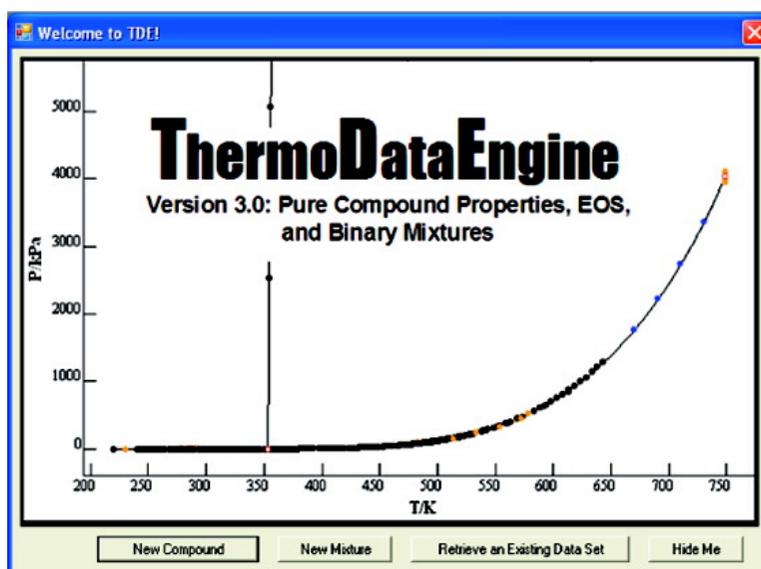## Article

ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 3. Binary Mixtures

Vladimir Diky, Robert D. Chirico, Andrei F. Kazakov, Chris D. Muzny, and Michael Frenkel

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ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 3. Binary Mixtures

Vladimir Diky, Robert D. Chirico, Andrei F. Kazakov, Chris D. Muzny, and Michael Frenkel*

Thermophysical Properties Division, National Institute of Standards and
Technology, Boulder, Colorado 80305-3328

ThermoData Engine (TDE) is the first full-scale software implementation of the dynamic data evaluation concept, as reported recently in this journal. The present paper describes the first application of this concept to the evaluation of thermophysical properties for binary chemical systems. Five activity-coefficient models have been implemented for representation of phase-equilibrium data (vapor−liquid, liquid−liquid, and solid−liquid equilibrium): NRTL, UNIQUAC, Van Laar, Margules/Redlich−Kister, and Wilson. Implementation of these models in TDE is fully described. Properties modeled individually are densities, surface tensions, critical temperatures, critical pressures, excess enthalpies, and the transport properties−viscosity and thermal conductivity. Extensions to the class structure of the program are described with emphasis on special features allowing close linkage between mixture and pure-component properties required for implementation of the models. Details of gas-phase models used in conjunction with the activity-coefficient models are shown. Initial implementation of the dynamic data evaluation concept for reactions is demonstrated with evaluation of enthalpies of formation for compounds containing carbon, hydrogen, oxygen, and nitrogen. Directions for future enhancements are outlined.

1. INTRODUCTION

As was discussed in the first two papers of this series,[1,2] *NIST ThermoData Engine* (TDE) software represents the first full-scale implementation of the dynamic data evaluation concept for thermophysical properties.[3,4] This concept requires large electronic databases capable of storing essentially all relevant experimental data known to date with detailed descriptions of metadata and uncertainties. The combination of these electronic databases with expert-system software, designed to automatically generate recommended property values based on available experimental and predicted data, leads to the ability to produce critically evaluated data dynamically or 'to order'.

The first version of TDE (version 1.0, released in 2004[5]) was limited to thermophysical properties of pure compounds. The second version (version 2.0, released in 2006[6]) expanded the implementation of dynamic data evaluation to on-demand generation of equations of state (EOS). To adequately represent a range of data scenarios, four equations of state of different complexities and precisions were selected: Peng−Robinson,[7] PC-SAFT,[8] Sanchez-Lacombe,[9,10] and fundamental equations based on the Helmholtz energy.[11,12] A dynamically updated *TDE-SOURCE*[2] data storage tool was developed, in part, with the multitier Web-Oracle dissemination system[13] recently established in development of the NIST Ionic Liquids Database, ILThermo[14] and NIST Web Thermo Tables.[15] All functional elements of TDE versions 1.0 and 2.0 have been further combined into TDE version 2.1.[16]

As previously described,[2] experimental data used by TDE are extracted from the *TRC-SOURCE*[17] data storage system and distributed as a local database (*TDE-SOURCE*) with the program. *TRC-SOURCE* is maintained at NIST and is continuously populated with new experimental data (using Guided Data Capture GDC software[18] developed at NIST). In order to more closely adhere to the requirements for dynamic data evaluation, TDE includes a mechanism for dynamically updating the local *TDE-SOURCE* based on additions and changes to *TRC-SOURCE* through a central server.

The present paper describes further expansion of TDE (version 3.0) in implementing the dynamic data evaluation concept for binary mixtures.[19] This expansion is a major step in the development of the TDE framework, broadening the scope of experimental properties considered from roughly 50 for pure compounds to about 120 for binary mixtures. In this development, numerous challenges were addressed related to enforcement of consistency among the phase equilibria properties of binary mixtures, which are expressed in a broad variety of ways in the experimental literature as well as enforcement of consistency between properties of the pure components and binary mixtures. This expansion is important from the standpoint of industrial applications in that it makes TDE suitable for use in a variety of engineering applications, including separation process design.

In addition to the expansion of TDE for binary mixtures, initial implementation of the dynamic data evaluation concept for reactions is demonstrated with evaluation of enthalpies of formation for compounds containing carbon, hydrogen, oxygen, and nitrogen. The framework described here will be extended to other reaction types in future releases of TDE. Directions for future enhancements are discussed.

* Corresponding author e-mail: frenkel@boulder.nist.gov.

2. SCOPE

While numerous industrially important inorganic compounds are within the scope of TDE, the focus of the program is organic compounds composed of the elements C, H, N, O, F, Cl, Br, I, S, and P. This is unchanged from the version limited to single components. The expansion of TDE (version 3) into property evaluations for binary mixtures has progressed along two paths: one for properties modeled individually (densities, surface tensions, critical temperatures, critical pressures, excess enthalpies, and the transport properties—viscosity and thermal conductivity) and one for properties modeled collectively (activity-coefficient models for phase equilibrium properties), including vapor liquid (VLE), liquid−liquid (LLE), and solid−liquid (SLE) equilibria. Excess enthalpies (and excess heat capacities) are not modeled collectively with the phase-equilibrium properties within TDE 3.0. This extension is planned for future development.

Fundamental thermodynamics, as expressed in the Gibbs phase Rule, specifies the maximum number of phases present and the number of independent variables required to fully specify a particular property for a system with a given number of components (chemical compounds). In the case of a binary chemical system, the maximum number of phases is four (an invariant state with no independent variables), and the maximum number of independent variables is three (for a single-phase system). These restrictions limit the number of system types to be considered, but a very large number of possible phase and variable combinations remain. This expansion of TDE targets systems with a maximum of two phases (i.e., VLE, LLE, and SLE but not vapor-solid equilibria). More complex equilibria, such as vapor−liquid−liquid (VLLE) or solid−liquid−vapor (SLVE), will be addressed in future releases. The present version (TDE 3.0) establishes the framework on which future extensions for mixtures will be based.

3. ALGORITHM

To model properties for binary mixtures, the properties of the pure components are required. In broad terms, the program algorithm involves full evaluation of the properties for each pure component (as described in the first two papers of this series[1,2]) followed by evaluation of the properties for the binary mixture. The molecular structures and property models for the pure components are essential for property estimations and modeling for the mixture.

Processing before Mixture Property Evaluation. The user initiates the evaluation process by selecting the two mixture components. Special features for the selection process, such as selection of components with known availability of experimental data, are described later. The first action of the TDE software is to retrieve all experimental data for the mixture and its components from the local database, *TDE-SOURCE*. The *TDE-SOURCE* archive of experimental data is a subset of the *TRC SOURCE* archive[17] which was designed and built as an extensive relational data archival system for experimental thermophysical, thermochemical, and transport properties reported in the world's scientific literature. Presently, *TDE-SOURCE* contains 2.0 million independent experimental property values for more than 31,000 mixtures. In addition, proprietary or other

experimental data can be added by the user. As described previously for pure-component evaluation,[1,2] property values can be modified (corrected) or selected for forced rejection by the user. Added or modified data are not added to *TDE-SOURCE* but are maintained separately to control the integrity of *TDE-SOURCE*. Property data are normalized, where possible, at the data-loading step, where mixture compositions are converted to x_1 (mole fraction of component 1), phases and variables are sorted, and different representations of the same property (e.g., density and molar volumes) are converted to a single property (density, in this example). Some composition variables require further processing. For example, densities are required to convert molarities to a mole fraction basis.

Before evaluating mixture properties, TDE evaluates properties of the components. This step is skipped for 70 compounds for which pre-evaluated properties are taken directly from the integrated REFPROP database.[20] (The user is informed by the program when this occurs.) These 70 compounds include water, many simple hydrocarbons (e.g., methane, ethane, etc.), light alcohols (methanol, ethanol), and other common chemicals. On-demand property evaluations for these compounds may be slow due to the large amount of available data. The REFPROP database provides high-quality models, plus there is little expectation of significant evaluation changes due to new measurements.

It is well-known that systematic errors in experimental mixture data relative to those of the pure components can lead to erroneous results, such as the prediction of azeotropic conditions where none exist or anomalous values for excess properties. To avoid such a scenario, each data point for the mixture is combined with property values for the pure components at the same conditions reported in the same data source (i.e., reported by the researchers in the same report or article) to calculate 'excess' values. These excess properties are used during evaluation instead of excess values calculated relative to pure-component properties evaluated by TDE. Not all reports provide pure-component properties, but this action yields at least partial compensation for systematic errors.

Additional sorting of the available experimental data is done for the convenience of the user. Property representation in TDE-SOURCE is designed to store individual properties as functions of appropriate state variables in accord with the Gibbs phase Rule. Experimental studies of phase equilibria often report results in multiproperty tabular form, such as *p*-*T*-*x*-*y* tables (pressure, temperature, liquid-phase composition, and gas-phase composition). The individual properties [e.g., $p = f(x, T)$ and $y = f(x, T)$ for VLE] from a given source at the same conditions are tied by special pointers that allow building of complete *p*-*T*-*x*-*y* tables. Similarly, separate liquid−liquid equilibrium properties are at times reported as "mutual solubility" tables. Such linked data sets are highlighted in special summary tables for the user. An example for VLE data is shown in Figure 1.

A final important step before evaluation of the mixture properties is identification of temperature and composition conditions for nonheterogeneity in the liquid state (i.e., the presence of liquid−liquid phase separation). Such regions are often not identified clearly (or at all) in the experimental literature. The TDE software combines available LLE data as phase-equilibrium temperatures $T = f(x_1)$ for pressures p

THERMODATA ENGINE. 3. BINARY MIXTURES

J. Chem. Inf. Model., Vol. 49, No. 2, 2009 **505**

Figure 1. Summary table for vapor−liquid equilibrium (VLE) data in TDE. Highlights indicate *p-T-x-y* data from a single data source.
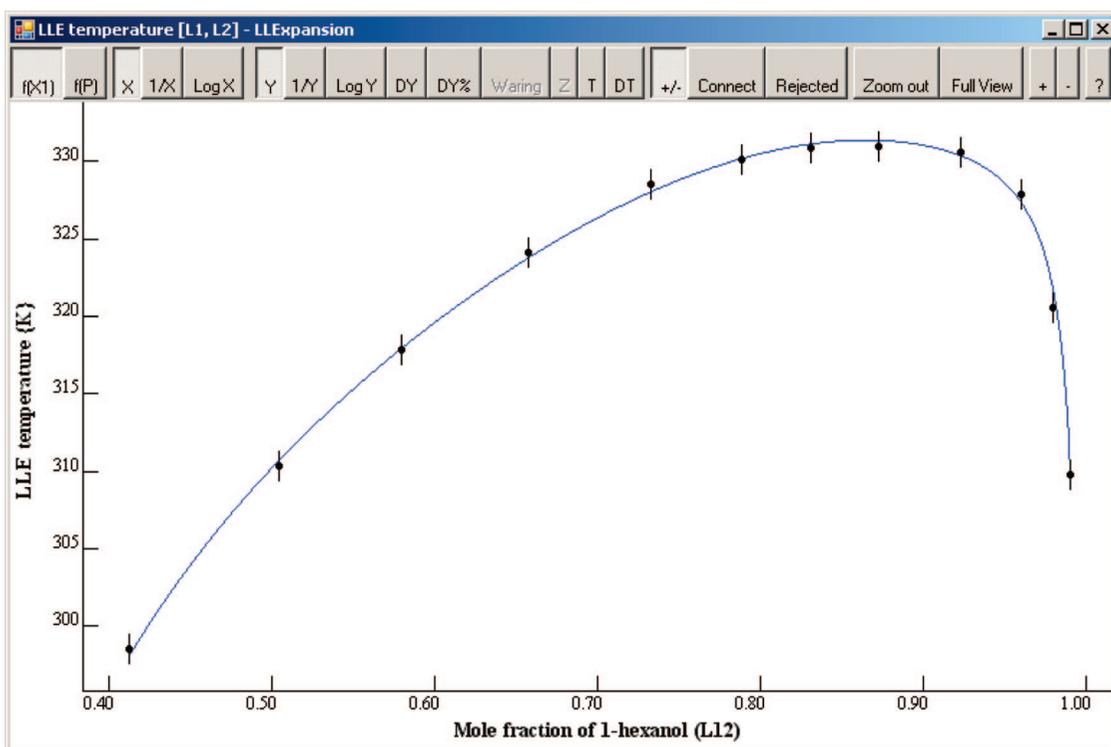
Figure 2. Experimental liquid−liquid equilibrium temperatures for the system (1-hexanol + 1-hexyl-3-methylimidazolium 1,1,1-trifluoro-N-[(trifluoromethyl)sulfonyl] methanesulfonamide) fitted with eq 1. The error bars are the uncertainties (estimated at NIST) for the experimental values.

near atmospheric and fits the following equation to the experimental values

$$(T/K) = A_0 + A_1/x_1 + A_2/x_2 + \sum_{i=3}^{n} A_i \cdot (x_1 \text{-} x_2)^i \quad (1)$$

where x_1 and x_2 are the mole fractions of the two components, and the upper limit of the summation n ($3 \leq n \leq 7$) is optimized by the program. Figure 2 shows a fit of this equation to LLE temperatures for the system (1-hexanol + an ionic liquid). The equation is used to delimit the composition ranges for the single-phase liquid state. The equation also serves as the basis for consistent association

of liquid compositions at LLE with a particular liquid phase. This is necessary because data from different literature sources stored in *TDE-SOURCE* may be based on different definitions of liquid-phase 1 and liquid-phase 2.

Evaluation with Single-Property Models. Properties for binary mixtures represented by single-property models in the present version of TDE are densities, viscosities, thermal conductivities, surface tensions, excess enthalpies, critical temperatures T_c, and critical pressures p_c. If not reported directly as excess properties, the experimental property values are converted for evaluation. As described earlier, pure-component property values from the same literature source

506 *J. Chem. Inf. Model.*, Vol. 49, No. 2, 2009

DIKY ET AL.
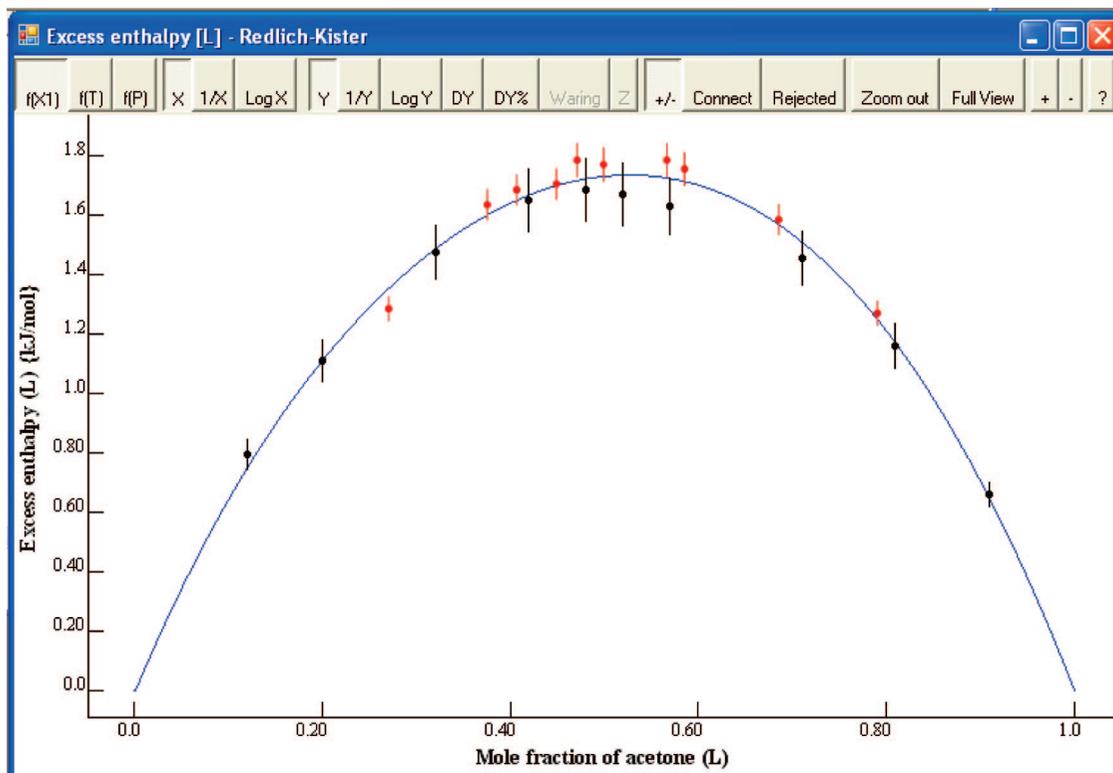
Figure 3. Excess enthalpies for the system (acetone + hexan-1-ol). The data points are experimental excess enthalpy values from multiple data sources, and the curve is the Redlich−Kister equation fitted by the TDE software. The error bars are the uncertainties (estimated at NIST) for the experimental values.

Figure 4. Interface for modification of activity-coefficient model details: number of terms for the Margules and Redlich−Kister equations, the form of the equation for temperature dependence of the activity coefficients (eq 3), and selection of the form (symmetric or asymmetric) of the Wilson, NRTL, UNIQUAC, and Van Laar equations.
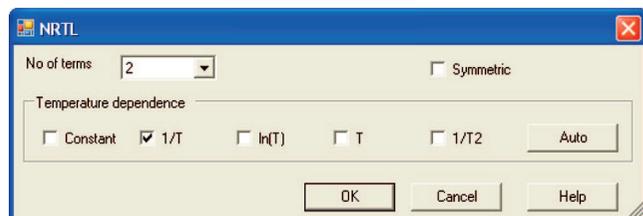
are used for conversion to excess properties, when possible, to compensate for systematic errors. Model parameters are pressure invariant and temperature dependent for all properties except T_c and p_c. High-pressure data (at pressures more than 5 MPa above the bubble-point pressures) currently are not processed. All excess properties are represented with the Redlich−Kister equation

$$\Psi = x_1 \cdot \Psi_1 + x_2 \cdot \Psi_2 + \sum a_i \cdot x_1 \cdot x_2 \cdot (x_1 - x_2)^i \quad (2)$$

where x_j and Ψ_j are the mole fraction and property value for pure component j, and the summation is from $i = 0$ to *nTerms*, with *nTerms* ≤ 4. Linear least-squares fitting is used with statistical weights proportional to the reciprocal squares of the uncertainties converted to excess property representation where necessary.

Figure 3 shows an example graph from the TDE software for an evaluated single property. The data points are experimental excess enthalpy values from two data sources, and the curve is the fitted Redlich−Kister equation. Fitted

parameters are provided to the user through the software interface, a text output computer file, and a file in ThermoML[21] format. ThermoML is the IUPAC data communication standard for thermophysical and thermochemical properties.

Evaluation with Activity-Coefficient (AC) Models. Properties associated with phase equilibria are fitted with AC models in the present version of TDE. AC models are widely used in industry for modeling a variety of phase equilibria, including VLE, LLE, and SLE. Phase equilibria and activity coefficients are described by AC models that express the composition dependence of the excess Gibbs energy for the liquid state. Many properties can be derived from AC models.[22] Presently, the following properties are supported in TDE: $p = f(x, T)$ or "bubble-point" pressure, $p = f(y, T)$ or "dew-point" pressure, gas-phase composition $y = f(x, T)$, activity coefficients in liquid state, and solid−liquid equilibrium temperature. Excess enthalpy and heat capacity will be included in the next version of TDE. A second type of model, equation-of-state (EOS) models,[22] will also be added to TDE in the next version to allow on-demand evaluations for properties of binary systems with a component at supercritical conditions for processes such as extraction with supercritical carbon dioxide.

A variety of AC models is provided in TDE for the convenience of the user: Margules,[23] NRTL,[24] Redlich−Kister,[25] UNIQUAC,[26] Van Laar,[27] and Wilson.[28] Mathematical implementations of the Margules and Redlich−Kister formulations are identical in TDE. A discussion of the efficacy of the various models for particular types of chemical systems is outside the scope of this work and is an active area of research in the chemical-engineering community. Some information on this topic is provided by Poling et al.[22] In the TDE 3.0 software,

THERMODATA ENGINE. 3. BINARY MIXTURES

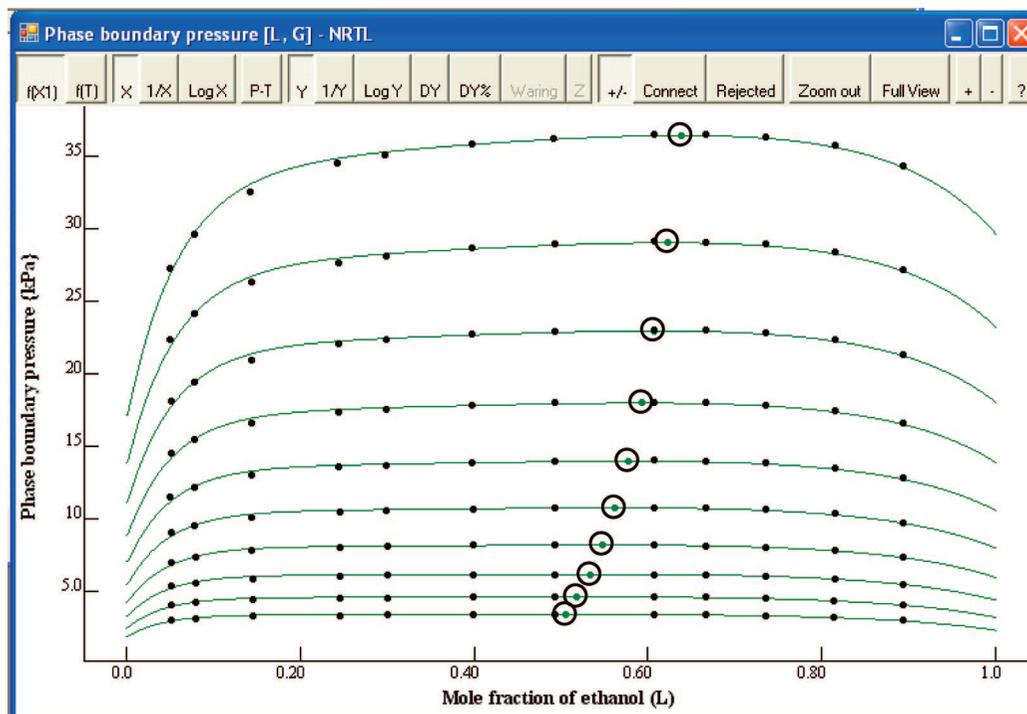*J. Chem. Inf. Model.*, Vol. 49, No. 2, 2009 **507**

Figure 5. Bubble-point pressures for the system (ethanol + 1-bromobutane). The curves represent model isotherms evaluated by the TDE software. The azeotropic conditions are identified by the TDE software and displayed on the graph. These conditions are circled here in the figure for clarity.

models for fitting are selected by the user. UNIFAC,[29,30] a predictive group-contribution method for activity coefficients that requires no fitting, is implemented in TDE with the form and parametrization given by Poling et al.[22]

Fitting of AC models is a much more complex process than that for single-property models. Preparation of property data for fitting is similar to that for single-property models and includes association with pure-component property values, assignment of statistical weights, and exclusion of data involving components at supercritical conditions. (Future development of TDE includes evaluations for such super-critical data.) In addition, consistency tests[31,32] are applied to p-T-x-y data. The weights of data showing departure from consistency are reduced in accordance with the magnitude of the departure.

Nonlinear fitting methods (Simplex or Simulated Annealing)[33] are used with least-squares objective functions. Special provision is made for application of the symmetric form of the NRTL and UNIQUAC models, if requested by the user. Details of these models are provided in the Appendix. A variety of gas-phase models may be selected by the user: Ideal-Gas, Virial Model,[34] Redlich-Kwong,[35] and Peng−Robinson.[7] Details of the equations for these models are also provided in the Appendix. The selected gas-phase model is used in an iterative refinement of the pressure p and gas composition y, except for the ideal-gas model, where the calculation is straightforward.

All AC model parameters are temperature-dependent. The dependence is represented in TDE with the following equation that includes up to five terms, where Θ represents any temperature-dependent parameter:

$$\Theta = A + B/T + C \cdot \ln(T) + D \cdot T + E/T^2 \qquad (3)$$

The program automatically selects the number of terms based upon the extent of available experimental data. A special

user interface is provided (Figure 4) to allow modification of the selected equation terms as well as specification of the number of parameters for the Margules/Redlich−Kister equation (see the Appendix) and selection of the symmetric form of the Wilson, NRTL, UNIQUAC, and Van Laar equations. The symmetric form is often chosen when experimental data are available for only one extreme of the composition range. In those cases, a reduced number of parameters is varied. Details of the symmetric form for each equation are included in the Appendix.

As the fitting process can be long, it is implemented as a separate programming thread that is monitored and controlled through a user interface that was described previously for EOS fitting. This interface was termed the *EOS Control Center*[2] for the fitting of equations of state. In TDE 3.0 (for binary mixtures), it is termed the *Multi-Property Model Control Center*, but the purpose is the same. Here, the user can monitor the fitting of properties as the model is adjusted, pause the fitting process to make modifications, and resume after modifications. Modifications can include correction or rejection of experimental data, changing relative weights of different properties, and selection of properties to include in the fit. The *Multi-Property Model Control Center* also allows direct access to the user interface for modification of AC model details (see Figure 4), such as the number of model parameters, the nature of the mathematical function for temperature dependence of the activity coefficients, and the symmetry status.

Figures 5, 6, and 7 show results of the application of activity-coefficient models to phase-equilibrium data involving VLE, LLE, and SLE, respectively. Each figure also demonstrates the display of properties for special conditions (azeotropic, consolute, and eutectic) evaluated in TDE. Figure 5 shows bubble-point pressures for the system (ethanol + 1-bromobutane). The azeotropic conditions are circled in the
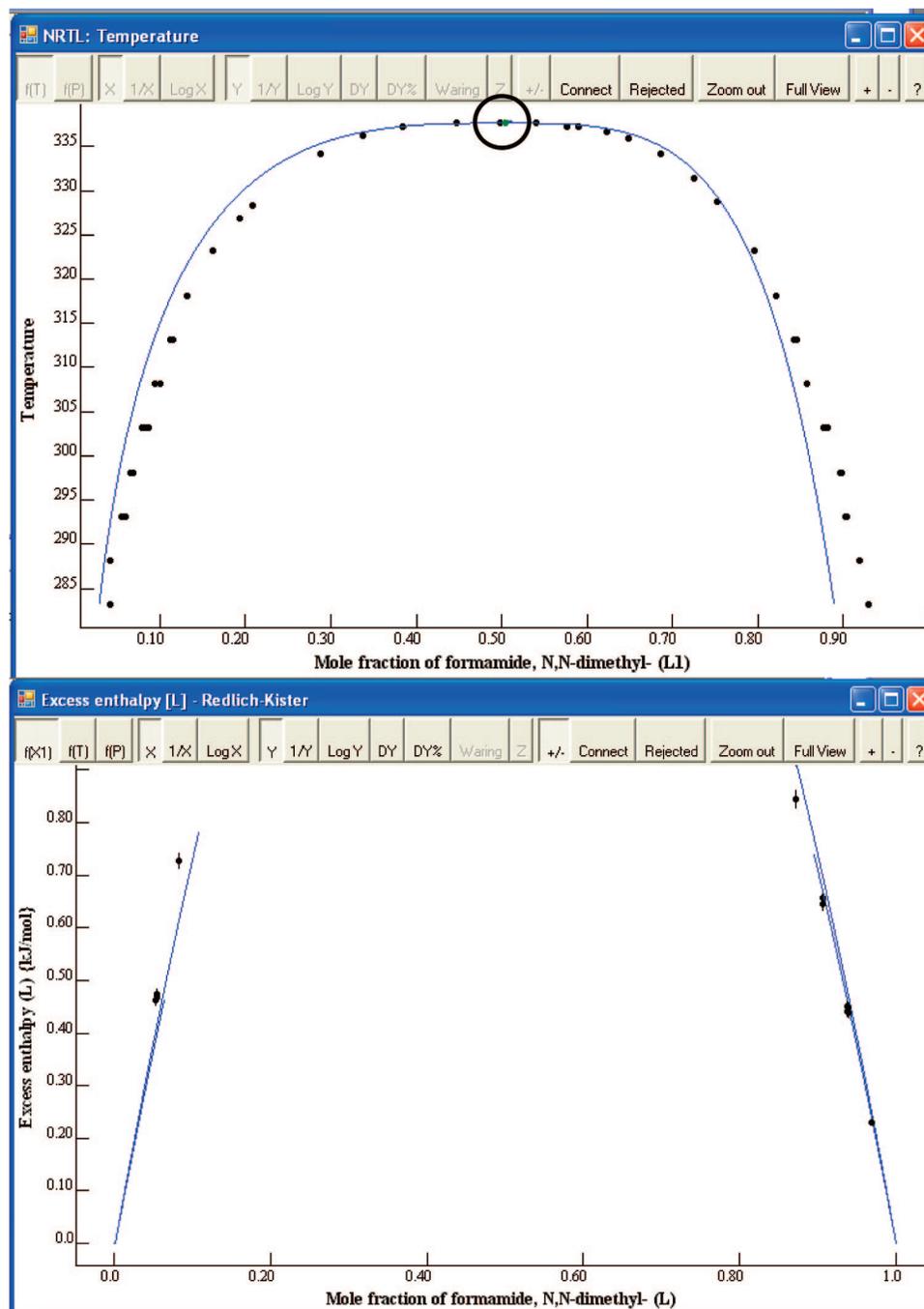
Figure 6. Liquid−liquid equilibrium temperatures (upper figure) and excess enthalpies (lower figure) for the system (2-methylpentane + N,N-dimethylformamide). The curves represent the models evaluated by the TDE software. The upper consolute conditions are indicated in the upper figure. These are identified by the TDE software, displayed on the graph, and are circled here in the figure for clarity. The error bars are the uncertainties (estimated at NIST) for the experimental values.

figure. Figure 6 shows liquid−liquid equilibrium temperatures (upper figure) and excess enthalpies (lower figure) for the system (2-methylpentane + N,N-dimethylformamide). The upper consolute conditions are indicated in the upper figure. The program uses the LLE results to limit the range of the fitted equation for the excess enthalpies shown in the lower figure. Figure 7 shows solid−liquid equilibrium temperatures for the system (benzene + naphthalene). The eutectic conditions evaluated by the TDE software are circled on the plot. At this time, solid solutions are not considered, and all solid phases are assumed to be stable crystals of the pure components.

If the necessary group parameters are available, the UNIFAC group-contribution method also can be valuable

in checking for data validity. The upper part of Figure 8 compares values calculated with the UNIFAC model implemented in TDE with experimental VLE data for the system (N,N-dimethylformamide + ethylbenzene), while the lower figure shows the results for a fit of the NRTL model to this system. Extension of the UNIFAC parameter set to allow representation of a wider range of chemical systems is an active area of research in chemical engineering.

4. SOFTWARE ARCHITECTURE

TDE software consists of three components, with each providing unique functionality. The first part contains core objects and data evaluation procedures and is written and

ThermoData Engine. 3. Binary Mixtures

J. Chem. Inf. Model., Vol. 49, No. 2, 2009 **509**
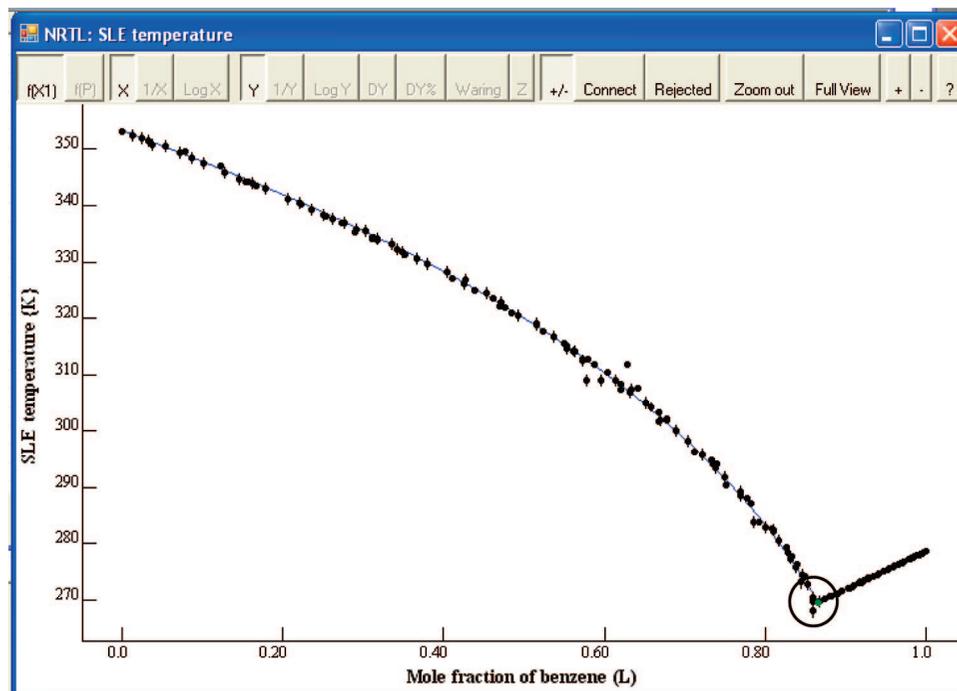
Figure 7. Solid−liquid equilibrium temperatures for the system (benzene + naphthalene). The curve represents the activity coefficient model fitted to the experimental data by the TDE software. The evaluated eutectic conditions are identified by the TDE software and displayed on the graph. These are circled here in the figure for clarity. The error bars are the uncertainties (estimated at NIST) for the experimental values.

maintained in ANSI standard C++, making it independent of platform and operating system. The second part contains data-access procedures that can be changed in order to accommodate different data sources (databases or other database connection tools). The third part is the graphical user interface, which is dependent on both the operating system and programming environment. In order to facilitate multithreading, the low-level TDE property fitting objects contain specific fields that allow their status to be monitored (e.g., for contribution to the objective function from each property) or that can be used as flags for controlling the fitting process (Stop flags). Using dynamic-link library (DLL) or other technologies, TDE can provide interactive, on-demand property evaluation to any application needing pure-component or mixture property data.

The software architecture for evaluation of pure-component properties in TDE was described in the first paper of this series.[1] Additions to accommodate EOS support, including specific C++ classes, were described in the second paper of the series.[2] In this section, further additions to accommodate evaluation of properties for binary mixtures are described.

The Mixture class is a new object in TDE. It is analogous to the Compound class, described previously,[2] which includes property data and models for fitting the property data. The general structure of the Mixture class is shown in Figure 9. The Mixture class includes two Compound objects for the mixture components, shown as Compound (1) and Compound (2) in Figure 9. The Compound objects were described previously[2] and include the chemical identification (name and formula), molecular structures, experimental property data, and models describing the pure-component properties. This information is a prerequisite for property evaluations for a mixture. There are single-property equations for description of one property, such as critical temperature or

excess volume as a function of composition (Single-Property Model in Figure 9), and multiproperty equations, such as AC models (Multi-Property Model in Figure 9). Single-Property Models belong to Mixture Property objects. In contrast, Multi-Property Models belong to the Mixture object and are associated with the group of properties that they describe, as indicated by the arrow in Figure 9.

A Property class (labeled as TDProperty) was described previously.[2] This class was modified and extended to meet the needs for mixtures. Property representation is based on that in *TRC-SOURCE*, which serves as the primary source of raw data for TDE. Namely, each property object is designed to store a single property as a function of state variables. Multiproperty data sets, such as p-T-x-y data for vapor−liquid equilibria, are stored in separate objects. The two data sets obtained from p-T-x-y data are $p = \mathrm{f}(x, T)$ for isotherms or $T = \mathrm{f}(x, p)$ for isobars and $y = \mathrm{f}(x, T)$ for the gas-phase composition. Other combinations of variables may not uniquely identify a state condition for some systems. For example, the p-T combination does not uniquely identify a state for mixtures forming azeotropes, where two different compositions correspond to the same p-T pair. Similarly, use of y-T or y-p as variables does not uniquely identify state conditions for equilibria involving a supercritical gas. In this case, a single gas-phase composition has two equilibrium states with the liquid. An example is provided in Figure 10.

The structure of the Mixture Property class is shown in Figure 11. A property of a binary mixture may be associated with a single phase or a specified condition of phase equilibrium, with a maximum of four phases existing simultaneously, in accord with the Gibbs phase Rule. In comparison with pure-compound properties, there is the additional variable of composition, which is associated with a particular phase at equilibrium. This is why State Variables are associated with phase on the right side of Figure 11. For

510 *J. Chem. Inf. Model., Vol. 49, No. 2, 2009*

DIKY ET AL.
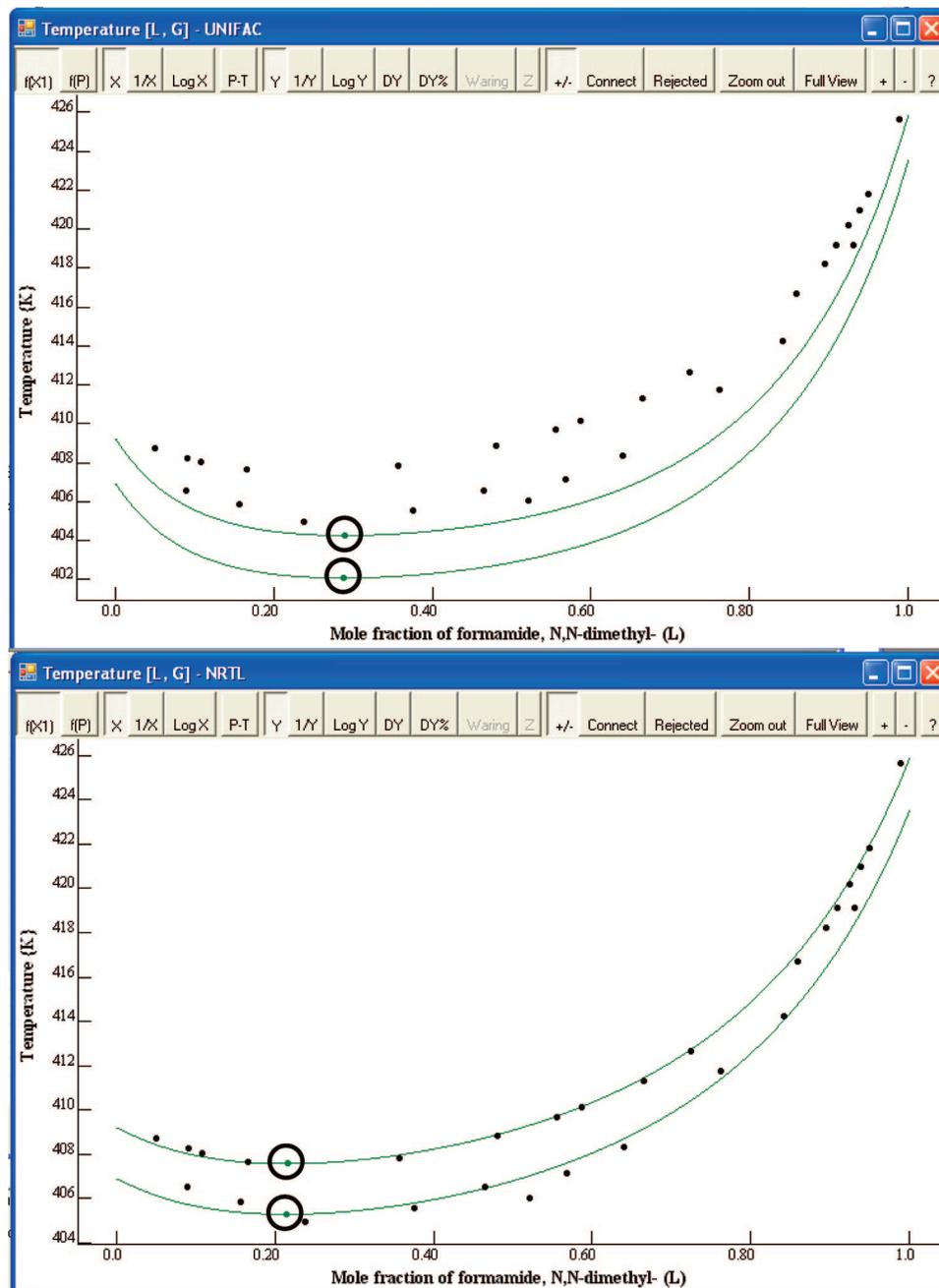
Figure 8. VLE data for the system (N,N-dimethylformamide + ethylbenzene). The upper figure compares values calculated with the UNIFAC model implemented in TDE (curves) with experimental VLE data (points) for the system (N,N-dimethylformamide + ethylbenzene). In the lower figure, the curves represent a fit of the NRTL model to this system by the TDE software. Azeotropic conditions evaluated with the models are displayed in the figures and are circled here for clarity.

some phase equilibria (e.g., solid−liquid equilibria) the crystal may be a pure component. This is why the phase element is associated with Component on the left side of Figure 11.

In analogy with the class structure for pure-component properties,[2] the Mixture Property class contains Data Sets (sets of property data from a given literature source), as represented in the center of Figure 11. Data Sets contain experimental data points, each with one property value and the values of the independent variables defining the state, as represented by Numerical Values in Figure 11. For the convenience of the user, complete VLE data (p-T-x-y) and complete LLE data (p-T-x'-x'', where the primes indicate a particular liquid phase) from a given data source are
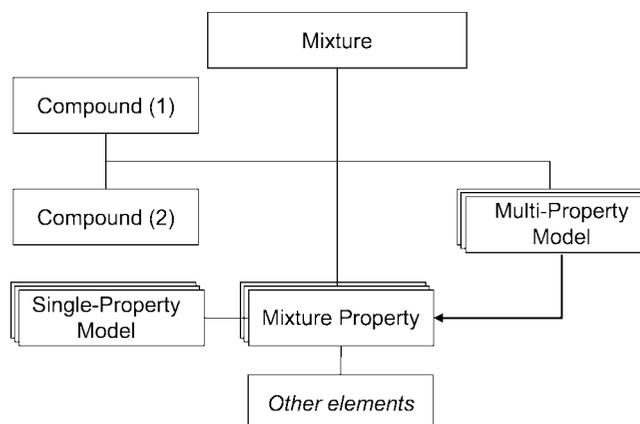
Figure 9. Structure of the Mixture class in TDE.

THERMODATA ENGINE. 3. BINARY MIXTURES

J. Chem. Inf. Model., Vol. 49, No. 2, 2009 **511**
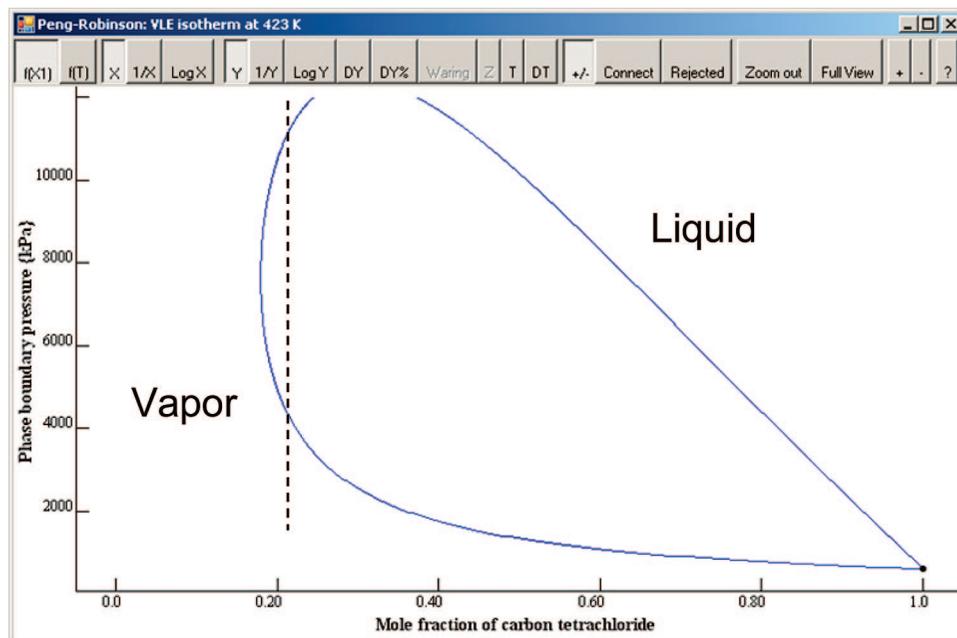
Figure 10. Isothermal vapor−liquid equilibrium for the system (carbon tetrachloride + ethene). The horizontal axis represents the mole fraction of carbon tetrachloride in the gas state. The intersections of the dashed line with the curve indicate two equilibrium states at a single gas-phase composition.
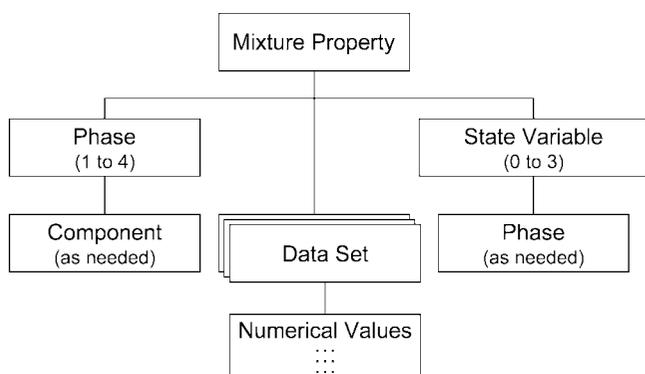
Figure 11. Structure of the Mixture Property class in TDE.
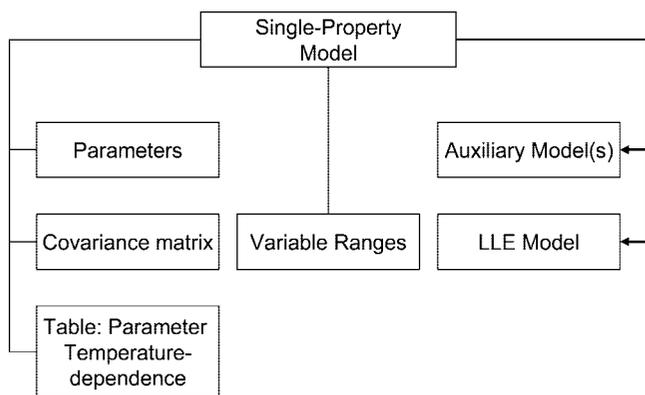
Figure 12. Structure of the Single-Property Model class in TDE.

identified. For this purpose each data point may contain a pointer to another data point, indicating the second property value.

The Single-Property Model class (Figure 12) also has additional features for mixtures. In addition to Parameters, the Covariance Matrix, and Variable Ranges (a table of validity ranges for state variable minima and maxima), it contains (1) a table indicating terms that express the temperature dependence of parameters, (2) pointers to
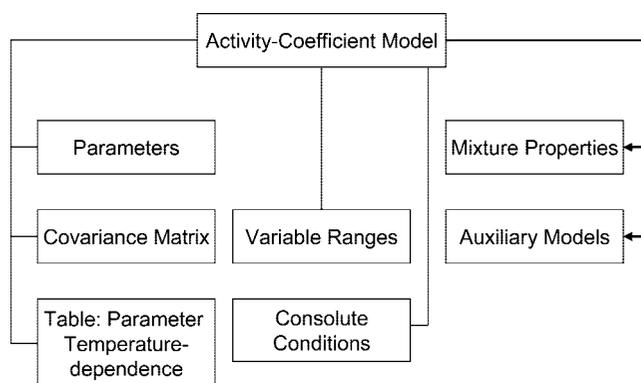
Figure 13. Structure of the Activity-Coefficient Model class in TDE.

Auxiliary Model(s) describing pure-component properties, and (3) a pointer to an LLE Model delimiting the composition range of the single-phase liquid, if a heterogeneous region is known to exist. The temperature dependence of the model parameters is expressed with eq 3. Any combination of the terms (*A* through *E*) can be selected by the user.

The structure of the Activity-Coefficient Model class (Figure 13) is based on the Multi-Property Model class (previously termed MultiModel[2]) used for EOS representation of pure compounds. Extensions for binary mixtures are analogous to those for the Single-Property Model class (Figure 12). In addition, consolute conditions (temperature and composition) derived from an AC model (if any) are included explicitly. The availability of this information decreases the computation time for many property calculations. The Auxiliary Models for an Activity-Coefficient Model (right side of Figure 13) are gas-phase models, which are described in the Appendix.

5. INTERFACE FEATURES FOR MIXTURES

The nature of thermophysical properties for binary mixtures presents multiple challenges in interface development,
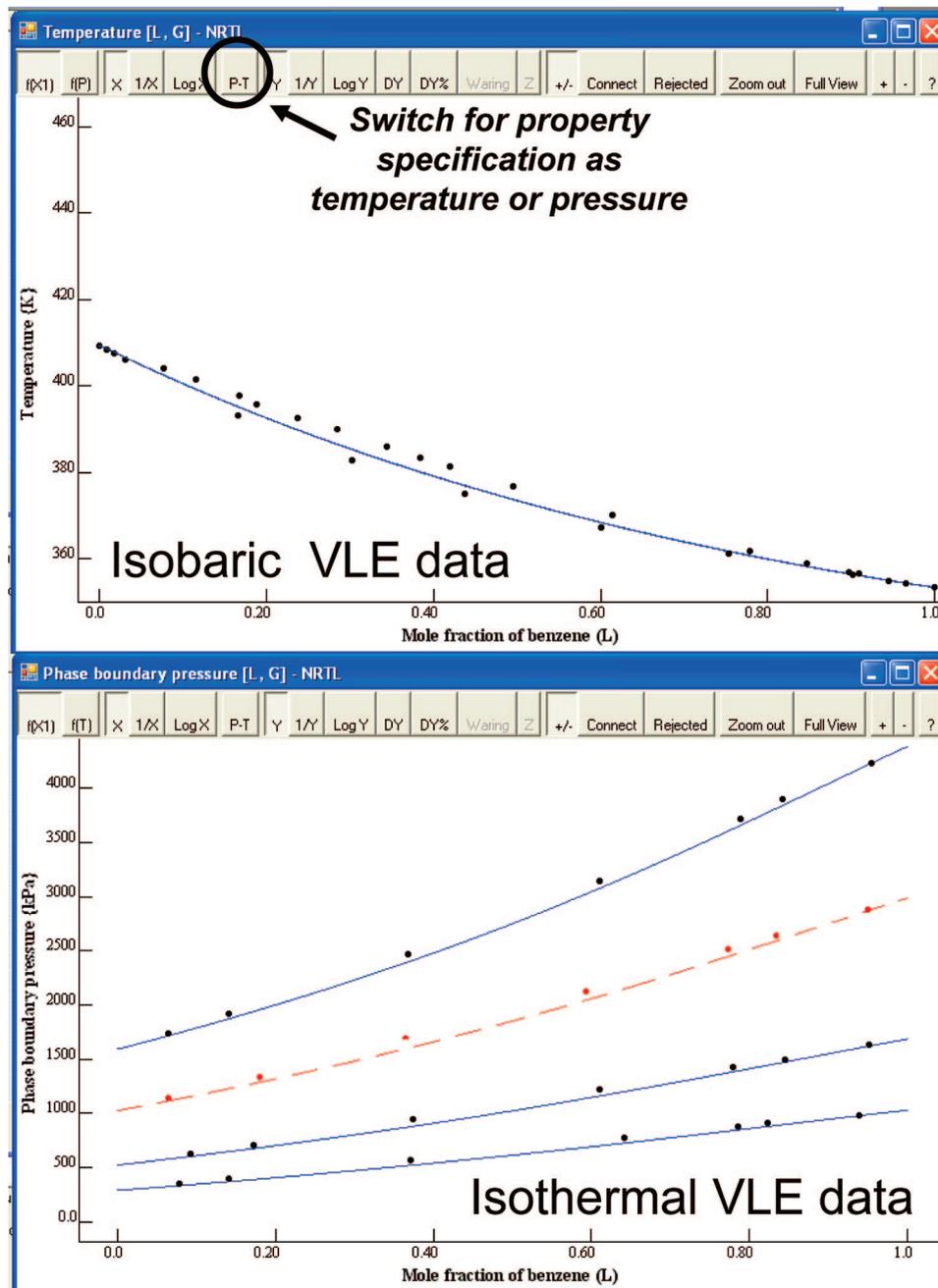
Figure 14. Isobaric and isothermal VLE data for the system (1,4-dimethylbenzene + propan-1-ol). The curves represent isobars (upper figure) and isotherms (lower figure) for the NRTL model evaluated with the TDE software. The $p \leftrightarrow T$ switch allows easy access to the alternative displays. Experimental data associated with particular isobars or isotherms can be highlighted, as shown by the dashed curve in the lower figure.

including user needs for identification of chemical systems with particular data types, full user access to mixture and pure-component information for model analysis and refinement, and effective display of model-experiment comparisons in a multivariable environment. Compound characteristics used for searching in TDE include name, formula, structure, and substructure. The availability of particular data types (e.g., VLE, LLE, transport properties, etc.) may be used as search criteria. A two-step search procedure first selects the compounds with desired data available and then refines the search result to the compounds matching the desired substructure and identification.

Effective display of comparisons between experimental data and models is a particular challenge for the representa-

tion of VLE (vapor−liquid equilibrium) data. The state variables that can be reported are p, T, x, and y. Experiments are commonly reported for either isothermal or isobaric conditions. Results at constant composition are reported also but much more rarely. To accommodate isobaric and isothermal VLE data comparisons, a simple $p \leftrightarrow T$ switch allows representation of the results with either state variable as the defined property for display. This feature, in combination with the ability to show isothermal or isobaric data sets only, greatly eases visual comparisons between experimental data and models. Figure 14 shows isobaric and isothermal VLE data for the system (1,4-dimethylbenzene + propan-1-ol). The two views show good agreement between the experimental data and the fitted NRTL model.

THERMODATA ENGINE. 3. BINARY MIXTURES

J. Chem. Inf. Model., Vol. 49, No. 2, 2009 **513**
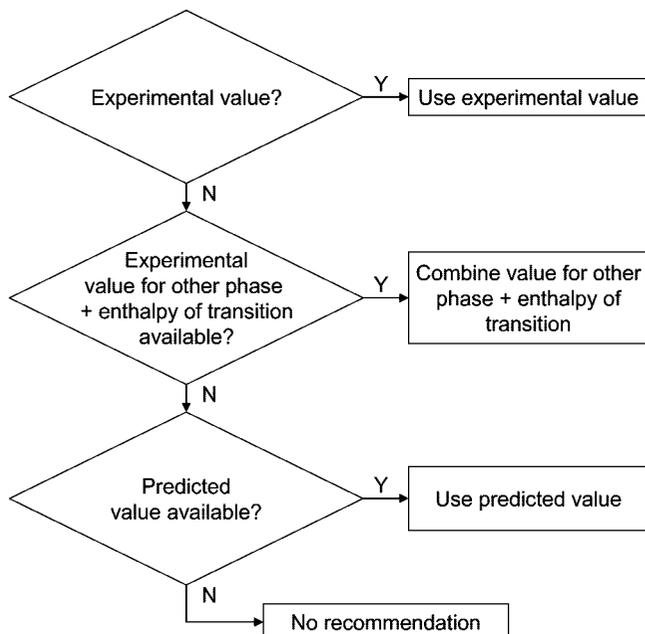
Figure 15. General algorithm for evaluation of the enthalpy of formation for CHON compounds.

6. PROPERTIES OF REACTIONS

Although the most important new features of TDE 3.0 involve evaluations of properties for binary mixtures, initial steps were made to provide capabilities for display and evaluation of reaction properties. Within TDE 3.0, enthalpies of formation are evaluated for compounds containing C, H, O, and N ("CHON compounds"). Enthalpies of formation are rarely measured directly but are commonly derived from enthalpy-of-combustion (in oxygen) studies. Enthalpies of combustion and formation for halogenated and sulfur-containing compounds will be included in a future release of TDE, where complexities associated with acid solutions as combustion products and issues related to the standard state of sulfur will be addressed fully.

The general reaction for the combustion of CHON compounds in oxygen is

$$C_aH_bO_cN_d(cr, l, or g) + [(4a + b - 2c)/4]O_2(g) = aCO_2(g) + (b/2)H_2O(l) + (d/2)N_2(g) \quad (4)$$
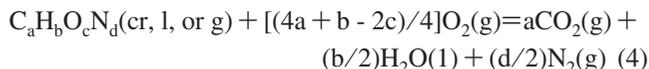
The enthalpy of this reaction is used within the TDE software in combination with the enthalpy of formation for $CO_2(g)$ [$-(393.51 \pm 0.13)$ kJ·mol^{-1}] and $H_2O(l)$ [$-(285.830 \pm 0.042)$ kJ·mol^{-1}], as assigned by CODATA,[36] to calculate the enthalpy of formation of $C_aH_bO_cN_d$ in the particular phase. Some authors report not the enthalpy of the combustion reaction but only the derived enthalpy of formation. In these cases, the reported enthalpy-of-formation values are stored in *TDE-SOURCE*.
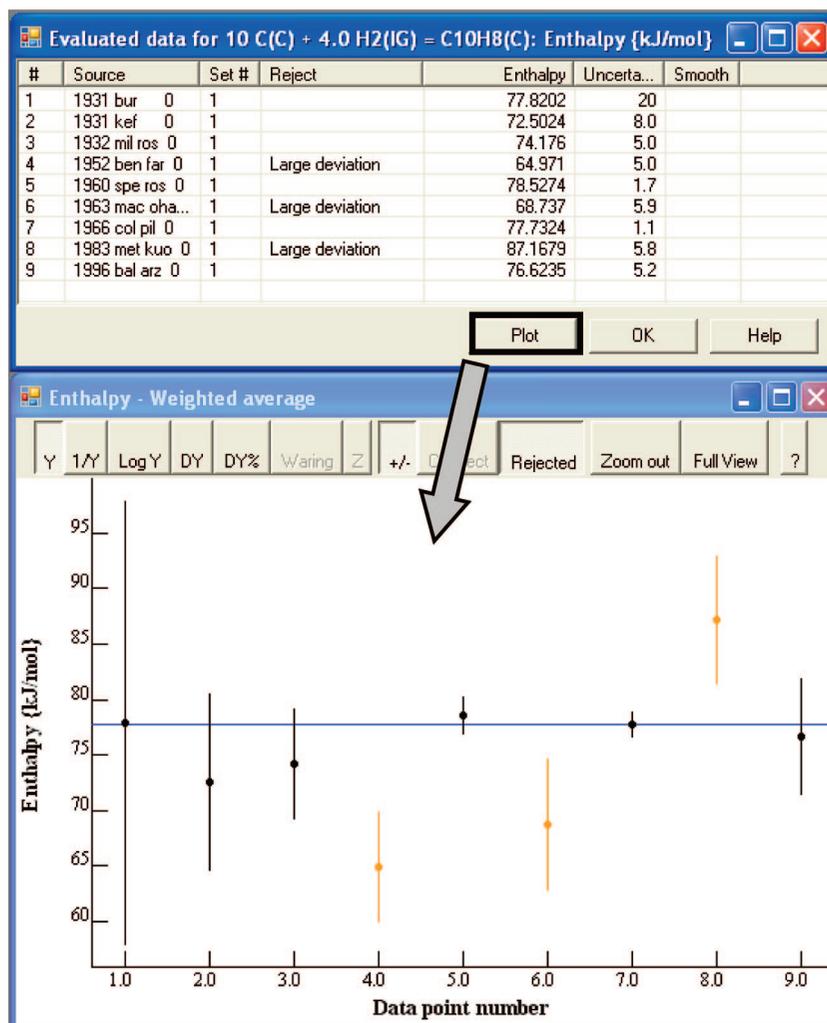
Figure 16. Experimental enthalpies of formation for naphthalene. The line represents the evaluated value. The error bars are the uncertainties (estimated at NIST) for the experimental values. Gray values in the figure were rejected in the analysis by the TDE software.

A Benson-type second-order group-contribution method[37] is used to generate predicted enthalpies of formation for validation of experimental data and to provide values when experimental data are not available. The original formulation by Benson was subsequently revised and extended.[38,39] The original gauche interaction parameters[39] were replaced by Roganov et al.[40] with the parameters for 1,4 and 1,5 interactions. This replacement facilitates automated processing of molecular structures and yields results equivalent to those of the original approach[39] and was used in TDE 3.0.

Evaluation Process for Enthalpies of Formation. Structural information (connectivity tables) for molecules with experimental property data are stored in *TDE-SOURCE*. The structural information is analyzed by the TDE software, and a table of Benson-type groups is built that includes terms for special features such as 1,4- and 1,5-interactions or adjustments for the presence of rings. Property prediction does not proceed if any group parameters are missing or if certain features are detected, such as high intramolecular strains that cannot be adequately described by group contributions (e.g., cage hydrocarbons with small rings). Uncertainties for the predictions are estimated based on analysis of deviations for a group of test compounds with reliable experimental values for the enthalpies of formation.

Generally, the implemented group-contribution method can predict enthalpies of formation at $T = 298.15$ K for three phases: gas, liquid, and crystal. Reliability of the prediction decreases from gas to crystal, due to increased uncertainty associated with intermolecular forces in the condensed states. It follows that if TDE can evaluate enthalpies of phase transitions (i.e., vaporization or sublimation at $T = 298.15$ K or fusion at a temperature near this value), those enthalpies in combination with more reliable predictions are used rather than the direct lower-quality predictions. The general algorithm for evaluation of the enthalpy of formation for CHON compounds is shown in Figure 15.

The user interface for reaction data is based on the existing infrastructure[1,2] and includes access through a navigation tree to data tables and plots. Because the enthalpy of formation is nearly always evaluated at the temperature $T = 298.15$ K, and pressure p near 0.1 MPa, property values are plotted chronologically relative to the recommended value, as shown in Figure 16 for naphthalene. Recommended values are included in ThermoML output,[21] and plain-text output provides the group-contribution parameters and all predicted values.

7. UNCERTAINTY ESTIMATES

Uncertainties are estimated for all properties evaluated with TDE. These uncertainties are based on the covariance approach, which was described fully in the first two papers of this series.[1,2] Both experimental uncertainties and curve deviations are taken into account when calculating statistical weights for the covariance matrix evaluation.

8. DYNAMIC UPDATES OVER THE WEB

Implementation of dynamic data evaluation requires regular updates of the experimental information in *TDE-SOURCE*. The mechanism for these updates over the Web was described in the previous paper of this series[2] and is unchanged for binary mixtures. However, because of the large amount of information for mixtures, the user is notified that the process can take considerable time, and a progress bar is shown in the user interface during download. As noted previously, the process engineer must always be able to reproduce calculations made for a particular system and time. This capability remains in TDE 3.0 for mixtures through control of the *TDE-SOURCE* version number, as described previously.[2]

9. CONCLUSIONS AND FUTURE DEVELOPMENT

The software framework of NIST ThermoData Engine for the implementation of the dynamic data evaluation concept has been further expanded to provide capabilities for on-demand critical evaluation of thermophysical properties of binary mixtures. Initial steps to expand software implementation of the concept to thermochemical properties were taken.

Immediate plans for future TDE development consist of further enhancement of the capabilities for binary mixtures, including simultaneous consideration of excess enthalpies and activity coefficients with phase equilibrium data and the application of equation-of-state technology and broadening the scope beyond the current limit of two phases to process more complex phase-equilibria data, such as VLLE and SVLE, as well as comprehensive extension of the software framework for chemical reactions, simultaneously processing both change-of-state and chemical equilibrium information. Long-term plans involve development of algorithms for strategic measurement planning using TDE technology.

MATHEMATICAL FORMULATION OF ACTIVITY-COEFFICIENT AND GAS-PHASE MODELS

Activity Coefficient Models. Phase equilibria and activity coefficients are described by activity-coefficients (AC) models that express the composition dependence of the excess Gibbs energy G^E for the liquid state. Symbols used in the following equations are as follows: gas constant R; temperature T; mole fraction of component 1 in the liquid phase x_1; and mole fraction of component 2 in the liquid phase x_2. Parameters are determined through fits to the experimental data, as described in the text.

THERMODATA ENGINE. 3. BINARY MIXTURES

J. Chem. Inf. Model., Vol. 49, No. 2, 2009 **515**

NRTL Equation.[24]

$$G^E/(RT) = x_1 \cdot x_2 \cdot (c_1 \cdot \exp(-k \cdot c_1)/(x_1 + x_2 \cdot \exp(-k \cdot c_1)) + c_2 \cdot \exp(-k \cdot c_2)/(x_2 + x_1 \cdot \exp(-k \cdot c_2))) \quad (A1)$$

The adjustable parameters are k (range -1 to 1), c_1, and c_2. The symmetric form of the equation has the constraint $c_1 = c_2$.

Margules[23]**/Redlich−Kister.**[25]

$$G^E/(RT) = \sum_{i=0}^{nTerms} a_i \cdot x_1 \cdot x_2 \cdot (x_1 - x_2)^i \quad (A2)$$

The adjustable parameters are a_i (array).
In TDE 3.0, *nTerms* cannot exceed 4.

UNIQUAC Equation.[26]

$$G^E/(RT) = -q_1 \cdot x_1 \cdot \ln(t_1 + t_2 \cdot t_{21}) - q_2 \cdot x_2 \cdot \ln(t_2 + t_1 \cdot t_{12}) + x_1 \cdot \ln(f_1/x_1) + x_2 \cdot \ln(f_2/x_2) + 5 \cdot (q_1 \cdot x_1 \ln(t_1/f_1) + q_2 \cdot x_2 \cdot \ln(t_2/f_2)) \quad (A4)$$

where

$$f_1 = (x_1 \cdot r_1)/(x_1 \cdot r_1 + (1 - x_1) \cdot r_2) \quad (A5)$$

$$f_2 = ((1 - x_1) \cdot r_2)/(x_1 \cdot r_1 + (1 - x_1) \cdot r_2) \quad (A6)$$

$$t_1 = (x_1 \cdot q_1)/(x_1 \cdot q_1 + (1 - x_1) \cdot q_2) \quad (A7)$$

$$t_1 = ((1 - x_1) \cdot q_2)/(x_1 \cdot q_1 + (1 - x_1) \cdot q_2) \quad (A8)$$

$$t_{12} = \exp(-u_{12}/(R \cdot T)) \quad (A9)$$

and

$$t_{21} = \exp(-u_{21}/(R \cdot T)) \quad (A10)$$

where the adjustable parameters are u_{12} and u_{21}, and the constant parameters r_1, r_2, q_1, and q_2 are related to molecular structures of the components and are taken from the UNIFAC parametrization. Other variables are intermediate. The symmetric form of the equation has the constraint $u_{21} = u_{12}$.

Van Laar Equation.[27]

$$G^E/(RT) = a_1 \cdot a_2 \cdot x_1 \cdot x_2/(a_1 \cdot x_1 + a_2 \cdot x_2) \quad (A11)$$

where the adjustable parameters are a_1 and a_2. The symmetric form of the equation has the constraint $a_1 = a_2$.

Wilson Equation.[28]

$$G^E/(RT) = -x_1 \cdot \ln(x_1 + a_2 \cdot x_2) - x_2 \cdot \ln/(x_2 + a_1 \cdot x_1) \quad (A12)$$

where the adjustable parameters are a_1 and a_2. The symmetric form of the equation has the constraint $a_1 = a_2$.

The model cannot be used to describe LLE, so applicability is limited to mixtures with complete miscibility.

UNIFAC Equation.[29,30]

$$G^E/(RT) = x_1 \cdot \ln(\gamma_1) + x_2 \cdot \ln/(\gamma_2) \quad (A13)$$

where

$$\gamma 1 = \gamma_{1,c} + \sum_{i=1}^{N} n_{1,i} \cdot (\gamma_i - \gamma_{1,i}) \quad (A14)$$

$$\gamma_2 = \gamma_{2,c} + \sum_{i=1}^{N} n_{2,i} \cdot (\gamma_i - \gamma_{2,i}) \quad (A15)$$

Calculations of γ_1 and γ_2 are based on group-contribution parameters, as described in detail by Poling et al.[41] That

description includes tables of the necessary parameters. The UNIFAC method is implemented in TDE 3.0 with the group parameters provided by Poling et al. The model is predictive, and there are no adjustable parameters.

Gas-Phase Models. The gas-phase models provide the means to apply approximate corrections for the nonideality of the gas phase.

Ideal Gas Model. If this model is chosen, fugacity coefficients are set equal to 1 in TDE.

Virial Model.[34] Application of the virial model is restricted to use of the second virial coefficient B, as shown in the following expression for the compressibility factor Z

$$Z = 1 + B(T)/V \quad (A27)$$

where

$$B = \sum_{i=1}^{2} \sum_{j=1}^{2} y_i \cdot y_j \cdot B_{ij} \quad (A28)$$

where B_{ii}, B_{ij}, and B are pure-component, interaction, and mixture virial coefficients at given temperature T and pressure p. V is the molar volume and Z is the compressibility factor pV/RT. Interaction virial coefficients are evaluated from experimental data, if available, or are estimated as the mean of the values for the pure components. Fugacity coefficients of the components are calculated as

$$\ln(\varphi_i) = [2\sum_{j=1}^{2} y_j \cdot B_{ij} - B] \cdot p/(RT) \quad (A29)$$

or

$$\ln(\varphi_i) = 2/V \cdot \sum_{j=1}^{2} y_j \cdot B_{ij} - \ln(Z) \quad (A30)$$

where B_{ij} are interaction virial coefficients and $B_{ii} = B_i$ by definition.

Redlich-Kwong Model.[35]

$$Z = 1 + B \cdot p - A^2 \cdot p \cdot (Z - B \cdot p)/[Z \cdot (Z + B \cdot p)] \quad (A31)$$

where

$$A^2 = a/(R^2 T^{2.5}) \quad (A32)$$

and

$$B = b/(RT) \quad (A33)$$

where T is the temperature, p is the pressure, and Z is the compressibility factor. The a and b parameters for mixtures are obtained from a_i and b_i parameters for pure components

$$a = \sum_{i=1}^{2} \sum_{j=1}^{2} y_i \cdot y_j \cdot a_{ij} \quad (A34)$$

and

$$b = \sum_{i=1}^{2} y_i \cdot b_i \quad (A35)$$

where

$$a_{ij} = (a_i \cdot a_j)^{1/2} \quad (A36)$$

Pure-component parameters are by definition

$$a_i = 0.4278 \cdot R^2 \cdot T_{c,i}^{2.5} / p_{c,i} \quad (A37)$$

and

$$b_i = 0.0867 \cdot RT_{c,i} / p_{c,i} \quad (A38)$$

where R is the gas constant, and $T_{c,i}$ and $p_{c,i}$ are the critical temperature and the pressure of pure compound, respectively. Fugacity coefficients of the components are calculated as

$$\ln(\varphi_i) = B_i/B \cdot (Z - 1) - \ln(Z - B \cdot p) -$$
$$A^2/B \cdot (2 \cdot A_i/A - B_i/B) \cdot \ln(1 + B \cdot p/Z) \quad (A39)$$

Peng−Robinson Model.[7]

$$Z = V/(V - b) - (a \cdot \alpha \cdot V)/((R \cdot T) \cdot (V^2 + 2 \cdot b \cdot V - b^2)) \quad (A40)$$

where T is the temperature, V is the molar volume, and Z is the compressibility factor. Values of $a \cdot \alpha$ and b for mixtures are obtained from $a_i \cdot \alpha_i$ and b_i values for pure components

$$a \cdot \alpha = \sum_{i=1}^{2} \sum_{j=1}^{2} y_i \cdot y_j \cdot (a \cdot \alpha)_{ij} \quad (A41)$$

and

$$b = \sum_{i=1}^{2} y_i \cdot b_i \quad (A42)$$

where

$$(a \cdot \alpha)_{ij} = ((a \cdot \alpha)_i \cdot (a \cdot \alpha)_j)^{1/2} \quad (A43)$$

Pure-component parameters are by definition

$$a_i = (0.45724 \cdot (RT_{c,i})^2) / p_{c,i} \quad (A44)$$

$$b_i = (0.0778 \cdot RT_{c,i}) / p_{c,i} \quad (A45)$$

$$\alpha_i = [1 + \{1 - (T/T_{c,i})^{0.5}\}(-0.26992 \cdot \omega_i^2 +$$
$$1.54226 \cdot \omega_i + 0.37464)]^2 \quad (A46)$$

where R is the gas constant, $T_{c,i}$ and $p_{c,i}$ are the critical temperature and the pressure of pure compound, and ω_i is the acentric factor. Fugacity coefficients of the components are calculated as

$$\ln(\varphi_i) = \frac{B_i}{B} \cdot (Z - 1) - \ln(Z - B) - \frac{A}{2^{3/2} \cdot B} \cdot$$
$$\left(\frac{2 \sum_{j=1}^{2} y_j \cdot a_{ij}}{a} - \frac{B_i}{B} \right) \cdot \ln\left(\frac{Z + 2.414 \cdot B}{Z - 0.414 \cdot B} \right) \quad (A47)$$

where

$$A = a \cdot \alpha \cdot p / (RT)^2 \quad (A48)$$

and

$$B = b \cdot p / (RT) \quad (A49)$$

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ThermoData Engine. 3. Binary Mixtures

J. Chem. Inf. Model., Vol. 49, No. 2, 2009 **517**

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