.0390	0.1180	0.8430	0.6803	0.1494	0.1703
		Calc.[2]	0.0351	0.1209	0.8440	0.6841	0.1464	0.1695
		Calc.[3]	0.0383	0.1488	0.8139	0.7326	0.1142	0.1533
500.00	429.91	Expt.	0.1140	0.5110	0.3750	0.5996	0.2892	0.1111
		Calc.[1]	0.1150	0.5056	0.3795	0.6437	0.2751	0.0812
		Calc.[2]	0.1144	0.5066	0.3791	0.6472	0.2727	0.0801
		Calc.[3]	0.0753	0.5238	0.4008	0.6811	0.2577	0.0612

APPENDIX B

(Continued)

Pressure (psia)	Temp. (^oR)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
500.00	429.91	Expt.	0.0950	0.1340	0.7710	0.7495	0.0950	0.1555
		Calc.[1]	0.0843	0.1256	0.7901	0.7769	0.1029	0.1202
		Calc.[2]	0.0770	0.1282	0.7948	0.7797	0.1004	0.1199
		Calc.[3]	0.0714	0.1469	0.7817	0.8176	0.0781	0.1043
700.00	429.91	Expt.	0.1280	0.1140	0.7580	0.8602	0.0240	0.1158
		Calc.[1]	0.1337	0.0823	0.7840	0.8356	0.0565	0.1079
		Calc.[2]	0.1230	0.0845	0.7925	0.8372	0.0547	0.1081
		Calc.[3]	0.1065	0.0964	0.7972	0.8663	0.0428	0.0910
700.00	429.91	Expt.	0.1720	0.4710	0.3570	0.6003	0.2261	0.1736
		Calc.[1]	0.2058	0.4549	0.3394	0.7156	0.2141	0.0703
		Calc.[2]	0.2065	0.4553	0.3382	0.7200	0.2106	0.0693
		Calc.[3]	0.1230	0.4921	0.3850	0.7449	0.2026	0.0526
300.00	400.03	Expt.	0.0580	0.1300	0.8120	0.8004	0.8502	0.1146
		Calc.[1]	0.0516	0.1195	0.8289	0.8155	0.0949	0.0895
		Calc.[2]	0.0442	0.1224	0.8334	0.8186	0.0922	0.0893
		Calc.[3]	0.0468	0.1447	0.8085	0.8551	0.0657	0.0792
300.00	400.03	Expt.	0.0820	0.4700	0.4480	0.7052	0.2190	0.0758
		Calc.[1]	0.0752	0.4631	0.4617	0.7035	0.2303	0.0663
		Calc.[2]	0.0713	0.4649	0.4638	0.7057	0.2291	0.0653
		Calc.[3]	0.0463	0.4821	0.4716	0.7432	0.2071	0.0497

APPENDIX B

(Continued)

Pressure (psia)	Temp. (^oR)		Liquid Mole Fractions			Vapor Mole Fractions		
			x_1	x_2	x_3	y_1	y_2	y_3
		Expt.	0.0960	0.1080	0.7960	0.8285	0.0629	0.1086
500.00	400.03	Calc.[1]	0.1057	0.1085	0.7858	0.8739	0.0587	0.0674
		Calc[2]	0.0909	0.1111	0.7980	0.8758	0.0568	0.0675
		Calc.[3]	0.0826	0.1241	0.7933	0.9024	0.0405	0.0571
		Expt.	0.1280	0.4660	0.4060	0.7642	0.1771	0.0587
500.00	400.03	Calc.[1]	0.1761	0.4482	0.3757	0.7952	0.1577	0.0472
		Calc.[2]	0.1706	0.4514	0.3780	0.7976	0.1558	0.0466
		Calc.[3]	0.0940	0.4862	0.4197	0.8185	0.1473	0.0343
		Expt.	0.2180	0.4150	0.3670	0.8567	0.0851	0.0582
700.00	400.03	Calc.[1]	0.3314	0.3421	0.3265	0.8365	0.1179	0.0456
		Calc.[2]	0.3295	0.3437	0.3268	0.8393	0.1155	0.0452
		Calc.[3]	0.1416	0.4222	0.4363	0.8534	0.1138	0.0329

[1] Modified van der Waals one-fluid mixing rules.

[2] Semiempirical exponent mixing rules.

[3] Semiempirical exponent mixing rules using the correlations given in Eqs. (VI-3) - (VI-5).