STATISTICAL THERMODYNAMIC APPROACH TO THE PREDICTION OF VAPOR-LIQUID EQUILIBRIA OF MULTI-COMPONENT MIXTURES

Shing-Shong Lan and G.Ali Mansoori
Department of Energy Engineering, University of Illinois at Chicago Circle, Chicago, IL 60680, U.S.A.

ABSTRACT
A Hard Sphere Expansion (HSE) conformal solution theory, which is a result of the application of statistical mechanics, is developed in order to predict the vapor-liquid equilibria properties of multicomponent mixtures. The HSE mixing rules are derived with consideration of the Kihara spherical-core function as the pair potential together with the 3-body potential function. Based on this HSE conformal solution theory, an equation of state for multi-component fluid is developed. In this conformal solution theory perturbation equation of state of pure fluids is used as the reference equation of state. The vapor-liquid equilibria properties of several properly chosen binary and ternary non-polar mixtures are predicted. These mixtures include: argon-krypton, argon-methane, methane-krypton, nitrogen-methane, nitrogen-argon, argon-neopentane, methane-neopentane, methane-perfluoromethane, carbon dioxide-ethylene, carbon dioxide-ethane, nitrogen-argon–oxygen, and nitrogen-argon-methane. The predicted results obtained in the present investigation compare quite favorably with the experimental vapor-liquid equilibria values. Furthermore, the present approach, being a purely molecular theory of fluid mixtures, provides detailed insight into the peculiar behavior of the azeotropic fluid mixture. It is shown that the vapor-liquid equilibria properties of multicomponent fluid systems may be predicted correctly through the present statistical mechanic approach provided that like- and unlike-interaction parameters of the species of the mixtures are known a priori. Generally, the present investigation shows that the use of the molecular theory of fluid mixtures in predicting the mixture properties is very promising.

INTRODUCTION
For optimum design of the equipment used in the separation processes, it is necessary to know the phase equilibria and other thermodynamic properties of the mixtures which are to be separated. Until quite recently, there has been little use for the fundamental molecular theories of fluids and fluid mixtures for predicting thermodynamic properties of real fluids, particularly at high pressures and in condensed states[1,2]. This has resulted from two factors; (i) complexity of the fundamental theories of fluids and (ii) the non-convergence of most of these theories in the case of condensed states. As a result, the general practice in phase equilibria and other thermodynamic property predictions has been the use of empirical methods. The basic approach of empirical techniques has been the development of correlations for thermodynamic properties of pure fluids. By the use of empirical mixing rules for the coefficients of pure fluid correlations, with respect to mole fractions, similar correlations for mixtures are developed.

Since the mid-sixties, there has been considerable development in the application of statistical thermodynamics in the predictions of thermodynamic properties of pure fluids and fluid mixtures. These methods, which are collectively termed as perturbation methods, yield excellent results when predicting thermodynamic properties of simple fluids and simple binary fluid mixtures[3–5]. While the perturbation equations of state for pure fluid possess simple forms, the perturbation relations for binary mixtures are rather complex, involving elaborate calculations. The use of the perturbation equations of state for the prediction of properties of multicomponent systems consisting of three components or more is extremely complicated at the present time.

As far as the practical applications are concerned, the most successful theories in predicting the equilibrium thermodynamic properties of multicomponent mixtures have been the corresponding states, or conformal solution theories of mixtures[6,7]. In the development of a conformal solution theory for mixtures, two principles are considered. One is the choice of an accurate equation of state for the reference pure system. The second is the choice of mixing

(1). Present address: Sargent & Lundy Engineers, Chicago, IL 60603, U.S.A. Email: shingslan@yahoo.com
(2). Email: mansoori@uic.edu
rules for the parameters of the pure reference equation of state, in order to generalize them for mixtures. The parameters of the pure reference equation of state are, usually, either intermolecular potential parameters or the critical properties.

The first conformal solution theory of mixtures was developed and proposed by van der Waals in the nineteenth century[8]. Since the original work of van der Waals, many other conformal solution theories have been devised. However, recently, investigators have demonstrated that van der Waals conformal solution theory of mixtures is theoretically and experimentally superior to other widely used conformal solution theories of non-polar mixtures[6, 7]. Recently, Mansoori and L&and [9] proposed a new conformal solution theory for mixtures. This theory is termed the hard sphere expansion (HSE) conformal solution theory. The HSE conformal solution theory is actually one which is more fundamental than the conventional conformal solution theories and is less complicated than the analytical theories of fluid mixtures. In one respect the HSE conformal solution theory is a refinement of van der Waals’ conformal solution theory and in other respect it utilizes the hard-sphere mixture equation of state and the perturbation equation of state of pure fluids in its formulation. Also, the HSE conformal solution theory is not limited to the conformal treatment of only two parameters as other conformal solution techniques are.

Initially, the HSE conformal solution theory was developed for predicting the excess thermodynamic properties of simple liquid mixtures. In comparing the predicted values of the excess thermodynamic properties of simple liquid mixtures with results of other theories of fluid mixtures the HSE technique proved to be substantially superior to the other theories[9]. Also the HSE technique is preferred over the analytic theories of fluid mixtures due to its applicability for mixtures containing more than two components. In the present report modifications and improvements are made in the formulation of the HSE conformal solution theory in order to apply it in predicting thermodynamic properties. Specifically the vapor-liquid equilibria properties of several realistic fluid mixtures which are of practical interest to engineers and scientists are predicted.

THE HARD SPHERE EXPANSION (HSE) CONFORMAL SOLUTION THEORY

According to Pitzer’s two-parameter corresponding states principle[10], the following relation can be written for the thermodynamic functions of a pure non-polar classical fluid

\[ X_r = X_r^p + f_i(T^*, p^*). \]  

(1)

In this equation \( X \) is a reduced thermodynamic function (i.e. compressibility, internal energy, or free energy), and \( T^* \) and \( p^* \) are reduced temperature and density, respectively. The reducing parameters in eqn (1) may be either the intermolecular potential parameters or the critical constants. The assumptions behind this two-parameter corresponding states principle are: (i) intermolecular energies are independent of density; (ii) quantum effects may be ignored; (iii) the intermolecular potential energy function of the molecules in the system is in the following form

\[ u(r) = \epsilon \left( \frac{r}{\sigma} \right). \]  

(2)

In order to apply the above idea to mixtures, the relations between \( \sigma \) and \( \epsilon \) (or \( V \) and \( T \)) of a pure reference fluid, and the composition and parameters of the components of the mixture should be derived. This procedure is based on the assumption that a pure fluid may exist hypothetically and possess the same properties as the mixture, provided the hypothetical pure fluid and the mixture are at the same temperature and pressure[6]. As a result, the intermolecular parameters (or the critical constants) of the hypothetical pure reference fluid are the pseudo-intermolecular potential parameters (or the pseudo-critical constants) of the mixture. The relations between the parameters of the hypothetical pure reference fluid and the composition and parameters of the mixture are termed the conformal solution mixing rules. Generally for the mixing rules of a non-polar, classical, mixture may be written as

\[ \bar{\epsilon} = \bar{\epsilon}(\bar{\epsilon}_i, \sigma_i, X_i, X, \rho, T) \]

\[ \bar{\sigma} = \bar{\sigma}(\bar{\epsilon}_i, \sigma_i, X_i, X, \rho, T) \]

\[ i, j = 1, 2, \ldots, m \]  

(3)

or

$$T_{pc} = T_{pc}(T_{ci}, v_{ci}, X_i, X_n, \rho, T)$$
$$v_{pc} = v_{pc}(T_{ci}, v_{ci}, X_i, X_n, \rho, T) \quad i, j = 1, 2, \ldots, m \quad (4)$$

where $\xi$, $\sigma$, and $T_{pc}$, $V_{pc}$ are the parameters of the reference pure fluid, $\varepsilon_{ij}$, $\sigma_{ij}$, and $T_{ci}$, $V_{ci}$ are the parameters of the components of the mixture, $X_i$ and $X_n$ are the mole fractions, and $m$ is the number of components of the mixture.

By application of the principles of statistical thermodynamics it has been possible to develop simple and analytical equations of state for pure fluids and fluid mixtures possessing hard-sphere intermolecular potential functions\[11, 12\]. The hard-sphere equations of state developed are quite accurate in predicting the thermodynamic properties of both pure hard-sphere fluid and hard-sphere fluid mixture. Due to the availability of the hard-sphere equations of state it will no longer be necessary to apply the principle of corresponding states to the excess properties over the ideal gas system as shown by eqn (1). Instead, one may replace eqn (1) with the following equation

$$X_p = X_{ps} + f_d(T^*, \rho^*), \quad (5)$$

where $X_{ps}$ is the pure hard-sphere thermodynamic function. In order to extend the applicability of eqn (5) to the case of mixtures one should replace $X_{ps}$ with $X_{ps}^n$, and the reducing parameters $\varepsilon$ and $\sigma$ (or $T_c$ and $V_c$) with $\xi$ and $\sigma$ (or $T_{pc}$, $V_{pc}$) appearing in the second term in the right-hand side of eqn (5). The corresponding states principle based on this idea is called the hard-sphere expansion (HSE) technique. In order to determine the mixing rules for the HSE conformal solution theory of mixtures, the equations of state for pure fluid and fluid mixtures as derived from statistical thermodynamics should be equated\[9\]. The following is a brief explanation of the procedure.

Consider a fluid with the following total intermolecular potential energy function

$$U = \sum_{j>i=1}^{N} u(r_{ij}) + \sum_{k>i>j=1}^{N} w(r_{ij}, r_{jk}, r_{ki}). \quad (6)$$

In the above equation $U(r_{ij})$ is the pair-potential function and $w(r_{ij}, r_{jk}, r_{ki})$ is the triplet-potential function. As in any conformal solution theory, it is necessary to assume certain functional forms for $u_{ij}$ and $w_{ijk}$. In the present work the following functional forms for $u$ and $w$ are assumed

$$u_{ij} = \varepsilon \phi_1\left(\frac{r_{ij}}{\sigma}, \frac{\gamma}{\sigma}\right) \quad (7)$$

and

$$w_{ijk} = \nu\sigma^{-2}\phi_2\left(\frac{r_{ij}}{\sigma}, \frac{r_{jk}}{\sigma}, \frac{r_{ki}}{\sigma}\right). \quad (8)$$

The above functional form for $u_{ij}$ is consistent with the most common form of a 3-parameter pair potential function such as the Kihara spherical-core potential function

$$u^s_{ij} = 4\varepsilon\left[\left(\frac{\sigma - \gamma}{r - \gamma}\right)^{12} - \left(\frac{\sigma - \gamma}{r - \gamma}\right)^{6}\right]. \quad (9)$$

The functional form chosen for $w_{ijk}$ is consistent with the Axilrod-Teller triple-dipole potential\[13\]

$$w^T_{ijk} = \nu\sigma^{-3}(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)(r_{ij}r_{jk}r_{ki}). \quad (10)$$

Axilrod-Teller triple-dipole potential function is the only 3-body function available at the

present time and it is expected to be the leading term of the 3-body potential. As a result, the total potential energy function will have the following relation

\[ U = \varepsilon \sum_{i<j<k} \phi \left( \frac{r_{ij}}{\sigma}, \frac{r_{ik}}{\sigma}, \frac{r_{jk}}{\sigma}, \theta_{ij}, \theta_{ik}, \theta_{jk} \right) \]  

(11)

According to statistical thermodynamics for the pure reference fluid with the total potential energy function given in the above equation, the following relation holds for compressibility factor \[ Z = 1 - \frac{2\pi \rho}{3kT} \int_0^{r_{12}} r_{12} \frac{du(r_{12})}{dr_{12}} g^{(2)}(r_{12}) dr_{12} - \frac{\rho^2}{6kT} \int \int g^{(3)}(123) w(123) \, dr_{12} \, dr_{13} + \cdots \]  

(12)

Similarly, for a mixture with \( m \) components the following relation holds for the compressibility

\[ Z_m = \frac{2\pi \rho}{3kT} \sum_{i<j} X_i X_j \int_0^{r_{ij}} r_{ij} \frac{du(r_{ij})}{dr_{ij}} g^{(2)}(r_{ij}) dr_{ij} \]

\[ - \frac{\rho^2}{6kT} \sum_{i<j<k} X_i X_j X_k \int \int g^{(3)}(123) w(123) \, dr_{12} \, dr_{13} \]  

(13)

In eqns (12) and (13), \( g^{(2)} \) stands for the radial distribution function and \( g^{(3)} \) stands for the triplet-distribution function.

In order to derive the mixing rules for the \( HSE \) conformal solution theory, at this point, we expand \( g^{(2)} \) and \( g^{(3)} \) (which appear in eqns (12) and (13)) with respect to the inverse powers of temperature. Next, we equate the coefficients of the equal powers of inverse temperatures in these two equations. The procedure and the assumptions involved in this regard are very much similar to the case of the original \( HSE \) conformal solution theory where the Lennard-Jones 2-parameter potential function was used as the pair potential [9, 15].

By equating the coefficients of the zeroth order terms with respect to \( 1/T \) (the hard-sphere terms) for the mixture and for the reference system, the following relation is obtained

\[ \sigma^3 = \sum_{i<j} X_i X_j \sigma_{ij}^3 \]  

(14)

By equating the coefficients of the first order terms with respect to \( 1/T \), the following relations are derived

\[ \varepsilon \sigma^3 = \sum_{i<j=k} X_i X_j \varepsilon_{ij} \sigma_{ij}^3 \]  

(15)

\[ \varepsilon \sigma^3 \gamma = \sum_{i<j=k} X_i X_j \varepsilon_{ij} \sigma_{ij}^3 \gamma_{ij} \]  

(16)

and

\[ \frac{E}{\sigma^3} = \sum_{i<j=k} X_i X_j \frac{V_{ij}}{(\sigma_{ij} \sigma_{jk} \sigma_{ki})} \]  

(17)

The relation obtained as a result of equating the coefficients of the leading terms of \((1/T)^2\) is as follows

\[ \varepsilon^2 \sigma^3 = \sum_{i<j=k} X_i X_j \varepsilon_{ij} \sigma_{ij}^3 , \text{ etc.} \]  

(18)

In observing the above equations, undoubtedly, the most important one for the prediction of mixture properties is eqn (14). This equation is actually the mixing rule for hard-sphere mixture. Due to the availability of the accurate equation of state of pure hard-sphere fluid and
hard-sphere fluid mixture, it would not be necessary to keep eqn (14) as a mixing rule for fluid mixture. As a result we may use eqns (15)-(18) in order to find the relations for $\bar{\sigma}$, $\bar{\epsilon}$, $\bar{\gamma}$ and $\bar{\nu}$ which will be needed for the HSE conformal solution theory. That is, from eqns (15)-(18), we can write

$$
\epsilon = \frac{\sum_{i,j=1}^{n} X_i X_j \sigma_{ij} \varphi_{ij}}{\sum_{i=1}^{m} X_i \sigma_{ii} \varphi_{ii}}
$$

(19)

$$
\bar{\sigma}^2 = \sum_{i,j=1}^{n} X_i X_j \sigma_{ij} \varphi_{ij} \bar{\epsilon}
$$

(20)

$$
\bar{\gamma} = \sum_{i,j=1}^{n} X_i X_j \sigma_{ij} \varphi_{ij} \bar{\gamma}_{ij} / (\bar{\sigma}^2 \bar{\epsilon})
$$

(21)

$$
\bar{\nu} = \bar{\sigma}^2 \sum_{i,j=1}^{n} X_i X_j X_k \nu_{ijk} / (\sigma_{ik} \sigma_{jk} \sigma_{kj}).
$$

(22)

In utilizing the above mixing rules when calculating the mixture properties, it is necessary to have available the like- and unlike-potential parameters of the components of the mixture which appear in these mixing rules. The like-pair potential parameters $\epsilon_{ii}$, $\sigma_{ii}$, and $\gamma_{ii}$ are usually calculated from the second virial coefficient data of pure gases when they are used for thermodynamic property predictions[16]. In the case of transport property predictions, it is more appropriate to derive these parameters from gas transport property data[16]. The like-triplet potential parameter $\nu_{iii}$ may be calculated by the following relation[13]

$$
\nu_{iii} = \frac{9}{16} I \alpha^3.
$$

(23)

Where $I$ is the ionization potential and $\alpha$ is the polarizability.

For the calculation of unlike-pair potential parameters it is preferable to have available the experimental data on the cross-second virial coefficients of mixtures readily accessible. For most of the mixtures which are under study in the present report, the cross-second virial coefficient data is not available. It is a usual practice to relate the unlike-pair potential parameters to the like-pair potential parameters. Such relationships are called the “combining rules”[17]. Various combining rules for unlike-pair interaction parameters have been proposed[18]. The most commonly used combining rules are the following

$$
\sigma_{ij} = \frac{1}{2} (\sigma_{ii} + \sigma_{jj})
$$

(24)

$$
\gamma_{ij} = \frac{1}{2} (\gamma_{ii} + \gamma_{jj})
$$

(25)

and

$$
\epsilon_{ij} = (1 - k_{ij})(\epsilon_{ii} \epsilon_{jj})^{1/2}.
$$

(26)

The validity of the combining rules (24) and (25) are obvious in the case of hard-sphere mixture and molecules with spherical-cores; respectively. It is expected that relations (24) and (25) are accurate for real mixtures with molecules close to spherical shapes. When $k_{ij} = 0$ the above combining rules are called the Lorentz–Berthelot combining rules which are valid for simple mixtures. Generally, $k_{ij}$ is not equal to zero and therefore should be calculated from the cross-second virial coefficient data or the excess thermodynamic properties of equimolar binary mixtures[17]. In calculating the unlike-triplet interaction parameter, $\nu_{ijk}$, the following relation may be used[13].

$$
\nu_{ijk} = \frac{3}{2} \frac{(I_i + I_j + I_k)(I_i I_j I_k) \sigma_{ii} \sigma_{jj} \sigma_{kk}}{(I_i + I_j)(I_i + I_k)(I_j + I_k)}.
$$

(27)

In the above relation $I_i$ is the ionization potential and $\alpha_i$ is the polarizability of a component $i$ of the mixture.
MIXTURE EQUATION OF STATE

As previously mentioned, the statistical thermodynamic perturbation equation of state has been quite successful in producing accurate equations of state for fluids possessing 2- and 3-body potential functions. The authors have improved the perturbation equation of state of pure fluids and have developed the following equation of state for the Helmholtz free energy of pure classical non-polar fluids possessing 2- and 3-body potential energy functions [15, 19]

\[
\frac{A_{m}^{\text{erm}}}{NkT} = \frac{A_{o}^{\text{erm}}(\eta)}{NkT} + \frac{6\eta}{T^{*}} 2[J_{d}(\theta, \gamma^{*}, c) - J_{d}(\theta, \gamma^{*}, c) + J_{d}(\theta, \gamma^{*}, c)]
\]

\[
- kT \left( \frac{\partial \rho}{\partial P} \right)_{T}^{*} \frac{1}{T^{*}} [J_{d}(\theta, \gamma^{*}, c) - J_{d}(\theta, \gamma^{*}, c) + J_{d}(\theta, \gamma^{*}, c)]
\]

\[
+ \frac{A_{3b}(\nu(T^{*}d^{*}), \eta)}{NkT} .
\]  

(28)

In the above equation, \(A_{m}^{\text{erm}}\) is the Helmholtz free energy of the pure classical non-polar fluid, according to perturbation theory; \(A_{o}^{\text{erm}}(\eta)\) is the pure hard-sphere Helmholtz free energy given by eqn (A1) of Appendix; \(T^{*} = kT/\epsilon\); \(\eta = (\pi/6) \times \rho \sigma^{3}\); \(c = d/\sigma\); and \(d\) is defined by the following relation

\[
d = \int_{0}^{\infty} \left[ 1 - \exp \left( - \frac{\mu(r)}{kT} \right) \right] dr.
\]

(29)

The functional forms for \(A_{o}^{\text{erm}}, J_{1}, J_{2}, J_{3}, \ldots J_{n}, kT(\partial \rho/\partial P)^{\nu}, \) and \(A_{3b}\) are, all, given in the Appendix.

When considering the above perturbation equation of state as the reference pure equation of state, the following relation will hold for the Helmholtz free energy of the mixture according to the HSE conformal solution theory

\[
A_{m} = A_{o}^{\text{erm}}(\rho, \sigma, \epsilon_{i}; \chi; i = 1, \ldots, m) + A_{m}^{\text{erm}}(\tilde{T}^{*}, \tilde{\eta}^{*}, \tilde{\epsilon}, \tilde{\nu}, \tilde{\tilde{\nu}}) - A_{o}^{\text{erm}}(\tilde{\eta}_{0}).
\]

(30)

In this equation, \(A_{m}^{\text{erm}}\) is the hard-sphere mixture Helmholtz free energy shown by eqn (A4) of the Appendix. Also in the above equation

\[
\tilde{T}^{*} = \frac{kT}{\epsilon}, \quad \tilde{\eta} = \frac{\pi}{6} \rho \sigma^{3} \chi^{3}, \quad \tilde{\eta}_{0} = \frac{\pi}{6} \rho \sigma^{3} \quad \text{and} \quad \tilde{\nu} = \tilde{\epsilon}/\tilde{\sigma} \quad \text{with}
\]

\[
\tilde{d} = \tilde{\sigma} \int_{0}^{\infty} \left[ 1 - \exp \left( - \frac{\mu(X)}{kT} \right) \right] dX, \quad \tilde{X} = \frac{r}{\sigma}.
\]

(31)

The HSE mixing rules for pseudo-potential parameters \(\tilde{\epsilon}, \tilde{\sigma}, \tilde{\nu}, \) and \(\tilde{\gamma}\) are given by eqns (19)-(22). With the availability of eqn (30) for the Helmholtz free energy of the mixture, one may calculate other thermodynamic properties of the mixture through classical thermodynamic relations. The compressibility of the mixture may be calculated from the Helmholtz free energy through the following equation

\[
Z_{m} = \rho \frac{\partial}{\partial \rho} \left[ \left( \frac{A_{m}}{NkT} \right) \right] T, \chi.
\]

(32)

Of particular importance in the thermodynamics of mixtures, are the excess properties of the mixture over the properties of an ideal mixture at the same temperature and pressure. The excess volume at constant temperature and pressure, \(V^{e}\), is given by the following relation

\[
V^{e} = V_{m} - \sum_{i=1}^{n} X_{i} V_{i}.
\]

(33)

where \(V_{m}\) and \(V_{i}\) are the volumes of the mixture and pure component \(i\), respectively, all at the same temperature and pressure. The excess Helmholtz free energy, \(A^{e}\), will be given by the
following relation

\[ A^E = \left( A_m - A_m^{vd} \right) \sum_{i=1}^m X_i \left( A_{pi} - A_{pi}^{vd} \right) - NkT \ln \left( \frac{V_m}{\prod_{i=1}^m V_{pi}} \right). \]  

(34)

From the relations for the excess volume and the excess Helmholtz free energy we get the following relation for the excess Gibbs free energy

\[ G^E = A^E + PV^E. \]  

(35)

When calculating the vapor–liquid equilibria properties of a mixture, it is necessary to derive relations for the fugacities of components of the mixture. For a binary mixture, the following relation holds for the fugacity of one of the components with respect to the Helmholtz free energy and compressibility of the mixture

\[ \ln \left( \frac{f_i}{X_i P} \right) = Z_m - 1 - \ln Z_m + \frac{A_m - A_m^{vd}}{NkT} X_i \frac{\partial}{\partial X_i} \left( \frac{A_m - A_m^{vd}}{NkT} \right)_{\tau, \rho} ; \quad (i \neq j) = (1, 2). \]  

(36)

For a ternary mixture, the following relation holds for the fugacity of one of the components

\[ \ln \left( \frac{f_i}{X_i P} \right) = Z_m - 1 - \ln Z_m + \frac{A_m - A_m^{vd}}{NkT} X_i \frac{\partial}{\partial X_i} \left( \frac{A_m - A_m^{vd}}{NkT} \right)_{\tau, \rho, X_k} - X_k \frac{\partial}{\partial X_k} \left( \frac{A_m - A_m^{vd}}{NkT} \right)_{\tau, \rho, X_k} ; \quad (i \neq j \neq k) = (1, 2, 3). \]  

(37)

For mixtures with larger number of components, similar relations for the fugacities of components can be derived. By joining the HSE equation of state for mixture, eqn (30), with the above thermodynamic relations it is possible to calculate thermodynamic functions of mixtures.

The major advantages of the HSE conformal solution theory over other theories of fluid mixtures are as follows: (a) The choice of perturbation equation of state, eqn (28), as the pure reference equation of state makes the HSE theory free from any empirical correlation, (b) Contributions of both 2- and 3-body interaction potentials are considered in the HSE theory; (c) The HSE theory is applicable to mixtures with any number of components; (d) Unlike the semiempirical approaches of thermodynamics, the relations based on the HSE theory are valid for both liquid and vapor phases and there is no need for auxiliary functions (i.e. activity and fugacity coefficients) in vapor–liquid equilibria property predictions of mixtures; (e) The computation time and the computer storage space needed for the HSE technique are considerably smaller than the other theories of mixtures in the mixture property predictions.

**PREDICTION OF VAPOR–LIQUID EQUILIBRIA (VLE) PROPERTIES OF MIXTURES**

The following is the necessary and sufficient condition for VLE of mixtures[1, 2]

\[ f_i'(P, T, X_1', X_2', \ldots, X_m') = f_i'(P, T, X_1', X_2', \ldots, X_m') , \quad i = 1, 2, \ldots, m \]  

(38)

with

\[ \sum_{i=1}^m X_i' = \sum_{i=1}^m X_i = 1.0. \]

Superscripts \( V \) and \( L \) stand for vapor and liquid phases, respectively.

For utilization of the HSE theory in the VLE prediction of mixtures, the only data necessary are values of the intermolecular potential parameters, ionization potentials, and polarizabilities of molecules of the species of the mixture. The usual multivariable regression techniques may be used to predict the VLE properties of mixtures through the application of eqn (38).
In Table 1 values of the Kihara potential parameters of different molecules under study here are listed. In Table 2 values of $\nu$, derived through eqn (23), are listed. In Table 3 values of $k_o$ defined by eqn (26) and calculated by the HSE technique and by other theories of fluid mixtures are reported for different interactions. In the absence of the cross-second virial coefficient data, $k_o$ values are calculated from excess thermodynamics properties by fitting the mixture equation of state to an excess property of a binary liquid mixture of equimolar composition.

The mixture of argon–krypton which basically satisfies the assumptions of the HSE theory, should provide a more rigorous test of this theory. On the other hand, mixtures of argon–methane and methane–krypton are interesting to study because of the existence of the globular-symmetric molecule of methane in these systems. Experimental VLE properties for these mixtures[29] are available at 115.77°K. In here, phase behaviors of these mixtures are predicted by carrying out bubble pressure calculations and the predicted isotherms are reported in Fig. 1 together with the experimental values. The use of suitable $k_o$ values has improved the predicted values of VLE properties of these mixtures considerably. Generally, the predicted values of VLE properties are in very good agreement with the experimental data.

The next group of mixtures under study here are binary mixtures of nitrogen–argon and nitrogen–methane. Each of these mixtures contains a component with diatomic molecules and another component with spherical or globular-symmetric molecules. The bubble temperature calculations are carried out here for nitrogen–argon mixture as shown in Table 4. In Fig. 2

### Table 1. Intermolecular potential parameters for Kihara spherical-core potential function

<table>
<thead>
<tr>
<th>Substance</th>
<th>$a^* (=\frac{\lambda}{\sigma^3})$</th>
<th>$\sigma. A^0$</th>
<th>$\epsilon/k, ^\circ K$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar (83-873°K)</td>
<td>0.125</td>
<td>3.314</td>
<td>147.20</td>
<td>20</td>
</tr>
<tr>
<td>Kr (113-873°K)</td>
<td>0.150</td>
<td>3.521</td>
<td>215.60</td>
<td>20</td>
</tr>
<tr>
<td>N$_2$ (123-873°K)</td>
<td>0.250</td>
<td>3.526</td>
<td>139.20</td>
<td>20</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.308</td>
<td>3.109</td>
<td>194.30</td>
<td>2</td>
</tr>
<tr>
<td>CH$_4$ (274-423°K)</td>
<td>0.20</td>
<td>3.620</td>
<td>204.30</td>
<td>20</td>
</tr>
<tr>
<td>CF$_4$ (273-423°K)</td>
<td>0.50</td>
<td>4.319</td>
<td>289.70</td>
<td>20</td>
</tr>
<tr>
<td>CO$_2$ (262.7-873.2°K)</td>
<td>0.615</td>
<td>3.760</td>
<td>424.16</td>
<td>20</td>
</tr>
<tr>
<td>C$_2$H$_6$ (2632-473.2°K)</td>
<td>0.0263</td>
<td>3.912</td>
<td>328.21</td>
<td>21</td>
</tr>
<tr>
<td>C$_2$H$_4$ (200-523.2°K)</td>
<td>0.397</td>
<td>3.977</td>
<td>425.32</td>
<td>21</td>
</tr>
<tr>
<td>C(CH$_3$)$_4$ (363-648°K)</td>
<td>0.550</td>
<td>5.785</td>
<td>554.20</td>
<td>21</td>
</tr>
</tbody>
</table>

### Table 2. Values of ionization potential, polarizability and $\nu$, the coefficient of the triple-dipole potential function calculated through eqn (23), for different substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>$I_1$ (ev)</th>
<th>$\alpha$ (Å$^3$/mole)</th>
<th>$\nu/k \times 10^4$ (Å$^3$K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>15.96</td>
<td>1.6244</td>
<td>44.669</td>
</tr>
<tr>
<td>Kr</td>
<td>13.94</td>
<td>2.465</td>
<td>134.850</td>
</tr>
<tr>
<td>N$_2$</td>
<td>15.51</td>
<td>1.734</td>
<td>52.265</td>
</tr>
<tr>
<td>O$_2$</td>
<td>12.063</td>
<td>1.60</td>
<td>32.265</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>13.16</td>
<td>2.699</td>
<td>168.959</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>13.769</td>
<td>2.65</td>
<td>167.327</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>10.50</td>
<td>4.26</td>
<td>530.074</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>11.50</td>
<td>4.47</td>
<td>670.722</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>10.35</td>
<td>10.14</td>
<td>7046.54</td>
</tr>
</tbody>
</table>

Table 3. Comparison of the experimental and theoretical values of excess thermodynamic properties at $P = 0$ and $x_1 = x_2 = 0.5$ for different binary mixtures. $G^e$ is in J/mole and $V^e$ is in cc/mole. The fifth column gives the $k_1$ values obtained from this investigation. The calculated excess properties in the brackets are the fitted values through which the $k_1$ values are calculated.

<table>
<thead>
<tr>
<th>System</th>
<th>Property</th>
<th>Exptl.</th>
<th>Calculated (HSE)</th>
<th>$k_1$(HSE)</th>
<th>$k_1$(other theories)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar + Kr</td>
<td>$G^e$</td>
<td>84.0</td>
<td>(84.0)</td>
<td>0.008</td>
<td>0.017 (Ref. [25])</td>
</tr>
<tr>
<td>(115.8 K)</td>
<td>$V^e$</td>
<td>-0.53</td>
<td>(Ref. [17])</td>
<td>-0.55</td>
<td></td>
</tr>
<tr>
<td>Ar + CH$_4$</td>
<td>$G^e$</td>
<td>74.0</td>
<td>(74.0)</td>
<td>0.021</td>
<td>0.028 (Ref. [25])</td>
</tr>
<tr>
<td>(91 K)</td>
<td>$V^e$</td>
<td>0.17</td>
<td>(Ref. [17])</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$ + Kr</td>
<td>$G^e$</td>
<td>28.66</td>
<td>(28.66)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(115.8 K)</td>
<td>$V^e$</td>
<td>-0.022</td>
<td>(Ref. [24])</td>
<td>-0.037</td>
<td>0.0026 (Ref. [26])</td>
</tr>
<tr>
<td>N$_2$ + CH$_4$</td>
<td>$G^e$</td>
<td>135.0</td>
<td>(135.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(91 K)</td>
<td>$V^e$</td>
<td>-0.21</td>
<td>(Ref. [17])</td>
<td>-0.53</td>
<td>0.021 (Ref. [26])</td>
</tr>
<tr>
<td>N$_2$ + Ar</td>
<td>$G^e$</td>
<td>34.0</td>
<td>(34.0)</td>
<td></td>
<td>0.030 (Ref. [26])</td>
</tr>
<tr>
<td>(84 K)</td>
<td>$V^e$</td>
<td>-0.18</td>
<td>(Ref. [17])</td>
<td>-0.09</td>
<td>0.0013 -0.001 (Ref. [25])</td>
</tr>
<tr>
<td>Ar + O$_2$</td>
<td>$G^e$</td>
<td>37.0</td>
<td>(37.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(84 K)</td>
<td>$V^e$</td>
<td>0.14</td>
<td>(Ref. [17])</td>
<td></td>
<td>0.010 0.013 (Ref. [25])</td>
</tr>
<tr>
<td>N$_2$ + O$_2$</td>
<td>$G^e$</td>
<td>42.0</td>
<td>(42.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(78 K)</td>
<td>$V^e$</td>
<td>-0.3</td>
<td>(Ref. [17])</td>
<td>-0.60</td>
<td>0.030 -0.002 (Ref. [25])</td>
</tr>
<tr>
<td>CF$_2$ + CH$_4$</td>
<td>$G^e$</td>
<td>360.0</td>
<td>(360.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(111°K)</td>
<td>$V^e$</td>
<td>0.88</td>
<td>(Ref. [17])</td>
<td>0.65</td>
<td>0.077 0.091 (Ref. [27])</td>
</tr>
<tr>
<td>CO$_2$ + CH$_4$</td>
<td>$G^e$</td>
<td>37.0</td>
<td>(37.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(244.4°K)</td>
<td>$V^e$</td>
<td>0.14</td>
<td>(Ref. [17])</td>
<td></td>
<td>0.010 0.013 (Ref. [25])</td>
</tr>
</tbody>
</table>

Table 4. Calculated and experimental vapor-liquid equilibria data for the binary mixture of nitrogen-argon at 6 and 18 atm

<table>
<thead>
<tr>
<th>Given properties</th>
<th>$T$ (°K)</th>
<th>$X_{c_{2}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calcd</td>
</tr>
<tr>
<td></td>
<td>$x_{c_{2}}$ (Ref. [31])</td>
<td>$k_0 = 0$</td>
</tr>
<tr>
<td>$P = 6$ atm</td>
<td>0.145</td>
<td>0.266</td>
</tr>
<tr>
<td></td>
<td>0.376</td>
<td>0.558</td>
</tr>
<tr>
<td></td>
<td>0.622</td>
<td>0.768</td>
</tr>
<tr>
<td></td>
<td>0.741</td>
<td>0.851</td>
</tr>
<tr>
<td></td>
<td>0.937</td>
<td>0.966</td>
</tr>
<tr>
<td>Average deviation†</td>
<td>0.7%</td>
<td>0.4%</td>
</tr>
<tr>
<td>$P = 18$ atm</td>
<td>0.167</td>
<td>0.250</td>
</tr>
<tr>
<td></td>
<td>0.271</td>
<td>0.373</td>
</tr>
<tr>
<td></td>
<td>0.458</td>
<td>0.576</td>
</tr>
<tr>
<td></td>
<td>0.620</td>
<td>0.715</td>
</tr>
<tr>
<td></td>
<td>0.871</td>
<td>0.915</td>
</tr>
<tr>
<td>Average deviation†</td>
<td>1.1%</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

† Average deviation = $\frac{1}{N} \sum_{i=1}^{N} \left[ \frac{|X_{\text{exptl}} - X_{\text{calcd}}|}{X_{\text{exptl}}} \right] \times 100$

Table 5. Experimental and calculated mixture critical data of argon-neopentane and methane-neopentane mixtures

<table>
<thead>
<tr>
<th>Argon-Neopentane at 50°C</th>
<th>Methane-Neopentane at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exptl†</td>
</tr>
<tr>
<td>Pressure (ATM)</td>
<td>252.0</td>
</tr>
<tr>
<td>Composition $X_{c_{2}}$</td>
<td>0.265</td>
</tr>
<tr>
<td>Density (Gmoles/l.)</td>
<td>11.3</td>
</tr>
</tbody>
</table>

† Ref. [33].
bubble pressure calculations for VLE property of nitrogen–methane mixture are reported. For these two mixtures, the HSE theory is also quite successful in predicting VLE properties.

It is interesting to study binary mixtures of argon–neopentane and methane–neopentane because of the substantial molecular size differences which exist between the components of these mixtures. Experimental data available for these mixtures are around their critical states[33]. Figure 3 exhibits the calculated isotherms for methane–neopentane system at 50°C and for argon–neopentane system at 25°C, respectively, on a P–X phase diagram. For \( k_i = 0 \), there exist considerable differences between predicted and experimental values of the saturated pressure of both of these mixtures. Nevertheless, predicted isotherms show the same trends as those of the experimental values. Improvements in the VLE predictions are possible with the knowledge of \( k_i \) values of these mixtures. Because of the lack of experimental data for the cross-second virial coefficient or the excess functions of mixing of these mixtures, their \( k_i \) values can not be calculated. In Table 5 predicted and experimental critical data for these mixtures are reported.

Mixture of carbontetrafluoride–methane consists of two components with globular molecules and considerable size difference between them. In Fig. 4 a predicted isotherm based on bubble pressure calculation together with the experimental data for this mixture[34] is reported. With the use of a suitable \( k_i \) value, the predicted equilibrium curves are altered from the case of \( k_i = 0 \), and the results are drastically improved. It should be pointed out that the available pair-potential parameters of both carbontetrafluoride and methane are valid only for the temperature range of 274–623 K. The calculations reported in Fig. 4 are for 98°C. The inaccuracy of the potential parameters at 98°C might be a reason for the deviation of predictions from experimental data.
The HSE technique in its present form may be applied to mixtures composed of molecules that interact with central potentials. Even so, it is still possible to predict the appearance of such singular states of mixtures like critical and azeotropic points through the application of the HSE theory. Mixtures of carbon dioxide–ethylene and carbon dioxide–ethane possess minimum boiling temperature (maximum boiling pressures) azeotropes. The VLE data for carbon dioxide–ethylene[35] are shown by a \( T - X \) diagram in Fig. 5 along with the calculations based on the HSE technique. For ethylene, there exist two sets of pair-potential parameters as reported in Table 1. The first set (with \( \gamma = 0 \)) is from the second virial coefficient data and the second set is from the combination of the second virial coefficient and viscosity data. In here the second set of parameters is used. By using the first set of parameters, no VLE for carbon dioxide–ethylene mixture was predictable. Calculation reported on Fig. 5 are for \( k_{ij} = 0 \), and \( k_{ij} = 0.06 \) (derived from the cross-second virial coefficient data[26]). With \( k_{ij} = 0 \), the predicted isobars are completely inadequate in describing the VLE behavior of this mixture and that no azeotropy is predicted. With \( k_{ij} = 0.06 \), the two predicted isobars possess azeotropic points which are also the case for the experimental isobars. Experimental data indicates that the positions of the minimum boiling points shift with temperature towards an azeotrope richer in the component with higher critical temperature (carbon dioxide in this case). The HSE theory correctly predicts the trend of the experimental data as it is indicated by the azeotropic locus on Fig. 5. Also, for carbon dioxide–ethane mixture the VLE properties are predicted when \( k_{ij} = 0 \) without showing any azeotropic behavior. The introduction of an appropriate \( k_{ij} \) value (\( k_{ij} = 0.21 \)) causes the change of the shape of isotherms in the \( P - X \) diagram, resulting in the
Fig. 3. Pressure-composition diagrams for argon-neopentane mixture at 50°C and methane-neopentane mixture at 25°C.

Fig. 4. Pressure-composition diagram for methane-carbontetrafluoride mixture at 98.01°K.
appearance of the maximum pressure boiling points as is shown in Fig. 6. Also Fig. 6 indicates that the predicted azeotropic locus has the same trend as the experimental locus [28, 36] for this mixture. In view of these results it may be concluded that satisfactory azeotropy predictions are possible through the HSE technique with the availability of reliable potential parameters for the components of the mixtures. Computations also indicate that while the 3-body potential

![Figure 5. Temperature-composition diagram for carbon dioxide-ethylene mixture at 20 and 40 atm.](image)

| Table 6. Experimental and calculated results of bubble temperature calculation of the ternary mixture of nitrogen-argon-oxygen |
|---|---|---|---|---|---|---|---|
| **Given properties** | **T(°K)** | **X₆₂** | **X₆₃** | **X₈₃** | **Exptl Ref.** | **Calculated** | **Exptl Ref.** | **Calculated** | **Exptl Ref.** | **Calculated** | **Exptl Ref.** | **Calculated** |
| | | **kᵣ = 0** | **kᵣ ≠ 0** | | | | **kᵣ = 0** | **kᵣ ≠ 0** | | | **kᵣ = 0** | **kᵣ ≠ 0** |
| **P = 6 atm** | | | | | | | | | | | | |
| 0.890 | 0.024 | 97.6 | 94.1 | 95.2 | 0.950 | 0.950 | 0.950 | 0.012 | 0.012 | 0.012 | 0.012 |
| 0.771 | 0.062 | 98.7 | 95.3 | 96.4 | 0.884 | 0.889 | 0.889 | 0.074 | 0.031 | 0.032 |
| 0.515 | 0.188 | 101.5 | 98.3 | 99.5 | 0.707 | 0.725 | 0.722 | 0.074 | 0.110 | 0.111 |
| 0.364 | 0.181 | 103.7 | 100.5 | 101.8 | 0.570 | 0.594 | 0.589 | 0.091 | 0.119 | 0.121 |
| 0.229 | 0.174 | 105.9 | 103.0 | 104.3 | 0.412 | 0.435 | 0.430 | 0.127 | 0.132 | 0.133 |
| Average deviation | 3.2% | 1.9% | 2.6% | 2.1% | | | | | | | | |
| **P = 18 atm** | | | | | | | | | | | | |
| 0.762 | 0.184 | 116.5 | 115.1 | 116.1 | 0.839 | 0.843 | 0.840 | 0.126 | 0.123 | 0.125 |
| 0.597 | 0.097 | 119.3 | 117.9 | 119.0 | 0.708 | 0.708 | 0.702 | 0.074 | 0.070 | 0.071 |
| 0.262 | 0.094 | 124.8 | 123.5 | 124.7 | 0.380 | 0.396 | 0.368 | 0.091 | 0.080 | 0.080 |
| 0.110 | 0.119 | 127.6 | 126.9 | 128.1 | 0.181 | 0.188 | 0.183 | 0.127 | 0.112 | 0.112 |
| 0.017 | 0.107 | 129.8 | 129.2 | 130.5 | 0.030 | 0.031 | 0.030 | 0.122 | 0.109 | 0.108 |
| Average deviation | 0.9% | 0.3% | 2.4% | 0.8% | | | | | | | | |

has quantitative effect on the location of azeotropic point it does not contribute to its appearance. It would also be interesting to apply the HSE technique in prediction of minimum boiling pressure (maximum boiling temperature) azeotropes. The only nonpolar mixture with this characteristic for which there is experimental data available is carbon dioxide-acetylene mixture[17]. Due to the unavailability of the Kihara intermolecular potential parameters for the components of this mixture, it was not possible to study this system by the HSE theory.

Table 7. Experimental and calculated results of bubble temperature calculation of the ternary mixture of nitrogen-argon-methane

| Given properties | \(T(\text{°K})\) | \(X_{c_w}^e\) | \(X_{c_w}^a\) |
|------------------|------------------|------------------|
| \(P(\text{atm})\) | \(X_{c_w}^e\) | \(X_{c_w}^a\) | \(X_{c_w}^e\) | \(X_{c_w}^a\) |
| 8.981            | 0.2180           | 0.7031           | 112.0          | 113.2          | 113.0 | 0.3802 | 0.3721 | 0.3773 | 0.6025 | 0.6136 | 0.6067 |
| 8.971            | 0.3003           | 0.4959           | 112.0          | 113.6          | 112.9 | 0.5313 | 0.5209 | 0.5336 | 0.4260 | 0.4416 | 0.4282 |
| 8.981            | 0.3595           | 0.3382           | 112.0          | 114.0          | 112.8 | 0.6455 | 0.6354 | 0.6545 | 0.6354 | 0.6545 | 0.6290 |
| 8.976            | 0.4156           | 0.1880           | 112.0          | 114.4          | 112.5 | 0.7592 | 0.7488 | 0.7726 | 0.1644 | 0.1747 | 0.1617 |
| 12.943           | 0.6546           | 0.3119           | 112.0          | 113.7          | 113.5 | 0.7763 | 0.7743 | 0.7743 | 0.2155 | 0.2191 | 0.2185 |
| 12.971           | 0.6916           | 0.2251           | 112.0          | 113.9          | 113.7 | 0.8299 | 0.8248 | 0.8248 | 0.1520 | 0.1593 | 0.1576 |
| 12.997           | 0.7234           | 0.5185           | 112.0          | 113.9          | 113.7 | 0.8672 | 0.8690 | 0.8690 | 0.1077 | 0.1120 | 0.1105 |
| 12.968           | 0.7595           | 0.0878           | 112.0          | 113.9          | 113.6 | 0.9408 | 0.9108 | 0.9081 | 0.0384 | 0.0624 | 0.0609 |

Average deviation 1.6% 1.1% 1.4% 1.1% 3.8% 1.6%
Table 8. Experimental and calculated results of bubble pressure calculation of the ternary mixture of nitrogen-argon-methane

<table>
<thead>
<tr>
<th>Given properties</th>
<th>Exptl</th>
<th>Calculated</th>
<th>Exptl</th>
<th>Calculated</th>
<th>Exptl</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ref.</td>
<td></td>
<td>Ref.</td>
<td></td>
<td>Ref.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[32]</td>
<td></td>
<td>[32]</td>
<td></td>
<td>[32]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(k_{ij} \neq 0)</td>
<td>(k_{ij} = 0)</td>
<td>(k_{ij} \neq 0)</td>
<td>(k_{ij} = 0)</td>
<td>(k_{ij} \neq 0)</td>
<td>(k_{ij} = 0)</td>
</tr>
<tr>
<td>(X_1)</td>
<td>0.218</td>
<td>0.703</td>
<td>8.981</td>
<td>8.523</td>
<td>8.531</td>
<td>0.380</td>
</tr>
<tr>
<td>(X_2)</td>
<td>0.300</td>
<td>0.496</td>
<td>8.971</td>
<td>8.356</td>
<td>8.459</td>
<td>0.531</td>
</tr>
<tr>
<td>(X_3)</td>
<td>0.416</td>
<td>0.188</td>
<td>8.976</td>
<td>8.065</td>
<td>8.420</td>
<td>0.759</td>
</tr>
<tr>
<td>Average deviation</td>
<td>7.7%</td>
<td>5.8%</td>
<td>4.0%</td>
<td>1.3%</td>
<td>2.6%</td>
<td>3.0%</td>
</tr>
<tr>
<td>(T = 112^\circ K)</td>
<td>0.655</td>
<td>0.312</td>
<td>12.94</td>
<td>12.05</td>
<td>12.71</td>
<td>0.777</td>
</tr>
<tr>
<td></td>
<td>0.692</td>
<td>0.225</td>
<td>12.97</td>
<td>11.94</td>
<td>11.97</td>
<td>0.830</td>
</tr>
<tr>
<td></td>
<td>0.723</td>
<td>0.159</td>
<td>13.00</td>
<td>11.92</td>
<td>11.98</td>
<td>0.867</td>
</tr>
<tr>
<td></td>
<td>0.760</td>
<td>0.088</td>
<td>12.97</td>
<td>11.92</td>
<td>12.02</td>
<td>0.941</td>
</tr>
<tr>
<td>Average deviation</td>
<td>9.2%</td>
<td>6.1%</td>
<td>1.0%</td>
<td>1.0%</td>
<td>1.7%</td>
<td>0.7%</td>
</tr>
</tbody>
</table>

The VLE properties of two non-polar ternary mixtures are also investigated through the HSE theory (argon-oxygen-nitrogen and argon-nitrogen-methane). The \(k_{ij}\) values for these mixtures are reported in Table 3. Calculated results along with the experimental data[31, 32] for the VLE properties of these mixtures are reported in Tables 6-8. The predicted results for these ternary mixtures are as reliable as the results for the binary mixtures reported above.

CONCLUSIONS

In applying the HSE theory for the prediction of VLE properties of mixtures, it may be concluded that:

1. The HSE theory, coupled with an accurate pair potential function, such as the Kihara potential, and the inclusion of the 3-body effects in the pure perturbation equation of state, in general, is capable of predicting mixture properties at critical regions, as in systems argon-neopentane and methane-neopentane; at cryogenic region, as in systems of nitrogen-argon-oxygen and nitrogen-argon-methane; at elevated pressures, as in nitrogen-argon system; and at low pressure, as in carbontetrafluoride-methane system.

2. The computation time necessary in applying the HSE theory to calculate VLE properties of mixtures is comparable with the empirical approaches and is considerably less time than that needed in the application of the other molecular theories of mixtures.

3. Application of the HSE theory for ternary mixtures yields quantitative predictions of phase equilibrium properties. Accuracy of the predicted values is comparable with those of its constituent binary mixtures. Contrary to other molecular theories of mixtures, the HSE theory can be employed to predict properties of mixtures having any number of components.

4. Advantages of using proper values of the unlike-pair interaction parameters, \(k_{ij}\)'s, for VLE predictions are shown in two ways: (a) When the predicted equilibrium curve on the phase diagram with \(k_{ij} = 0\) shows the same trend as the experimental measurements, the use of suitable \(k_{ij}\) value will bring the calculated results closer to the experimental values. This is observed in the investigation of systems argon-krypton, methane-krypton, argon-methane and nitrogen-methane; (b) When the calculated equilibrium curve on the phase diagram with \(k_{ij} = 0\) is obtained, but shows completely different shape from that of the experimental measurements, use of suitable \(k_{ij}\) values will change the shape of the predicted equilibrium curve such that the experimental and the theoretical results will have the same trends. This is observed through the studies of carbon-tetrafluoride-methane, carbon dioxide-ethylene and carbon dioxide-ethane mixtures. Perhaps the most profound effect of the suitable \(k_{ij}\) values is on the prediction of azeotropic points of mixtures of carbon dioxide-ethylene and carbon dioxide-ethane. When \(k_{ij} = 0\), the equilibrium curves obtained through the HSE technique for these mixtures are incapable of predicting any azeotropic state, while with using suitable values of \(k_{ij}\), the HSE theory predicts the appearance of the azeotropic points. The authors also performed computations on mixtures based on the Lennard-Jones potential function, rather
than the Kihara spherical-core potential function. With the use of Lennard-Jones potential function (i.e. $\gamma_u = 0$) no 2-phase region could be predicted for most of the mixtures studied.

(5) Consideration of 3-body potential has no effect on the prediction of VLE or azeotropic points although it improves the predictions.

(6) Application of the HSE technique for more complex mixture is subject to the detailed knowledge about the intermolecular potential functions of the components of mixtures which is lacking at the present time. With the employment of more realistic pair- and triplet-potential functions, as they may become available, and with a better understanding of the nature of the unlike-interaction parameters one may improve the working equations of the hard sphere conformal solution theory for application to the case of more complex mixtures.

Acknowledgement—The authors appreciate the support of this research by the U.S. National Science Foundation, grant GK-43139.

NOMENCLATURE

- $a^*$: $y/(\sigma - \gamma)$
- $A$: Helmholtz free energy
- $c$: $d\sigma$
- $c_i$: $c(1 + a^*)$
- $d$: hard-sphere diameter
- $f_i$: fugacity of component $i$ in the mixture
- $g$: radial distribution function
- $g^{0^m}_n$: distribution function
- $G$: Laplace transform of $y\phi_d(\pi, \gamma)$
- $I$: ionization potential
- $J_i$: defined by eqns (A5)-(A10)
- $k$: Boltzmann's constant
- $k_o$: geometric-mean correction factor as defined in eqn (26)
- $m$: number of components in a mixture
- $N$: number of molecules
- $P$: pressure
- $r$: intermolecular distance
- $T$: absolute temperature
- $u$: pair-intermolecular potential energy function
- $U$: total intermolecular potential energy function
- $U^*_1$: inverse Laplace transform of $yU^*(c, \gamma)$
- $U^*_2$: inverse Laplace transform of $yU^*(s, \gamma)$
- $V$: volume
- $w$: triplet-intermolecular potential energy function
- $X_i$: mole fraction of component $i$
- $\chi$: $r\sigma$
- $y$: $rf_d$
- $Z$: compressibility

Greek symbols

- $\alpha$: polarizability
- $\gamma$: Kihara spherical-core diameter
- $\gamma^*$: $y\sigma$
- $d_{\theta_0}$: correction term of $g_0$
- $e$: energy parameter of pair-potential energy function
- $\eta$: $\Pi_{\alpha}d_{16}$
- $\eta$: $\eta(1 - \eta)/16$
- $\rho$: $NI/V$ (number density)
- $\sigma$: length parameter of pair-potential energy function
- $\nu$: parameter of triple-dipole potential energy function

Subscripts and superscripts

- $0$: hard-sphere reference system
- $c$: dimensionless property
- $c$: critical property
- $m$: mixture
- $ij$: molecules $i$ and $j$
- $id$: ideal gas
- $L$: liquid phase
- $pY$: Percus–Yevick
- $p$: pure substance
- $V$: vapor phase

Helmholtz free energy of the hard-sphere pure fluid is [12]

\[
\frac{A_s^*-A_s^w}{NkT} = \frac{(4-3\eta)\eta}{(1-\eta)^3}.
\]

where

\[
\eta = \frac{\pi}{6} \rho a^3.
\]

Compressibility coefficient for the hard sphere pure fluid is [12]

\[
kT \frac{\partial^2 \rho}{\partial \rho^2} |_{\rho} = \frac{(1-\eta)^3}{(1+2\eta^2-\eta(4-\eta))}.
\]

Contribution to the Helmholtz free energy due to 3-body interactions [13] is as follows

\[
\frac{A_{3b}}{NkT} = \frac{\eta \pi^2}{kT a^2} \frac{9.87748 + 11.76739}{1-1.12789\eta + 0.73166\eta^2}.
\]

Helmholtz free energy of the hard-sphere mixture \(A_s^*/NkT\) is given by the following relation [12]

\[
\frac{A_s^*-A_s^w}{NkT} = -\frac{3}{2} \frac{1}{(1-y_1+y_2+y_3)+\frac{3y_1+2y_2+\frac{3}{2}(1-y_1-y_2-y_3)}{(1-\xi)}+\frac{1}{(1-\xi)}} + (y_s-1)\ln(1-\xi).
\]
where

\[ \xi = \sum_{i=1}^{n} \xi_i, \]
\[ \xi_i = \Pi_{k \neq i} \xi_k, \]
\[ y_i = \sum_{j=1}^{n} \Delta_{yj} \frac{\sigma_{yj} + \sigma_{yi}}{\sigma_{yj}}, \]
\[ \Delta_{yi} = \left[ \sum_{j=1}^{n} \xi_j \frac{\sqrt{\sigma_{yj}}}{\sigma_{yj}} \right], \]
\[ y_i = \left[ \sum_{j=1}^{n} \left( \xi_j \xi_i \right)^{1/2} X_i \right]. \]

and

\[ \Delta_{yi} = \left[ \sum_{j=1}^{n} \xi_j \frac{\sqrt{\sigma_{yj}}}{\sigma_{yj}} \right]. \]

The terms \( J_1, J_2, \ldots, J_4 \) appearing in eqn (28) are given by the following relations:[19]

\[ J_{i}(\theta, c) = \int_{0}^{\theta} G(\theta, S)U_{i}(S, S) \, dS, \quad (A5) \]
\[ J_{i}(\theta, c) = \int_{0}^{\theta} \theta^{i-1} G(\theta, y)u^{*}(c, y)y^{i-1} \, dy, \quad (A6) \]
\[ J_{i}(\theta, c) = \int_{0}^{\theta} G(\theta, s)U_{i}(c, s) \, ds, \quad (A7) \]
\[ J_{i}(\theta, c) = \int_{0}^{\theta} \theta^{i} G(\theta, y)u^{*}(c, y)y^{i} \, dy, \quad (A8) \]
\[ J_{i}(\theta, c) = \int_{0}^{\theta} \delta_{i}(\theta, y)u^{*}(c, y)y \, dy, \quad (A9) \]
\[ J_{i}(\theta, c) = \int_{0}^{\theta} \delta_{i}(\theta, y)u^{*}(c, y)y^{2} \, dy. \quad (A10) \]

In the above relations

\[ \theta = \eta \left( 1 - \frac{\eta}{16} \right), \]
\[ u^{*}(c, y) = 4\frac{(c_y - \rho^*)^{-2} - (c_y - \rho^*)^{-4}}{c_y}, \]
\[ U_{i}(c, s) = \frac{\delta_{i}^n}{c_i} e^{\frac{s a^*_i}{c_i}} \left[ \frac{1}{c_i^{10}} \left( 1 + \frac{s a^*_i}{11 c_i} \right) - \frac{1}{4!} \left( 1 + \frac{s a^*_i}{3 c_i} \right) \right], \]
\[ U_{i}(c, s) = 16 \frac{\delta_{i}^n}{c_i^{1}(1 + \rho^*)^2} e^{\frac{s a^*_i}{c_i}} \left[ \frac{a^*_i}{22} \left( 1 + \frac{s a^*_i}{23 c_i} \right) \right] - 2 \frac{s^{11}}{c_i^{17}} \left( 1 + \frac{s a^*_i}{17 c_i} \right) - \frac{1}{10} \left( 1 + \frac{s a^*_i}{11 c_i} \right), \]

and

\[ c_i = c(1 + a^*) \]

\[ G(d, s), \] the Laplace transform of \( \eta \delta_{i}(d, y) \), is given by the following relation[11]

\[ G(d, s) = \frac{sL(s) e^{\frac{s d}{c_i}}}{12\eta L(s) e^{\frac{s d}{c_i}} + S(s)}, \]

where

\[ L(s) = \left( 1 + \frac{1}{2} \eta \right) s + (1 + 2\eta), \]
\[ S(s) = (1 - \eta)^2 \frac{s^2}{4} + 6\eta(1 - \eta)s + 18\eta^2 s - 12\eta(1 + 2\eta). \]

The hard-sphere radial distribution function in the range \( 1 \leq \rho \leq 2 \) is as the following[11]

\[ \delta_{i}(d, y) = \frac{e^{\frac{s d}{c_i}}(H_0 + H_1 + H_2) + e^{\frac{s d}{c_i}}2D_s \cos A_2 - 2D_s \sin A_2}{3\eta(1 - \eta)^2} \]

Prediction of vapor-liquid equilibria of multi-component mixtures

where

\[ A_1 = \frac{2\eta}{(1 - \eta)} (y - 1)(-1 + X_1 + X_2), \]

\[ A_2 = \frac{2\eta}{(1 - \eta)} (y - 1) \times \gamma(X_2 - X_3), \]

\[ A_3 = \frac{2\eta}{(1 - \eta)} (y - 1)(-1 - 0.5(X_3 + X_4)), \]

\[ D_1 = H_0 - 0.5(H_1 + H_2), \]

\[ D_2 = \frac{\sqrt{2}}{2} (H_1 - H_3), \]

\[ H_0 = 1 + \frac{1}{2} \eta, \]

\[ H_1 = \left[ \frac{-1}{4\pi(1 + 1.05)} \right] \left[ X_2(1 - 3\eta - 4\eta^2) + X_1 \left( 1 - \frac{5}{2} \eta \right) \right], \]

\[ H_2 = \left[ \frac{1}{4\pi(1 + 1.05)} \right] \left[ X_2(1 - 3\eta - 4\eta^2) + X_1 \left( 1 - \frac{5}{2} \eta \right) \right], \]

\[ X_1 = \left[ \left( f + \frac{\beta}{8} \right)^{\frac{1}{1 - \eta}} \right]^*, \]

\[ X_2 = \left[ \left( f - \frac{\beta}{8} \right)^{\frac{1}{1 - \eta}} \right]^*, \]

and

\[ f = \frac{3 + 3\eta - \eta^2}{4\eta}, \]

The correction term to the Percus-Yevick result of the hard-sphere radial distribution function, \( \delta g^*(\theta, y) \), is given by the following relation\[34\]

\[ \delta g^*(\theta, y) = \frac{B}{y} e^{-y - \theta} \cos \mu (y - 1), \]

where

\[ B = \frac{3\theta^2(1 - 0.7176 - 0.1168\theta^2)}{(1 - \theta)^2} \]

and

\[ \mu = \frac{2\lambda B}{\delta g^*(\theta, 1)}. \]