A Helmholtz energy equation of state for calculating the thermodynamic properties of fluid mixtures

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Abstract

A new approach has been developed for calculating the properties of mixtures based on an equation of state explicit in reduced Helmholtz energy. This approach allows for the representation of the thermodynamic properties over a wide range of fluid states and is based on highly accurate equations of state for the pure components combined at the reduced temperature and density of the mixture. The reducing parameters used for temperature and density depend on composition. For simple mixtures (those that closely follow Raoult’s law), a very accurate representation of all thermodynamic properties has been achieved with relatively simple functions. For nonideal mixtures, the reducing functions for density and temperature were modified, and a departure function was added to the equation of state. Generally, the model is able to represent liquid and vapor states with uncertainties of 0.1% in density, 1% in heat capacities and 1% in bubble point pressures if experimental data of comparable uncertainties exist. Two applications of the mixture model concepts were developed independently by the authors in the United States and Germany over the same time period. These applications include the development of individual equations for each binary system and a generalization of the model which is valid for a wide variety of mixtures. The individual approaches are presented with an explanation of the similarities and differences. Although the paper focuses mainly on binary systems, some results for ternary mixtures are also presented. © 1999 Published by Elsevier Science B.V.

Keywords: Equation of state; Density; Helmholtz energy; Mixture model; Thermodynamic properties; Vapor–liquid equilibria

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1. Introduction

Equations of state using the dimensionless Helmholtz energy, $\alpha = A/RT$, have been successfully employed to describe the thermodynamic properties of pure fluids with high accuracy over a wide range of temperatures and pressures. These equations allow the calculation of all thermodynamic properties from a single mathematical relation. Equations of state can have a large number of adjustable coefficients, e.g., equations with up to 58 terms [23] have been reported. The effort required to establish an equation can be considerable, and the equations are usually developed only for fluids for which there is a large body of reliable experimental data over a wide range of thermodynamic states. One purpose of this type of equation is to serve as a reference equation for the calculation of property tables and charts. When modern optimization methods are used to establish its structure, the accuracy of the equation of state is restricted only by the accuracy of available measurements.

Due to their complexity, wide-ranging equations of state with many coefficients have generally been applied only to pure fluids. High-accuracy equations of state have been developed for only about 30 pure substances, in part because of the extensive data required. Only a few attempts have been made to describe mixture properties using multiparameter equations of state. Plocker et al. [18] used a one-fluid theory applied to modified Benedict–Webb–Rubin (mBWR) equations of state with a mixing rule for the pseudo-critical temperature to calculate vapor–liquid equilibria and enthalpies at high pressures. Platzer and Maurer [17] generalized the 20-term Bender equation of state to predict properties of multicomponent mixtures. The extended corresponding states model as applied by Huber and Ely [7] to refrigerants is based on a wide-ranging mBWR equation of state.

This work presents a mixture model based on existing high-accuracy pure fluid equations of state for the pure components. Since these equations of state are generally explicit in Helmholtz energy, this type of equation was adopted for the mixture. With a simple integration of pressure to obtain the Helmholtz energy, pressure-explicit equations of state (such as modified BWR equations) can also be used. A fixed structure of the pure fluid equation is not required since the model does not use mixing rules for the terms in the equation, but rather combination rules for the Helmholtz energy functions of the mixture components. This approach leads to a single mathematical expression from which all thermodynamic properties of the fluid phases of a mixture can be calculated over the entire thermodynamic space.

The general form of the Helmholtz energy model has been developed independently by both authors during overlapping periods of time. The work of Tillner-Roth [29] was focused mainly on developing an accurate formulation for individual binary mixtures for which a large amount of accurate experimental data was available. Several modifications were proposed in his work which led to an accuracy comparable to that of a pure fluid equation of state. The work of Lemmon [11] was focused on developing a generalized model capable of accurate property calculation for a large number of fluid mixtures which are well-characterized by experimental data and on prediction of properties of additional mixtures with limited data sets. The present paper gives additional detail and background about the models, especially concerning the ideal mixture, and contrasts the differences between the models.
2. The Helmholtz energy for mixtures

2.1. Basic structure

Before the mixture model is presented, the structure of the pure component equations of state will be outlined due to its importance in understanding the mixture approach. Equations of state for the pure fluids used here are given in terms of the dimensionless Helmholtz energy:

\[
\frac{A}{RT} = \alpha(\tau, \delta) = \alpha^0(\tau, \delta) + \alpha^r(\tau, \delta),
\]

where \( A \) is the molar Helmholtz energy and \( R \) is the universal gas constant. This equation has been split into an ideal part \( \alpha^0 \) and a residual part \( \alpha^r \) using the dimensionless variables \( \tau = T_n/T \) and \( \delta = \rho/\rho_n = V_n/V \). The equations for these contributions are generally given in the form:

\[
\alpha^0(\tau, \delta) = \ln \delta + c_1 \ln \tau + \sum_{k=2}^{k_1} c_k \tau^{m_k} + \sum_{k=k_1+1}^{k_2} c_k \ln[1 - \exp(-a_k \tau)] \tag{2}
\]

\[
\alpha^r(\tau, \delta) = \sum_{k=k_1+1}^{k_3} c_k \delta^{n_k} \tau^{m_k} + \sum_{k=k_3+1}^{k_4} c_k \delta^{n_k} \tau^{m_k} \exp(-\delta^{c_k}). \tag{3}
\]

It is common to use measured critical properties for the reducing parameters \( T_n \) and \( V_n \). All thermodynamic properties can be derived from the equation of state using exact thermodynamic relations, as given by Setzmann and Wagner [25] or Tillner-Roth and Baehr [31].

It is not necessary that the pure fluid equations of state be given in this form for use with the mixture model. A thermal equation of state:

\[
p = p(V, T) \text{ or } p = p(\rho, T) \tag{4}
\]

can be transformed into the Helmholtz energy form by integrating the relation:

\[
p = \rho RT \left[ 1 + \delta \left( \frac{\partial \alpha^r}{\partial \delta} \right)_\tau \right] \tag{5}
\]

and combining this with an expression for the ideal gas heat capacity.

For the mixture model presented here, the structure given by Eq. (1) has been used, i.e., the dimensionless Helmholtz energy of a mixture is given as:

\[
\alpha = \alpha^0 + \alpha^r, \tag{6}
\]

where \( \alpha \) of the mixture also depends on composition.

In subsequent sections, only molar quantities are considered. Pure fluid properties are indicated by subscripting, for example, \( \alpha^r_1 \) is the residual part of the dimensionless Helmholtz energy of component 1. No index is used for mixture properties. The mole fractions identify the component number by a lowercase index. The mole fraction vector for the mixture is \( \mathbf{x} = \{x_1, x_2, \ldots\} \). For pure fluid equations, \( \delta \) is generally defined as a reduced density. For our mixture model, we use the definition \( \delta = V_n/V \) (\( = \rho/\rho_n \)) as the inverse reduced molar volume.

\[\]
2.2. The ideal gas mixture

Ideal gas properties for a mixture are obtained analytically from functions for the ideal gas properties of the pure fluids. The ideal parts $\alpha^0_i$ are combined at constant temperature $T$ and constant molar volume $V$ according to:

$$\alpha^0 = \alpha^0(T, V, x) = \sum_{i=1}^{l} x_i \alpha^0_i(T, V) + \sum_{i=1}^{l} x_i \ln x_i$$

(7)

for a mixture of $l$ components, where $\alpha^0_i = A_i^0/RT$. The second sum in this equation is related to the entropy of mixing for the ideal gas mixture. The ideal parts of the mixture expression are usually transformed to allow the use of the independent reduced variables $\tau$ and $\delta$, consistent with those generally used for the ideal parts of the pure fluid equations. There are subtle differences in the reduced variable sets used by Tillner-Roth and by Lemmon, although the formulations are substantially equivalent. Details of each method are given in the original publications by Lemmon [11] and Tillner-Roth [29].

2.3. The residual Helmholtz energy

The general form of the residual Helmholtz energy was chosen as:

$$\alpha^r(\tau, \delta, x) = \sum_{i=1}^{l} x_i \alpha^r_i(\tau, \delta) + \Delta \alpha^r(\tau, \delta, x),$$

(8)

which is a linear combination of the pure fluid residual Helmholtz energies $\alpha^r_i$, taken from the pure component equations, weighted by the mole fractions $x_i$ of the components in the mixture. The pure fluid residuals, $\alpha^r_i$, are evaluated at the same values of $\tau$ and $\delta$ for each component $i$. The departure function $\Delta \alpha^r$, which depends on $\tau$, $\delta$, and composition $x$, accounts for the interaction of different species in the mixture. The uniqueness of this approach is the combination of the residual parts $\alpha^r_i$ at specified reduced variables $\tau$ and $\delta$. Since different pure fluid equations of state use different reducing parameters $T_n,i$ and $V_n,i$, each pure fluid equation of state is evaluated at a different temperature and molar volume when the same values for $\tau$ and $\delta$ are used. This feature is similar to the corresponding states principle established by Leland et al. [10] which used a reference equation mapped over the surface of a fluid or mixture. Shape factors translate $T$ and $V$ of a fluid into $T_r$ and $V_r$ of the reference fluid. The most simple shape factors are the ratios of the critical properties. For example, the temperature $T_r$ at which the reference fluid equation is evaluated is:

$$T_r = T \cdot h = \frac{T_{n,r}}{T_n},$$

(9)

where $h$ is the shape factor and $T_{n,r}$ and $T_n$ are the critical temperature for the reference fluid and the fluid under consideration. After rearrangement,

$$\tau_r = \frac{T_{n,r}}{T_r} = \frac{T_n}{T} = \tau.$$  

(10)

Thus, both fluid properties are evaluated at the same reduced temperature.
Till now, we have assumed that we knew $\tau$ and $\delta$ while evaluating $\alpha_i'$ of each pure component. Suitable reducing parameters for $T$ and $V$ are necessary to obtain $\tau$ and $\delta$. The reducing parameters (or critical parameters) of the pure fluid (or critical parameters) of the pure fluid equations are not the same as the reducing functions of the mixture. The parameters $\tau$ and $\delta$ vary with composition,

$$\tau(\mathbf{x}) = \frac{T_n(\mathbf{x})}{T} \quad \text{and} \quad \delta(\mathbf{x}) = \frac{V_n(\mathbf{x})}{V},$$

but must converge to the pure fluid values, $\tau_i$ and $\delta_i$, as $x_i$ approaches 1,

$$T_n(\mathbf{x}) \rightarrow T_{n,i} \quad \text{and} \quad V_n(\mathbf{x}) \rightarrow V_{n,i} \quad \text{(12)}$$

or

$$\tau(\mathbf{x}) \rightarrow \tau_i \quad \text{and} \quad \delta(\mathbf{x}) \rightarrow \delta_i. \quad \text{(13)}$$

These functions could be called pseudo-critical parameters because measured critical parameters are often chosen for $T_{n,i}$ and $V_{n,i}$. We prefer to call $T_n(\mathbf{x})$ and $V_n(\mathbf{x})$ reducing functions. The true shape of the critical locus of a mixture can be significantly different from the shape of the line representing the reducing functions.

With any two functions $T_n$ and $V_n$ which converge to the pure fluid values, the Helmholtz energy model is complete. All thermodynamic properties can be calculated from this equation of state. Relations for calculating selected thermodynamic properties from the current mixture model are given in Table 1. The parameter $n$ in the fugacity equation is the number of moles in the mixture and the subscript $j$ specifies that the mole fraction of each component in the mixture is held constant during differentiation except that for component $i$. The partial derivative in this equation is generally evaluated numerically at constant temperature and total mixture volume (not molar volume).

Table 1
Thermodynamic properties calculated from the Helmholtz energy model [abbreviations: $\alpha_i' = (\partial \alpha_i' / \partial \alpha_i')_x$, $\alpha_i'' = (\partial \alpha_i'' / \partial \alpha_i'' )_x$, $\alpha_i''_0 = (\partial \alpha_i'' / \partial \delta_0)_x$, $\alpha_i''_s = (\partial \alpha_i'' / \partial \tau)_s$, $\delta = \delta(x)$, $\tau = \tau(x)$]

| Ideal gas properties | | Real gas properties |
|----------------------|-----------------------|
| Internal Energy $U^0 = \sum_{i=1}^{n} x_i \tau_i (\partial \alpha_i' / \partial n_i)$ | Compressibility factor $Z = pV/RT = 1 + \delta \alpha_i''_s$ |
| Enthalpy $H^0 = RT = \sum_{i=1}^{n} x_i \tau_i (\partial \alpha_i' / \partial n_i)$ | Fugacity of component $i$ $f_i = x_i \rho RT \exp (\vartheta(n \alpha_i'/n_i))_{T,aV,n_i}$ |
| Entropy $S^0 = R = \sum_{i=1}^{n} x_i \tau_i (\partial \alpha_i' / \partial n_i)$ | Internal energy $U/RT = (U^0/RT) + \tau \alpha_i''_s$ |
| Isochoric heat capacity $C_V^0 = 1$ | Entropy $S/RT = (S^0/RT) + \tau \alpha_i'' + \delta \alpha_i''_s$ |
| | Isochoric heat capacity $C_V/RT = (C_V^0/RT) - \tau \alpha_i''_s$ |
| | Isobaric heat capacity $C_p/RT = (C_p^0/RT) + \left( \frac{1 + \delta \alpha_i''_s - \delta \alpha_i''_s}{1 + 2 \delta \alpha_i'' + \delta \alpha_i''_s} \right)$ |
| | Speed of sound $w^2M/RT = (C_v/C_p) \left[ 1 + 2 \delta \alpha_i'' + \delta \alpha_i''_s \right]$ |
3. The linear mixture model

The simplest functions for $T_n$ and $V_n$ are linear combinations of the pure fluid parameters,

$$T_n(x) = \sum_{i=1}^{l} x_i T_{n,i}$$

and

$$V_n(x) = \sum_{i=1}^{l} x_i V_{n,i}.$$  \hspace{1cm} (14) \hspace{1cm} (15)

When these linear reducing functions are used and a departure function $\Delta \alpha^{r}$ in Eq. (8) is omitted, the mixture model does not have any adjustable parameters. We will call this special form a linear mixture model.

Before dealing with more involved forms of the mixture model, we will compare the thermodynamic properties obtained from the linear model with some experimental data for three binary mixtures. The mixture 1,1,1,2-tetrafluoroethane (R-134a) + difluoromethane (R-32) has been chosen as an example of a simple mixture which closely follows the behavior of an ideal solution. The mixture ethane + carbon dioxide was selected to show azeotropic behavior. The mixture water + ammonia was selected as a mixture of polar components showing large mixing effects and a wide two-phase region (Fig. 1). For all of these mixtures, a variety of experimental data is available. Wide-ranging, accurate equations of state are available for each component summarized in Table 2.

The vapor–liquid equilibrium is obtained from the Helmholtz energy model for a given $p$ and $T$ by equating the liquid and vapor fugacities. Calculated values of composition are shown in Fig. 1 along with experimental data for comparison. The linear mixture model gives excellent results for the system R-134a + R-32 (Fig. 1a) which behaves like an ideal solution. Measurements on the dew and bubble point curves are equally well-represented.

For the mixture water + ammonia (Fig. 1b) the linear mixture model predicts the dew curve well but exhibits large deviations along the bubble curve, especially at compositions for mole fractions of

![Fig. 1. Experimental and calculated VLE state points from the linear mixture model. (a) R-134a + R-32: ○, ● Holcomb et al. [6]. (b) Water + ammonia: ○, ● Smolen et al. [26]. (c) Ethane + carbon dioxide: ○, ● Fredenslund and Mollerup [3].](image-url)
ammonia near 0.5. The good representation of the dew curve is attributed to the high ammonia concentration in the vapor phase at high equilibrium pressures where the dew curve is determined almost completely by the ammonia equation of state. At lower pressures, the vapor is nearly an ideal

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Equation of state</th>
<th>$T$ range (K)</th>
<th>Maximum $p$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-134a</td>
<td>Tillner-Roth and Baehr [31]</td>
<td>169.85–500</td>
<td>70</td>
</tr>
<tr>
<td>R-32</td>
<td>Tillner-Roth and Yokozeki  [33]</td>
<td>136.34–435</td>
<td>70</td>
</tr>
<tr>
<td>Water</td>
<td>Pruss and Wagner [20]</td>
<td>273.16–1275</td>
<td>1000</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Tillner-Roth et al. [30]</td>
<td>195.495–700</td>
<td>1000</td>
</tr>
<tr>
<td>Ethane</td>
<td>Friend et al. [4]</td>
<td>90.352–625</td>
<td>70</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>Span and Wagner [27]</td>
<td>216.592–1100</td>
<td>800</td>
</tr>
</tbody>
</table>

Fig. 2. Density deviations between experimental data and densities calculated from the linear mixture model. (a) Subcritical R-134a + R-32 ($T = 333.15$ K, $x = 0.5$): ×, ○ Kleemiss [9]; ■ Magee and Haynes [15]. (b) Supercritical R-134a + R-32 ($363 < T$ (K) < 413, $x = 0.5$): ×, ○ Kleemiss [9]. (c) Liquid water + ammonia ($273 < T$ (K) < 333, $p < 40$ MPa): ○ Harms-Watzenberg [5].
gas. The linear mixture model cannot describe azeotropic behavior, e.g., for ethane + carbon dioxide (Fig. 1c) it incorrectly predicts nearly ideal VLE similar to the results for R-134a + R-32.

Comparisons of the linear mixture model with \((p,V,T,x)\) properties for selected mixtures are shown in Fig. 2. In the subcritical range (Fig. 2a), vapor densities of R-134a + R-32 are represented well at low pressures where ideal gas behavior is approached. For increasing pressures in the vapor (increasing real fluid behavior), the absolute deviations increase to about 1%. However, excellent agreement between calculated and experimental liquid densities is observed. Deviations are within \(\pm 0.1\%\) over the entire range of pressure. Deviations for supercritical densities (Fig. 2b) are larger. Around 5 MPa, near the critical pressure, density deviations from the linear mixture model exceed 6%. At pressures greater or less than 5 MPa, deviations decrease according to the behavior observed for subcritical temperatures. Systematic deviations are also observed for the liquid density in the system water + ammonia (Fig. 2c). Densities obtained from the linear mixture model deviate between \(-1\%\) and \(+3\%\) from experimental values. The largest deviations occur for ammonia mole fractions around 0.7.

Results for caloric properties are shown in Fig. 3. The isochoric heat capacity of R-134a + R-32 (Fig. 3a) is represented by the linear mixture model within \(\pm 1\%\) (about the experimental uncertainty). For ethane + carbon dioxide (Fig. 3b), the representation of \(C_v\) is less accurate. Generally, outside of the critical region, results from the linear mixture model are about 2% greater than the experimental

![Fig. 3. Deviations between measured caloric properties and values calculated from the linear mixture model. (a) Liquid R-134a+R-32 \(C_v\) \((x = 0.5)\): □ Magee and Haynes [15]. (b) Isochoric heat capacity for ethane + carbon dioxide: ○ Magee [13]. (c) Excess enthalpy in liquid water + ammonia \((T = 298.15\text{ K}, \ p = 5\text{ MPa})\): ● Staudt [28].](image-url)
data values. Around 300 K, close to the critical region, deviations increase sharply and those for several data points fall outside the limits of Fig. 3b. The excess enthalpy of liquid water + ammonia is shown in Fig. 3c. The linear mixture model predicts a positive excess enthalpy, although measurements indicate large negative values. The reason for this error may be related to the poor representation of the VLE for water + ammonia by the linear mixture model.

4. Enhancements to the mixture model

Although the linear mixture model is just a combination of pure fluid equations without any adjustable parameters, it yields good results for simple mixtures which closely follow ideal-solution behavior. The thermodynamic properties for more complex mixtures, however, are sometimes represented poorly, especially those for mixtures exhibiting large mixing effects or azeotropes. In such situations, the linear mixture model can be modified in order to represent the thermodynamic properties accurately.

4.1. Reducing functions

As a first modification, the linear functions (14) and (15) can be replaced by:

\[
T_n(x) = \sum_{i=1}^{l} \sum_{j=1}^{l} x_i x_j T_{n,ij} \quad \text{and} \quad (16)
\]

\[
V_n(x) = \sum_{i=1}^{l} \sum_{j=1}^{l} x_i x_j V_{n,ij}, \quad (17)
\]

where the pure fluid parameters, \(T_{n,i}\) and \(V_{n,i}\), are used when \(i = j\). The parameters with mixed indices \((i \neq j)\) can be expressed by:

\[
T_{n,ij} = k_{T,ij} \frac{1}{2} (T_{n,ii} + T_{n,ji}) \quad \text{and} \quad (18)
\]

\[
V_{n,ij} = k_{V,ij} \frac{1}{2} (V_{n,ii} + V_{n,ji}). \quad (19)
\]

The parameters \(k_{T,ij}\) and \(k_{V,ij}\) are adjusted using experimental data. When \(k_{T,ij}\) and \(k_{V,ij}\) are equal to 1, the quadratic functions reduce to the linear model given in Eqs. (14) and (15).

Fig. 4 shows how varying \(k_{T,ij}\) and \(k_{V,ij}\) affects the Helmholtz energy model for the VLE of ethane + carbon dioxide. The solid lines correspond to the VLE calculated from the linear mixture model \((k_{T,12} = 1\) and \(k_{V,12} = 1\)). The strongest influence is observed for a variation of the parameter \(k_{T,12}\). The azeotropic behavior of ethane + carbon dioxide is described well with a value of \(k_{T,12} = 0.9\) (and \(k_{V,12} = 1.0\)). For \(k_{T,12}\) greater than 1, a negative pressure azeotrope can be modeled. A variation of \(k_{V,12}\) has a much smaller effect. When it is increased, the dew–bubble curves are shifted to slightly higher saturation pressures while for values below 1 they are shifted in the other direction.
Fig. 4. Influence of the parameters $k_{T,12}$ and $k_{V,12}$ in the quadratic reducing function on the VLE of ethane + carbon dioxide: ◇ Fredenslund and Mollerup [3]; solid line: $k_T = 1.0$, $k_V = 1.0$.

Deviations of calculated values from the $C_V$ measurements of Magee [13] for the mixture ethane + carbon dioxide were recalculated using $k_{T,12} = 0.9$ and $k_{V,12} = 1$ (obtained from the optimization to VLE data), and the isochoric heat capacities, shown in Fig. 5, were represented with an average absolute deviation of 1.4% as opposed to 8% without adjusting $k_{T,12}$. The systematic offset observed in Fig. 3c has been substantially reduced, improving the data representation especially in the critical region. This result verifies the close connection between the representation of VLE and caloric properties in the liquid, as already indicated in the previous section for the water + ammonia system.

A further modification of the reducing functions for binary mixtures was introduced by Tillner-Roth [29] by supplementing the quadratic expressions (16) and (17) with exponents $\beta_T$ and $\beta_V$ according to:

\[
T_n(x) = x_1^2 T_{n,1} + x_2^2 T_{n,2} + 2 x_2 (1 - x_2^{\beta_T}) T_{n,12}
\]

\[
V_n(x) = x_1^2 V_{n,1} + x_2^2 V_{n,2} + 2 x_2 (1 - x_2^{\beta_V}) V_{n,12}.
\]

The effect of these exponents on the shape of the expression $x_2 (1 - x_2^{\beta_T})$ is shown in Fig. 6 for different values of the exponent $\beta_T$. The quadratic form corresponds to $\beta_T = 1$. If $\beta_T$ differs from 1,
the influence of \( T_{n,12} \) or \( V_{n,12} \) becomes asymmetric with respect to composition. This modification is effective when the mixture properties exhibit asymmetries. The additional flexibility allows fine tuning of the mixture model, significantly increasing the accuracy of calculated properties. More complicated reducing functions, such as cubic and higher order polynomials were tested as well. Although slight improvements were observed when additional parameters were introduced, the convergence behavior of the optimization process became worse.

During the development of the generalized model by Lemmon [11], the linear reducing functions, Eqs. (14) and (15), were modified and are given by:

\[
T_n(x) = \sum_{i=1}^{l} x_i T_{n,i} + \sum_{i=1}^{l-1} \sum_{j=i+1}^{l} x_i^\beta_{ij} x_j \xi_{ij} \quad \text{and} \\
V_n(x) = \sum_{i=1}^{l} x_i V_{n,i} + \sum_{i=1}^{l-1} \sum_{j=i+1}^{l} x_i x_j \xi_{ij}
\]

for a mixture of \( l \) components. The parameters \( \xi_{ij} \), \( \xi_{ij} \), and \( \beta_{ij} \) modify the shapes of the reducing functions in a form similar to that of the parameters \( k_v \) and \( k_r \) in Eqs. (18) and (19). When the parameter \( \beta_{ij} \) is set equal to one, \( \xi_{ij} \) and \( \xi_{ij} \) are directly related to \( k_{r,ij} \) and \( k_{v,ij} \) of Eqs. (18) and (19) by:

\[
\xi_{ij} = (T_{n,i} + T_{n,j})(k_{r,ij} - 1) \quad \text{and} \\
\xi_{ij} = (V_{n,i} + V_{n,j})(k_{v,ij} - 1).
\]

For the methane + ethane system, \( \xi_{ij} \) and \( \xi_{ij} \) were arbitrarily set to zero. For the ethane + propane system, a nonlinear fit showed that these parameters were also close to zero. Thus, the general characteristic of the ethane + propane system should be similar to that of the methane + ethane system. However, with the azeotropic mixture ethane + carbon dioxide, the value of \( \xi_{ij} = -67.4 \) K was large and negative, and over certain ranges of composition, the values of \( T_n \) fell below the critical
temperatures of the pure fluids. Using the value of $\zeta_{ij} = -67.4$ K for ethane + carbon dioxide, the corresponding value for $k_{T,12}$ in Eq. (24) is about 0.89, which is in good agreement with the value of 0.9 (obtained from a fit of VLE only) from the example given in Section 4.

Initially, the parameters $\zeta_{ij}$ and $\xi_{ij}$ were determined using only experimental ($p,V,T,x$) data. However, comparisons of VLE data with values calculated from the equation for the methane + propane mixture showed large systematic deviations for the bubble point pressures. These deviations were about 20% at $x_{CH_4} = 0.15$ and about −10% at $x_{CH_4} = 0.75$. In order to improve these deviations, the parameter $\beta_{ij}$ was included in the regression. Since VLE calculations rely heavily on derivatives of the Helmholtz energy with respect to composition, the asymmetric shape caused by the $\beta_{ij}$ parameter was ideal for modifying the reducing temperature line. The change in deviations of the available ($p,V,T,x$) data was insignificant, but comparisons to VLE data improved substantially. Thus, although only a limited amount of ($p,V,T,x$) data was required to accurately describe the full ($p,V,T,x$) surface of a binary mixture, it could not be assumed that VLE states would also be accurately predicted. Data must be available for comparison to verify this aspect of the model. Fortunately, VLE data for mixtures are generally readily available. Likewise, fitting only VLE data does not insure that the ($p,V,T,x$) data will be well-represented.

4.2. Departure function for the Helmholtz energy

The basic Helmholtz energy model for mixtures can be supplemented by a departure function:

$$\Delta \alpha^i = \Delta \alpha^i(\tau, \delta, x)$$

in order to improve its overall accuracy. This function should contribute only to mixture properties and should have no effect at the pure fluid limits. The following compositional dependence of $\Delta \alpha^i$ was chosen:

$$\Delta \alpha^i(\tau, \delta, x) = \sum_{i=1}^{l-1} \sum_{j=i+1}^{l} x_i x_j \Delta \alpha_{ij}(\tau, \delta, x_i, x_j).$$

According to this relation, the departure function of a multicomponent mixture is composed of the departure functions of the constituent binary pairs. The function $\Delta \alpha_{ij}$ not only depends on $\delta$ and $\tau$, but also on the mole fractions of the components $i$ and $j$. For mixtures containing more than two components, ternary or higher order departure functions are conceivable. Although these have not been necessary for an accurate description of the mixtures studied to date, we cannot a priori exclude this possibility for strongly nonideal systems. The following sections consider only departure functions for the binary constituents in the mixture.

The magnitude of the departure function is generally at least one order smaller than the residual dimensionless Helmholtz energy $\alpha^i$. The departure function is modeled in a process similar to that used in developing an equation of state. First, the structure must be determined. The regression analysis developed by Wagner [34] is especially suited to this task. This strategy allows the selection of a subset of terms for $\Delta \alpha_{ij}$ from a much larger “bank of terms” which represents a given set of experimental data with the lowest standard deviation. Such an equation may be further optimized using a nonlinear technique to fit directly all experimental mixture data. A suitable nonlinear method is the modified Marquardt–Fletcher algorithm as developed by Dennis et al. [1].
In setting up the bank of terms, we used terms of the form:

\[ \delta^{n_k \tau^{m_k}} \text{ and } \delta^{n_k \tau^{m_k}} \exp(-\delta^{e_k}) \]  

(28)

where \( k \) is the term number and the values of the exponents ranged from 1 to 10 for \( n_k \), -2 to 20 for \( m_k \), and 1 to 4 for \( e_k \). Additional terms might be included for other applications, but these terms were sufficient to formulate \( \Delta \alpha_{ij} \) functions which accurately described the mixture properties for a large variety of systems.

5. Applications of the enhanced model

The discussion above describes the similarities of the models resulting from this work and the differences in the reducing functions applied by each author. Further discussion is given here on the unique features of the models by describing applications of the enhanced model by each author and assessing the strengths and weaknesses of the differing approaches.

5.1. Applications by Tillner-Roth

Tillner-Roth [29] introduced an exponent \( \gamma \) in the expression which precedes the terms of the departure function for a binary mixture, resulting in:

\[ \Delta \alpha^\gamma(\tau, \delta, x) = x_2(1 - x_2^\gamma) \Delta \alpha_{ij}(\tau, \delta, x_i, x_j). \]  

(29)

This terms allows asymmetric influences of the departure function to be modeled, and proved to be very effective for simple systems, such as R-152a + R-134a [29]. Although an acceptable data representation might also be achieved without this modification, the introduction of the exponent \( \gamma \) reduced the number of terms in the departure function. This modification has been applied only to binary systems to date. The extension to multicomponent mixtures would require further research.

For mixtures which deviate significantly from the linear mixture model, the terms of the departure function can include a further compositional dependence. For water + ammonia, functions of the form:

\[ x \delta^{n_k \tau^{m_k}} \exp(-\delta^{e_k}) \text{ and } x^2 \delta^{n_k \tau^{m_k}} \exp(-\delta^{e_k}) \]  

(30)

were used in the bank of terms, where \( x \) is the mole fraction of ammonia. However, these terms resulted in a significant increase in the number of terms required in the regression analysis, and should be avoided when the terms given by Eq. (28) are sufficient to develop an accurate equation. Other problems may occur during nonlinear optimization of the coefficients of the terms given in Eq. (30) when the exponent \( \gamma \) is used. Since these terms depend on composition, they interact with the exponent, often leading to poor convergence behavior.

This Helmholtz energy approach for individual binary mixtures has been applied to only a few binary mixtures to date. Its original development was carried out based on a comprehensive data set for the mixture R-152a + R-134a. For this mixture, a departure function and the reducing functions given by Eqs. (20) and (21) were needed with a total of nine adjustable parameters. Typical uncertainties of the model were about 0.2% in density and 0.3% in equilibrium pressures. A complete set of comparisons for this system is given by Tillner-Roth [29].
Some results have been obtained for the mixture R-134a + R-32. Although this mixture shows almost ideal solution behavior, a departure function is needed to represent experimental data within their uncertainties, especially in the near-critical and supercritical regions. For this system a five-term departure function:

\[
\Delta \alpha'(\tau, \delta, x) = x(1 - x^y) \left[ \sum_{k=1}^{2} c_k \delta^{n_k \tau} m_k + \sum_{k=3}^{5} c_k \delta^{n_k \tau} m_k \exp(-\delta^{e_k}) \right]
\]

was developed. The coefficients and exponents required to implement this model are given by Tillner-Roth [29]. The improvement in accuracy over the linear model shown in Fig. 2 is illustrated in Fig. 7 for \((p, V, T, x)\) data. In the liquid and vapor regions, density deviations are within ±0.1%. Deviations in the critical region also decreased drastically from more than −6% to ±0.4%. Representations of VLE and \(C_V\) in the liquid are about the same as with the linear mixture model, which were already within the experimental uncertainty of measured values.

For the mixture water + ammonia, which exhibits a large two-phase region and significant mixing effects in the liquid, the following 14-term departure function was used:

\[
\frac{\Delta \alpha'(\tau, \delta, x)}{x(1 - x^y)} = c_1 \delta^{n_1 \tau} m_1 + \sum_{k=2}^{6} c_k \delta^{n_k \tau} m_k \exp(-\delta^{e_k}) + x \sum_{k=7}^{13} c_k \delta^{n_k \tau} m_k \exp(-\delta^{e_k}) + c_{14} x^2 \delta^{n_{14} \tau} m_{14} \exp(-\delta^{e_{14}}).
\]

In addition to the exponent \(\gamma\), a separate compositional dependence term had to be included in the departure function. The modified quadratic expressions, Eqs. (20) and (21), were used, yielding a total of 19 adjustable parameters. A complete description of the model for water + ammonia is given by Tillner-Roth and Friend [32]. For the VLE close to the critical locus, differences from the linear

Fig. 7. Deviations between densities of R-134a + R-32 and values calculated from the Helmholtz energy model \((x = 0.5)\):
- Liquid densities of Kleemiss [9]: ●
- Vapor densities of Kleemiss [9]: ×
mixture model are quite significant, as illustrated in Fig. 8a. The improved representation of excess enthalpies for this system is shown in Fig. 8b, as compared with Fig. 3 where the predicted excess enthalpies were positive.

In addition to these features, a significant number of terms was needed to describe the low temperature range. When properties close to the solid–liquid–vapor boundary are calculated, the lower temperature limits of the mixture may be considerably less than the lower temperature limits of the pure components, as illustrated in the (T,x) diagram in Fig. 9. Two lines which correspond to the triple-point temperatures of the pure components, modified by the reducing parameters of the pure fluid and of the mixture, are included in the figure. Properties calculated at temperatures below these lines are extrapolations of the equation of state. For ammonia, the equation of state was extrapolated by about 110 K below its triple-point temperature. Thus, any deficiencies in the pure fluid equations due to extrapolation must be compensated by the departure function to reliably represent properties, such as the triple point pressure, at low temperatures (Fig. 9).

5.2. Applications by Lemmon

The model of Lemmon [11] used a single generalized departure function valid for a large variety of mixtures. The nature of the generalization enables the prediction of properties of mixtures with limited experimental data. The model includes mixtures of nitrogen, carbon dioxide, oxygen, argon, methane, ethane, propane, n-butane, and i-butane, and mixtures of the refrigerants R-32, R-125, R-134a, R-143a, and R-152a.

For an accurate description of the properties of mixtures of these fluids, individual departure functions could be developed for every binary mixture of interest as described in Section 5.1. However, this requires experimental data that cover the entire surface, including (p,V,T,x) data, caloric data, and measurements of VLE states. Such a database exists for only a few mixtures:
methane + ethane, methane + nitrogen, and mixtures of the refrigerants R-32, R-125, R-134a, and R-152a. For most other mixtures, such an extensive and highly accurate database is not available. Therefore, a relatively short generalized departure function $\Delta \alpha^i$ was developed which was not only applicable to the mixtures to which it was fitted, but could also be used to predict properties of other binary mixtures with limited data.

The generalized departure function $\Delta \alpha^i$ has the form:

$$\Delta \alpha^i(\tau, \delta, x) = \sum_{i=1}^{l-1} \sum_{j=i+1}^{l} x_i x_j F_{ij} \Delta \alpha_{ij}(\tau, \delta),$$

where

$$\Delta \alpha_{ij}(\tau, \delta) = \sum_{k=1}^{10} c_k \delta^{n_k} \tau^{m_k}.$$  \hspace{1cm} (34)

The coefficients, $c_k$, and the structure of Eq. (34) were determined from extensive and accurate experimental data for various mixtures. Additional details and comparisons to experimental data are given by Lemmon and Jacobsen [12] along with the coefficients and exponents required to implement this model.

The coefficients $c_k$ and exponents $n_k$ and $m_k$ in Eq. (34) are the same for all mixtures in the model. Binary systems are characterized by different values of the parameter $F_{ij}$. Once the function given in Eq. (34) is fixed, only the parameter $F_{ij}$ and the parameters of the reducing functions need to be determined to apply the mixture model to additional mixtures. In addition, only a few experimental
data are sufficient for this purpose, thus enabling the model to be extended to mixtures with limited databases. An example is given in Fig. 10 for the propane + n-butane system. Eleven liquid \((p,V,T,x)\) data points of Magee [14] were used to determine the mixture parameters. Comparisons of the mixture model using these parameters to vapor data by Parrish [16] and liquid data by Magee [14] for the propane + n-butane system showed that the average absolute deviation of the model from the selected \((p,V,T,x)\) data shown in Fig. 10a was less than 0.04\%. The liquid data by Parrish [16] deviate from the more recent values by Magee [14] by as much as 0.4\%, and are not shown in Fig. 10a. Although no VLE data were used to determine the mixture parameters, the average absolute deviation in bubble point pressure for the data of Kay [8] was 0.4\% as shown in Fig. 10b.

A linear regression of the available data for each binary mixture was performed to determine the consistency among different data. The global fitting of these data began with the methane + ethane database in order to establish a preliminary set of coefficients \(c_k\) by linear regression. Other binary mixtures were then added to the fit one at a time to ensure a consistent fit in the generalization by nonlinearly fitting the generalizing parameters \(F_{ij}\) and the parameters \(\zeta_{ij}\) and \(\xi_{ij}\) to a small set of \((p,V,T,x)\) data. This set was made up of 20 to 100 data points selected from the available data to cover the entire fluid surface. Generally, only the \(F_{ij}\), \(\zeta_{ij}\), and \(\xi_{ij}\) parameters were needed to fit the \((p,V,T,x)\) data. However, accurate representation of VLE data often required the use of the \(\beta_{ij}\) parameter. While maintaining the parameters from the nonlinear fit, the linear regression was again performed including data for these other binary mixtures along with the data for the methane + ethane system. The output of the linear regression was the coefficients \(c_k\) of Eq. (34). The nonlinear fit was then repeated to improve the values of \(F_{ij}\), \(\zeta_{ij}\), \(\xi_{ij}\), and \(\beta_{ij}\). This procedure of performing a linear regression and a nonlinear fit continued until the differences between values calculated from the equation and experimental data were less than the experimental uncertainty in the measurements. At this point, data for another binary mixture were added to the regression and the analysis was repeated for each step of the process.

![Fig. 10. The mixture propane + n-butane. (a) Deviations between liquid densities and values predicted from the Helmholtz energy model: ● Parrish [16] (283 < \(T\) (K) < 333, 0.15 < \(x_{\text{propane}}\) < 0.75); ○ Magee [14] (244 < \(T\) (K) < 400, \(x_{\text{propane}}\) = 0.6). (b) Deviations between bubble point pressures and values predicted from the Helmholtz energy model: ● Kay [8] (332 < \(T\) (K) < 425).](image-url)
Fig. 11. Deviations between experimental densities for the ternary system R-134a + R-125 + R-32 and values predicted from the Helmholtz energy model: ● Kleemiss [9] (243 < T (K) < 353); ○ Magee and Haynes [15] (200 < T (K) < 400).

The uncertainty of the equation reported by Lemmon [11] is generally 0.2% in density where there are measured data to confirm this assessment, 0.1% in the speed of sound at pressures below 10 MPa, 0.5% in the speed of sound for higher pressures, and 1% in heat capacities. In the region from 250 to 350 K at pressures up to 30 MPa, uncertainties in calculated densities are within 0.1% for most gas phase mixtures. For mixtures where the critical temperatures of the pure components are within 100 K of each other, uncertainties in calculated bubble point pressures are generally within 1%–2%. For mixtures with critical points at temperatures farther apart, calculated bubble point pressures are generally within 5%–10%. In regions outside the fitted binary mixture data, the uncertainty is estimated to be of the same magnitude. However, this must be verified by data when measurements become available. This is especially true for binary mixtures for which the mixture parameters \( F_{ij}, \xi_{ij}, \epsilon_{ij} \) are large, i.e., nonideal mixtures, and the uncertainties will increase in proportion to the size of the mixture parameters. Although the equation was developed using mostly binary data, it is accurate in calculating the properties of multicomponent mixtures. An example is illustrated in Fig. 11 for the \((p,V,T)\) properties of the ternary refrigerant mixture R-134a + R-125 + R-32.

6. Conclusions

An equation of state for mixtures in terms of the Helmholtz energy has been developed and applied to several fluid systems by two different research groups. All thermodynamic properties can be calculated from this equation over a wide range of fluid temperature, density, and composition. The model is based on accurate pure-fluid equations of state.

The model can be established individually for single binary systems for which comprehensive, accurate data are available using the approach proposed by Tillner-Roth [29]. Using this approach, the thermodynamic properties of the mixture can be represented within their experimental uncertainties. Furthermore, a generalized model was presented by Lemmon [11] which accurately predicts the
thermodynamic properties of mixtures, including those for which only limited data are available. Accurate prediction of the properties for multicomponent mixtures is also possible. These two applications of the model may be considered to be substantially equivalent for specific mixture properties.

The model described here has been applied to binary mixtures of relatively simple molecules, such as hydrocarbons and refrigerants. Preliminary research has shown that the model may be effective in predicting liquid–liquid equilibria. The prediction of the properties of ternary and higher systems studied to date was based only on the data for binary subsystems.

Future research will be concerned with the application of the model presented here to more nonideal systems such as mixtures of associating species or of molecules which greatly differ in size and polarity. For complex multicomponent mixtures, it may be necessary to revise or extend the current mixing rules. Accurate wide-range equations of state are desired for all fluids to be investigated in future research using the model described in this work.

7. List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$A$</td>
<td>Molar Helmholtz energy</td>
</tr>
<tr>
<td>$c_k$</td>
<td>Coefficients</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Molar isobaric heat capacity</td>
</tr>
<tr>
<td>$C_v$</td>
<td>Molar isochoric heat capacity</td>
</tr>
<tr>
<td>$e_k$</td>
<td>Exponents</td>
</tr>
<tr>
<td>$f_i$</td>
<td>Fugacity of component $i$</td>
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<tr>
<td>$F$</td>
<td>Binary characterization parameter</td>
</tr>
<tr>
<td>$H$</td>
<td>Molar enthalpy</td>
</tr>
<tr>
<td>$k_T$, $k_V$</td>
<td>Coefficients of reducing functions</td>
</tr>
<tr>
<td>$l$</td>
<td>Number of fluids in a mixture</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar mass</td>
</tr>
<tr>
<td>$m_k$, $n_k$</td>
<td>Exponents</td>
</tr>
<tr>
<td>$n$</td>
<td>Number of moles</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
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<tr>
<td>$R$</td>
<td>Universal gas constant</td>
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<td>$S$</td>
<td>Molar entropy</td>
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<td>$T$</td>
<td>Temperature</td>
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<td>Molar internal energy</td>
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<td>$V$</td>
<td>Molar volume</td>
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<tr>
<td>$Z$</td>
<td>Compressibility factor</td>
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<tr>
<td>$w$</td>
<td>Speed of sound</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Mole fraction of component $i$</td>
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<tr>
<td>$Z$</td>
<td>Compressibility factor</td>
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<td>$\beta$</td>
<td>Exponent</td>
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<tr>
<td>$\gamma$</td>
<td>Exponent</td>
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<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\Delta \alpha$</td>
<td>Reduced Helmholtz energy departure function</td>
</tr>
</tbody>
</table>
$\alpha$ Reduced Helmholtz energy
$\delta$ Inverse reduced volume or reduced density
$\tau$ Inverse reduced temperature
$\xi, \zeta$ Coefficients of reducing functions

Subscripts
n Reducing property
r Reference fluid
i Pure component $i$
calc Calculated

Superscripts
0 Ideal gas
E Excess
r Residual

References
