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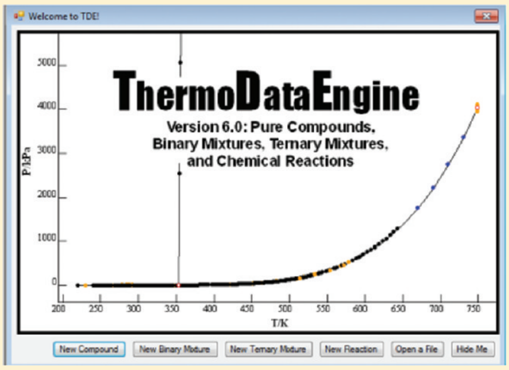
ThermoData Engine (TDE) Software Implementation of the Dynamic Data Evaluation Concept. 7. Ternary Mixtures

Vladimir Diky,[†] Robert D. Chirico,[†] Chris D. Muzny,[†] Andrei F. Kazakov,[†] Kenneth Kroenlein,[†] Joseph W. Magee,[†] Ilmutdin Abdulagatov,[†] Jeong Won Kang,[‡,§] and Michael Frenkel*[,†]

[†]Thermophysical Properties Division, National Institute of Standards and Technology, Boulder, Colorado 80305-3337, United States
[‡]Department of Chemical and Biological Engineering, Korea University, 5-1 Anam-Dong, Sungbuk-Ku, Seoul 136-701, South Korea

ABSTRACT: ThermoData Engine (TDE) is the first full-scale software implementation of the dynamic data evaluation concept, as reported in this journal. The present paper describes the first application of this concept to the evaluation of thermophysical properties for ternary chemical systems. The method involves construction of Redlich–Kister type equations for individual properties (excess volume, thermal conductivity, viscosity, surface tension, and excess enthalpy) and activity coefficient models for phase equilibrium properties (vapor–liquid and liquid–liquid equilibrium). Constructed ternary models are based on those for the three pure component and three binary subsystems evaluated on demand through the TDE software algorithms. All models are described in detail, and extensions to the class structure of the program are provided. Reliable evaluation of properties for the binary subsystems is essential for successful property evaluations for ternary systems, and algorithms are described to aid appropriate parameter selection and fitting for the implemented activity coefficient models (NRTL, Wilson, Van Laar, Redlich–Kister, and UNIQUAC). Two activity coefficient models based on group contributions (original UNIFAC and NIST-KT-UNIFAC) are also implemented. Novel features of the user interface are shown, and directions for future enhancements are outlined.



INTRODUCTION

As discussed in the first six papers of this series,[1−6] the NIST ThermoData Engine (TDE) software represents the first full-scale implementation of the concept of dynamic data evaluation for thermophysical properties.[7,8] 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'.

TDE has evolved from a first release, limited to thermophysical properties of pure compounds,[9] to on-demand generation of equations of state (EOS),[10] dynamic web-based updates of local data resources[10] through the TRC-SOURCE data storage system,[11] support for binary mixtures, including phase equilibria,[12] properties of chemical reactions,[13] and experiment planning and product design tools[14] as well as dynamic web-based dissemination of properties of pure components through the NIST Web Thermo Tables.[15] Currently, TDE is used in a multitude of applications varying from data quality assurance[16] and validation of new experimental data[17] to chemical process and product design.[18,19] It is also a core component in implementation of the concept of Global Information Systems in Science with application to the field of thermodynamics.[20]

The present paper describes an extension of TDE (version 6 released in 2011)[21] to critical evaluation of thermophysical properties of ternary mixtures through on-demand dynamic evaluation of the properties of the binary subsystems. Other additions described here are a vapor–liquid equilibrium (VLE) data modeling test that complements consistency tests implemented previously for low-pressure/subcritical VLE data[14,22] as well as addition of the NIST-KT-UNIFAC prediction method[23] for VLE data, which was developed based on data quality factors (i.e., data set weighting factors) described previously[22] and automatic decomposition of molecular structures into KT-UNIFAC groups and subgroups.[24]

SCOPE

The types of compounds within the scope of TDE are unchanged since the first release of the program.[1] The focus of the program is organic compounds composed of the elements C, H, N, O, F, Cl, Br, I, S, and P, plus industrially important inorganic compounds, such as ammonia and water, are included. In analogy to the approach used for binary mixtures in TDE (version 3),[3] the expansion into property evaluations for ternary mixtures (version 6) has progressed along two paths: one for properties modeled individually (volumetric properties, transport

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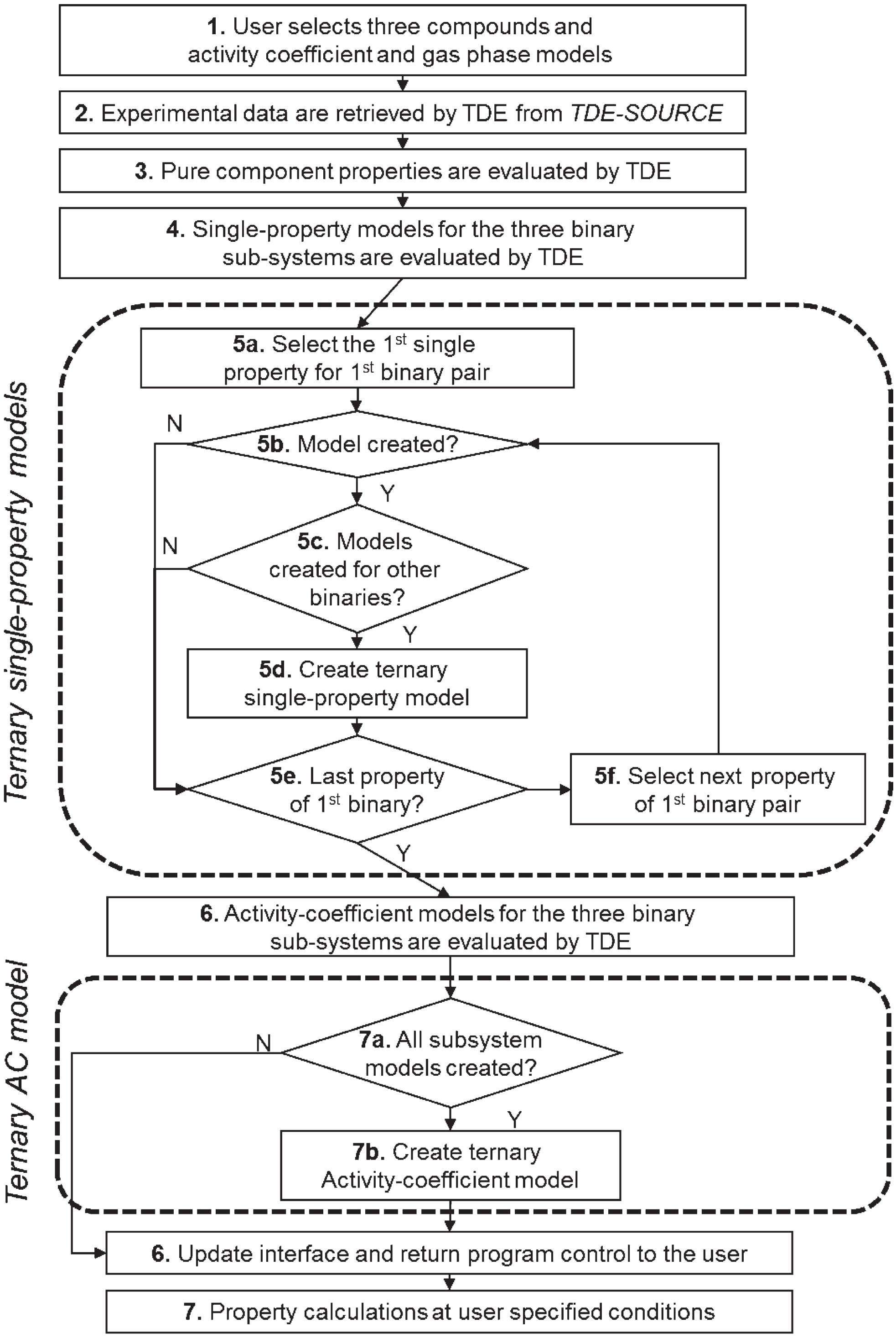


Figure 1. Algorithm for property evaluations for ternary chemical systems with TDE.

properties, etc.) and one for properties modeled collectively with activity coefficient (AC) models for phase equilibrium properties.

The Gibbs phase rule specifies the maximum number of phases present and the number of independent variables required to fully define a property for a system with a given number of components (chemical compounds). In the case of a ternary chemical system, the maximum number of phases is five (an invariant state with no independent variables), and the maximum number of independent variables is four (for a single-phase system). These restrictions limit the number of possible system types, but the number of potential phase and variable combinations is very large for ternary mixtures. The extensions to the TDE software described here target systems with a maximum of two phases: vapor—liquid equilibrium (VLE) and liquid—liquid equilibrium (LLE). Solid—liquid equilibrium (SLE) is not included for ternary mixtures at this time. Single-phase properties (excess volume, thermal conductivity, viscosity, surface tension, and enthalpy of mixing) at low pressures (<10 bar) are considered for the liquid phase.

■ ALGORITHM

To model properties for a binary mixture, the properties of the two pure components are required.[3] Similarly, to model properties for a ternary mixture, the properties of the three binary subsystems must be available and modeled. The program algorithm involves three major steps: (1) evaluation of the properties for the three pure components, as described in the first two papers of this series;[1,2] (2) evaluation of the properties for the three binary subsystems (described in the third paper of this series,[3] with additions described here); and (3) calculation of the properties of the ternary system at specified conditions with uncertainty assessment. Experimental property data for the ternary system may be compared with the values derived from the combined binary models, but the ternary experimental data are not used in model fitting.

The general algorithm for property evaluations for ternary chemical systems with TDE is shown in Figure 1. The major steps are numbered in the figure and are described in the paragraphs that follow.

Step 1: Compound Selection by User. The user initiates the evaluation process by selecting the three components for the mixture. Special features of this selection process, such as selection of components with known availability of experimental data, are analogous to those described previously for binary systems.[3] The only other required user action is selection of the AC model and gas-phase model to be used for representation of the phase equilibrium properties (VLE and LLE). (If application of an AC model is not of interest to the user, this action can be skipped.) A variety of common AC models are available for selection: NRTL, Redlich—Kister, UNIQUAC, Van Laar, Wilson, and the UNIFAC group contribution method. Gas-phase models are the ideal gas, virial, Redlich—Kwong, Peng—Robinson, and Hayden—O'Connell models. The AC and gas-phase models implemented in TDE for binary systems were described previously.[3]

Recently, this research group reported development of a method for generation of UNIFAC-type group parameters based on data quality factors (i.e., data set weighting factors)[22] and automatic parsing of molecular structures into KT-UNIFAC groups and subgroups.[23] The resulting new parametrization for the KT-UNIFAC framework was labeled NIST-KT-UNIFAC,[23] and this method is now implemented in TDE. New group parameters for NIST-KT-UNIFAC will be included in future releases of TDE, as newly published experimental data allow their determination.

Step 2: Experimental Data Are Retrieved From TDE-SOURCE by TDE. Following compound selection by the user, the TDE software retrieves (loads) all experimental data for the ternary mixture, its components, and the binary subsystems from the local database, TDE-SOURCE. TDE-SOURCE is an archive of experimental data and is a subset of the TRC SOURCE archive,[11] which is a relational data archival system for experimental thermophysical and thermochemical properties reported in the scientific literature. Presently (August, 2011), TDE-SOURCE contains 4.3 million experimental property values, including those for 37 000 binary mixtures and 10 000 ternary mixtures. In addition, proprietary or other experimental data can be added by the user. As described previously,[1,2] property values can be modified (corrected) or selected for forced rejection by the user. Added or modified data are not transferred to the TDE-SOURCE database but are maintained separately to ensure traceability and database integrity. Property data are normalized at the data-loading step, where mixture compositions are converted to mole fractions, phases and variables are sorted, and equivalent representations of the same property (e.g., density and molar volume) are converted to a single property (density, in this example).

Step 3: Pure-Component Properties Are Evaluated by TDE. Following retrieval and basic processing of the available experimental data, the properties of the pure components are evaluated automatically. The dynamic evaluation of pure component properties was described in the first two articles of this series.[1,2] This step is bypassed if evaluated properties for the compounds are available from the NIST REFPROP database.[25] There are 105 such compounds included in TDE version 6, and these 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 with TDE may be slow due to the large amount of available data, and the REFPROP database provides high-quality models; plus, there is little expectation of significant changes in the evaluated properties due to new measurements for these compounds.

Step 4: Single-Property Models for Binary Subsystems Are Evaluated by TDE. Application of the concept of dynamic data evaluation to properties for binary chemical systems was first described in the third article of this series.[3] For properties represented by single equations, Redlich—Kister type equations are used to represent the properties of of the binary subsystems. The equations used and the fitting procedures were described fully in the earlier article,[3] and those procedures were used here, except for viscosities, where a revised equation is given in Appendix A.

Step 5: Creation of Ternary Single-Property Models. The portions of the algorithm that are specifically related to formulation of the ternary models are shown within the dotted rectangles in Figure 1. The general program flow for single-property models is shown in steps 5a through 5f. Because a model for a ternary system can be created only if models were successfully created for all three binary subsystems, the process involves checking for the existence of the requisite binary models and formulating the composite ternary model, once all are determined to exist. The mathematical details of the composite ternary models are provided in Appendix A. The ranges (temperature and pressure) of validity of the various binary models are not considered at this juncture. The ranges are considered only when properties are calculated at the request of the user. Values for conditions outside the region of mutual overlap of the binary systems are labeled extrapolated by the software, and users can decide whether the extrapolated values meet their purposes.

Step 6: AC Models for Binary Subsystems Are Evaluated by TDE. In the initial development of the TDE software for application of AC models (i.e., multiproperty models), substantial user interaction with the software was necessary to optimize fitting of the models to experimental phase equilibrium data. Procedures for automatic evaluation (i.e., without user intervention) have been improved to increase their reliability. The improvements are described in the following paragraphs.

Successful creation of an AC model requires many considerations, including the extent of the available experimental data, selection of an appropriate mathematical function to represent temperature dependence of the activity coefficients, chemical nature of the components (hydrogen bonding, reactivity, etc.), availability of required auxiliary data (virial coefficients for some gas-phase models, densities for Poynting corrections, etc.), data

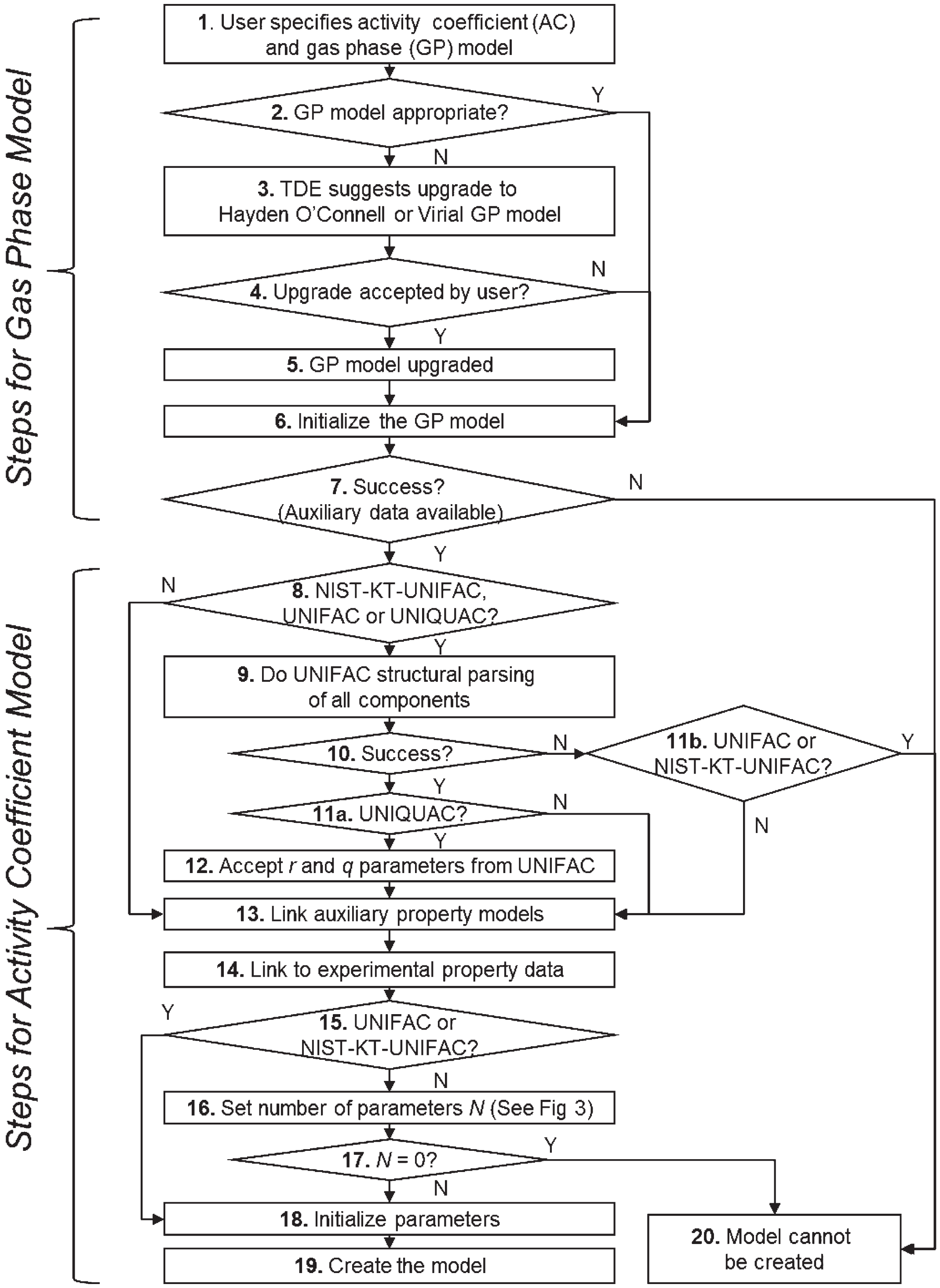


Figure 2. Algorithm for creation of an AC model for a binary chemical system with TDE.

gaps, and others. Figure 2 shows the algorithm used in TDE for creation of an AC model for a binary system. After selection of the pure components, the user is required to select an AC model and a gas-phase model (step 1, Figure 2 or step 1, Figure 1). Steps 2−7 of the algorithm (Figure 2) involve selection and initialization of the gas-phase model. In step 2, the program provides a warning if a binary pair is suspected of being reactive and cannot be correctly represented by an AC model. Presently, this includes any mixtures containing methanal and mixtures of amines with acids. If the selected gas-phase model seems inappropriate for a binary pair, an alternative model (an "upgrade") is suggested to the user before fitting. For example, the program may suggest an upgrade from the ideal gas to virial model for a mixture containing alcohols or to the Hayden−O'Connell gas-phase model for mixtures containing formic or acetic acid (steps 2−5, Figure 2.)

The TDE software includes many stored molecular structures (presently, ~20 000) that can be parsed for application in various

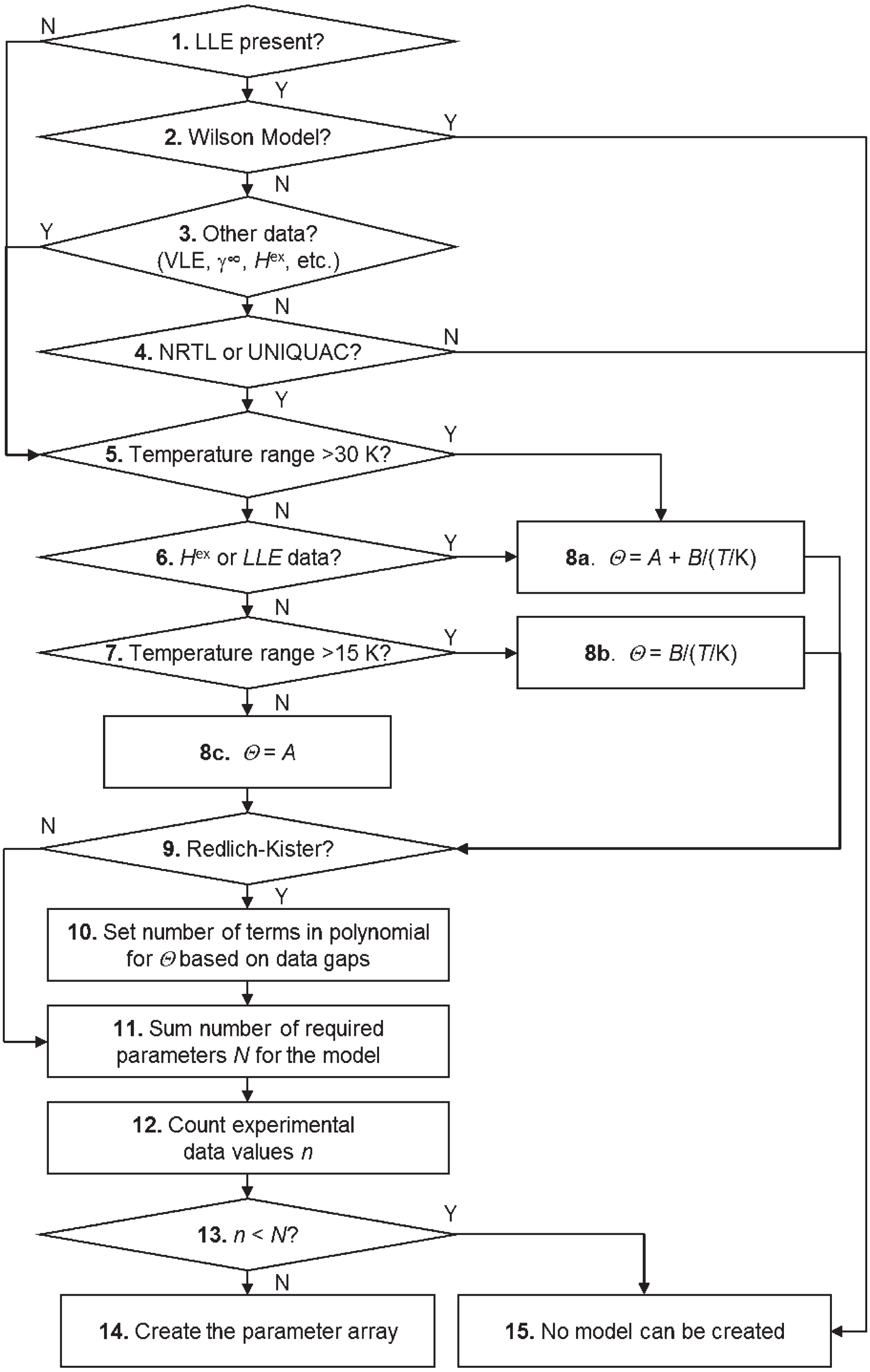


Figure 3. Algorithm for determination of the appropriate number of parameters for creation of an AC model for a binary system with TDE.

group contribution methods[1] as well as a structure drawing tool to add new compounds. This structural information is the key component in provision of guidance by the software in the selection of models. Guidance provided in the present version of TDE (version 6) represents only the initial application of TDE technology to model selection. At present, guidance for the selection of an appropriate AC model based on the chemical nature of the pure components is outside the scope of TDE but is an active area of research by this group.

The initialization of gas-phase models (step 6, Figure 2), plus enumeration of any required auxiliary data for those models, was described previously.[3] If the gas-phase model can be created (step 7, Figure 2), formulation of the AC model (steps 8−19, Figure 2) begins. If a gas-phase model cannot be created (step 20, Figure 2), the algorithm is terminated, and the user is informed. Steps 8−12 of the algorithm (Figure 2) involve the UNIFAC, UNIQUAC, and NIST-KT-UNIFAC models, which use group parameters for structural fragments determined from connectivity

Table 1. Requirements for Application of Data Quality Tests Used in TDE[a]

requirement	Herrington	van Ness	point	infinite dilution	end point	EOS
complete $p-T-x-y$ set	●	●	●	●	○	●
subcritical	●	●	●	●	●	○
composition span	0.5	0.5	0.5	0.5	0.5 or end points	0.3
composition gaps less than 0.8	●	●	●	●	○	○
isovariable type[b]	T or p	T or p	T only	T or p	T or p	T or p
$p < 0.5\,p_c$[c]	●	●	●	●	○	○
more than 5 points	●	●	●	●	or end points	●
pure component data	●	●	●	●	●	●
end point gaps <0.3[d]	○	○	○	○	●	●

[a] ● indicates the requirement is necessary for the test; ○ indicates that the requirement is not necessary. [b] T indicates that the test can be applied to isothermal data set, and p indicates that the test can be applied to isobaric data sets. [c] p_c is the critical pressure for the component with the lower value of p_c. [d] An end point gap is defined as the range in mole fraction between an end point (i.e., mole fraction $x = 0$ or 1) and the first experimental binary data value. This implies that some experimental binary data must exist for $x < 0.3$ and $x > 0.7$.

tables for the mixture components. Absence of required group parameters causes the algorithm to terminate for the UNIFAC and NIST-KT-UNIFAC models (steps 10 and 11b, Figure 2).

At step 13 (Figure 2), program links are made to auxiliary pure component property models that may be necessary for the particular AC model. Details of the AC model and auxiliary data were described earlier.[3] Step 14 (Figure 2) involves linking (accessing) of the experimental data (VLE, LLE, SLE, activity coefficients, and excess enthalpies) needed for the model fit. Steps 15−18 (Figure 2) involve setting the number and type of parameters to be fit for a particular AC model. Figure 3 shows details of step 16 (Figure 2). Since the group contribution methods (UNIFAC and NIST-KT-UNIFAC) involve no fitting to experimental data, steps 16 and 17 (Figure 2) are bypassed for those methods. In steps 18 and 19, all parameters are initialized, and the model is created.

Key steps in achieving a successful fit of an AC model to experimental phase equilibrium data are selection of an AC (and gas phase) model that is appropriate for the chemical system and selection of an appropriate form for the temperature dependence of the activity coefficient that will neither under fit the experimental data, resulting in a crude representation, nor overfit the data, resulting in unphysical property predictions. This is an area of continuous research in our development of dynamic data evaluation in TDE, and the sophistication and reliability of the algorithm will continue to be enhanced. The present status is described here to demonstrate how some of the major considerations are implemented. AC models with parameters fitted to experimental data in TDE are UNIQUAC, NRTL, Redlich−Kister, Wilson, and Van Laar. Features of each of these models are considered in determination of an appropriate number and type of fitted parameters, as described in the following paragraphs.

The algorithm for determination of the appropriate number of parameters for creation of an AC model for a binary system with TDE is shown in Figure 3. The Wilson model is an inappropriate choice for systems involving LLE, and steps 1 and 2 of the algorithm address this. In steps 3 and 4, the choices for AC model are reduced to only the NRTL or UNIQUAC models when additional experimental data are not available. Steps 5−7 establish the form of the temperature dependence for any AC model parameter Θ, as represented in steps 8a−8c. The formulation for $\Theta = f(T)$ ranges from a two-parameter fit (step 8a), when the temperature range exceeds 30 K or excess enthalpy or LLE are available, to a simple constant (step 8c), when few data are available. In steps 9 and 10, the number of terms in the polynomial for Θ within the Redlich−Kister model is set based on the distribution of the available data, as described earlier.[3] Finally, in steps 11−15, the total number of parameters to be determined is compared with the amount of available experimental data. If sufficient data are not available, no model can be created, and the user is notified.

Another key aspect in the fitting of AC models to experimental phase equilibrium data is appropriate weighting of data sets when multiple sets are available for a given binary system. Recently, this research group described a quality assessment algorithm for binary VLE data that combines four widely used tests of data consistency based on the requirements of the Gibbs−Duhem equation with a check of consistency between the VLE data and the vapor pressures of the pure components.[22] Results of the five tests were given numerical scores that were combined algebraically to yield an overall data quality factor Q_{VLE}, which then could be used to weight diverse experimental data sets in the fitting of AC models. Though valuable for many systems, application was limited to low-pressure (<1 MPa) subcritical systems.

A sixth test for binary VLE is added here specifically for high-pressure ($p > 1$ MPa) data sets, including those for which the conditions are supercritical for one component. The background and mathematical formulation of this test is given in Appendix B. Calculation of the quality factor Q_{VLE} is now modified relative to the original description[22] to ease addition of new tests. Previously, all tests were included in the calculation of Q_{VLE}, including default contributions for tests that were not applicable to the particular data scenario. As different consistency tests have different requirements, their applicability is now considered individually. Data requirements for each test are summarized in Table 1. The overall quality factor Q_{VLE} is now calculated only from the results of applicable consistency tests through the following equation:

$$Q_{\mathrm{VLE}} = q_{\mathrm{pure}} \frac{1}{N} \sum_{i=1}^{N} q_i \qquad (1)$$

where q_{pure} represents consistency with pure component vapor pressures (value: 0.1−1), N is the number of applicable tests, and q_i are the numerical results of the applicable individual tests. Full descriptions of all tests and calculation of q_i values have been published.[22]

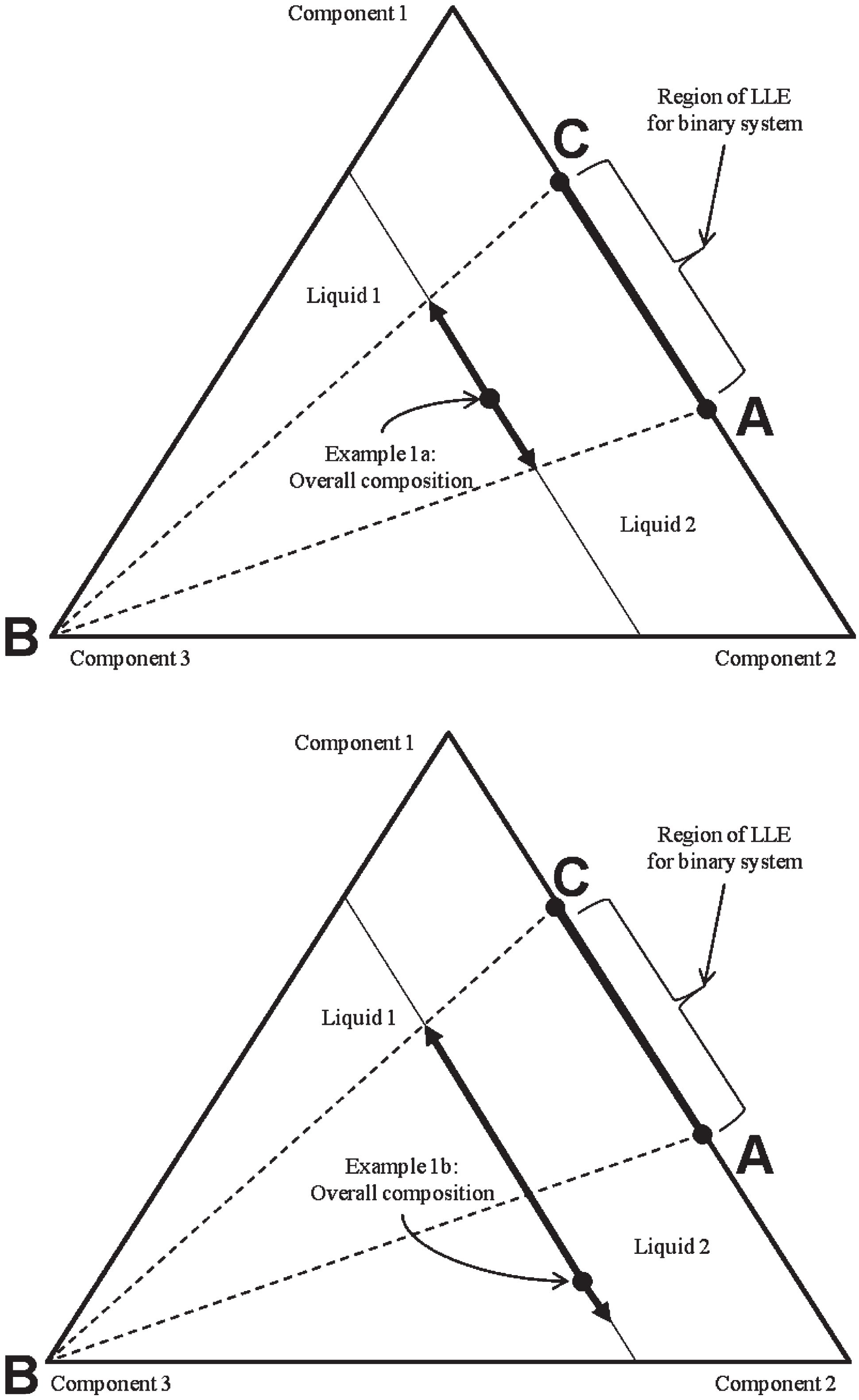


Figure 4. Basis of initial approximations for calculation of phase compositions with liquid−liquid phase splitting based on AC models. The example shows phase splitting for one binary subsystem.

Step 7: Creation of ternary AC models. Creation of a ternary AC model requires successful model creation for all of the binary subsystems (step 6, Figure 1). Steps 7a and 7b (Figure 1) indicate this requirement in Figure 1. The mathematical formulations for the ternary AC models available in TDE (version 6) are given in Appendix A.

Step 8: Update the User Interface and Return User Control. At this step the user can review all results, including those for the pure

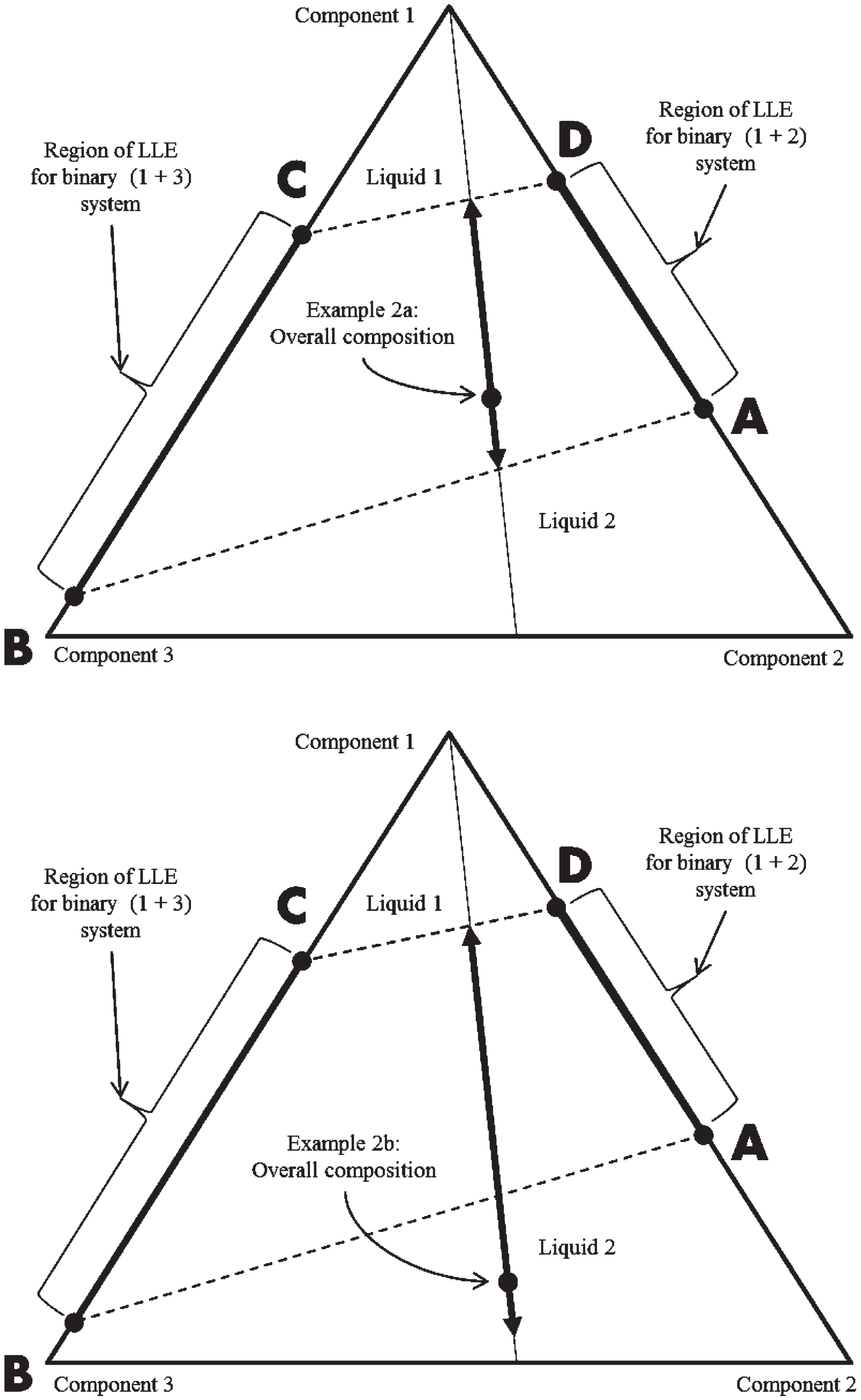


Figure 5. Basis of initial approximations for calculation of phase compositions with liquid−liquid phase splitting based on AC models. The example shows phase splitting for two binary subsystems.

components and binary subsystems. Features of the TDE interface for display of experimental data, deviation plots, fitted models, etc., have been described in earlier articles of this series.[1−3] An alternative AC model can be chosen, but this model (and the gas-phase model) must be applied to all of the binary systems. A mixture of models cannot be used in the calculation of the properties for the ternary mixture.

Step 9: Properties Are Calculated at User-Specified Conditions. Ternary properties are calculated in accordance with the

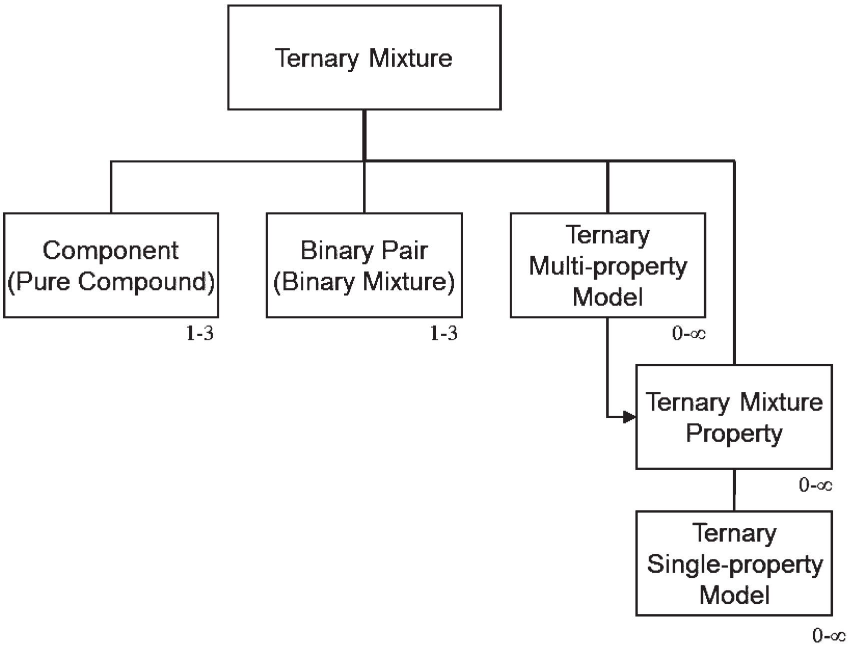


Figure 6. Structure of the ternary mixture class in TDE. Numerical values below the substructure elements indicate the possible indices for the element.

equations given in the Appendix A. The equations for representation of single properties (eqs A1−A4) are analogous to those for the binary properties. The equations for AC models (eqs A5−A20) involve calculation of activity coefficients of the components within a multicomponent (ternary) mixture. Calculation of LLE compositions is a special case. These compositions are calculated explicitly when specified by the user and also as part of the calculation for other properties supported by AC models in order to get the compositions of the coexisting liquid phases.

Calculation of phase compositions for two coexisting liquid phases is now supported by TDE. The calculation consists of an initial approximation for the phase compositions, followed by a series of refining steps. The initial approximations to the two liquid-phase compositions are built based on the evaluated binary LLE compositions and the overall composition of the ternary mixture. If only one binary pair shows LLE splitting at a given temperature, it is assumed that the same proportion of the split components exists in the ternary LLE, as represented by the sector ABC in Figure 4 (upper figure). If the overall composition lies outside of this two-phase region, the initial composition of one phase is modified, as shown in Figure 4 (lower figure). Figure 5 shows the analogous constructs for the initial estimates of the phase compositions for the case involving the presence of LLE in two binary subsystems. Here, the initial approximation for the two-phase region is represented by area ABCD in the figure. The possibility of LLE occurring in all three subsystems is not addressed in this release. Such systems are rare, and the user is notified that no model can be created by the software.

Refining iterations are applied to one mole of the ternary mixture with preservation of the overall composition. At each step, an amount of each component is transferred between the liquid phases. The amount transferred Δn from liquid phase 1 to liquid phase 2 is determined as

$$\Delta n_{\mathrm{L1}\rightarrow\mathrm{L2}} = -\frac{\gamma_{\mathrm{L2}}x_{\mathrm{L2}} - \gamma_{\mathrm{L1}}x_{\mathrm{L1}}}{\gamma_{\mathrm{L1}}N_{\mathrm{L1}} + \gamma_{\mathrm{L2}}N_{\mathrm{L2}}} \tag{2}$$

where γ_{L1} and γ_{L2} are its activity coefficients in liquids 1 and 2, x_{L1} and x_{L2} are its mole fractions in phases 1 and 2, and N_{L1} and N_{L2} are amounts of liquid phases 1 and 2. Refinement is complete when activities of all components are equal in both liquid phases within a narrow tolerance: 1×10^{-6}. If the liquid compositions are equal within the tolerance or the amount of one liquid is less than the tolerance level, it is concluded that one liquid phase exists at the considered overall composition.

SOFTWARE ARCHITECTURE

Previous articles in this series described pure compound,[2] binary mixture,[3] and chemical reaction[4] objects. In the present work, a fourth object is added: ternary mixture. The new ternary mixture class (Figure 6) includes objects representing the three pure components, the three binary mixture subsystems, and the ternary properties. Pure components are represented by compound classes containing all relevant information (identification, molecular structure, property data, and models: equations and covariance matrix). Binary subsystems are represented by binary mixture objects containing links to the components, property data, and models. Models for the calculation of properties for ternary mixtures are divided into two groups: those used for representation of single properties (e.g., viscosity, excess volume, etc.) and those used to represent multiple properties simultaneously (i.e., AC models used to represent VLE and LLE). This is analogous to the approach described previously for binary mixtures.[3] The class structure was designed to allow application to mixtures with an unlimited number of components n with specification of n component classes and $(n^2 - n)/2$ binary pair classes. It is planned that models for all multicomponent mixtures will be based on those for the binary subsystems. In the figures showing class structures (Figures 6−8), connecting arrows indicate links to external objects, and lines indicate objects belonging to the parent object.

In analogy to the class structure for binary mixture properties (Figure 11 of ref 3), the ternary mixture property class (Figure 7)

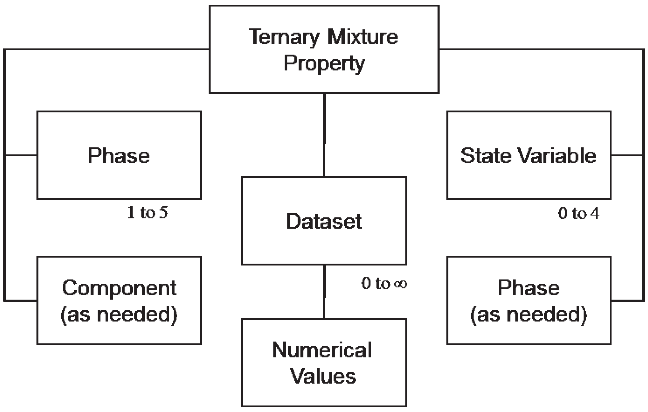


Figure 7. Structure of the ternary property class in TDE. Numerical values below the substructure elements indicate the possible indices for the element.

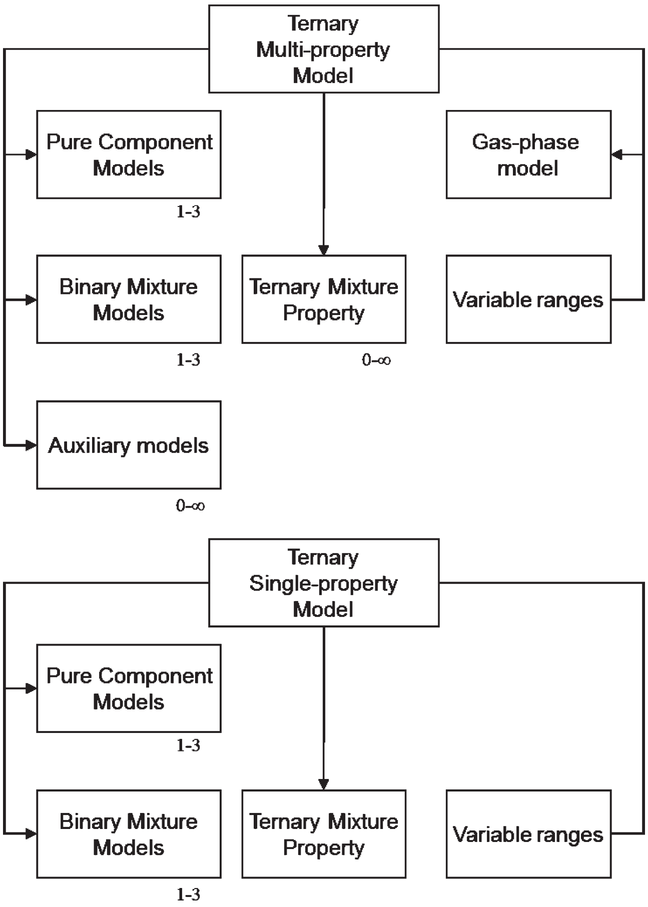


Figure 8. Structure of the ternary property class in TDE. Numerical values below the substructure elements indicate the possible indices for the element.

contains data sets (sets of property data from a given literature source), as seen in the center of Figure 7. Data sets contain a collection of property values, each with values of independent variables and phases that define the state. The number of possible independent variables and phases is related through the Gibbs phase rule with maximum values of four and five, respectively. Models in TDE for ternary systems are presently restricted to those involving a maximum of two phases, with the further restriction that models involving solid phases are not considered.

Structures of the ternary multiproperty and single property model classes are shown in Figure 8. Ternary mixture property models are synthesized from, and linked to, binary and pure component models. Auxiliary models are included as needed, and at present, the only such models used are for liquid densities of pure components needed for calculation of Poynting corrections[26] required for modeling of VLE. Consequently, auxiliary models appear only in the upper section of Figure 8. Similarly, a model for the gas phase is required for representation of VLE with an AC model. Such a model is not needed for the single property models (lower section of Figure 8).

INTERFACE FEATURES FOR TERNARY MIXTURES

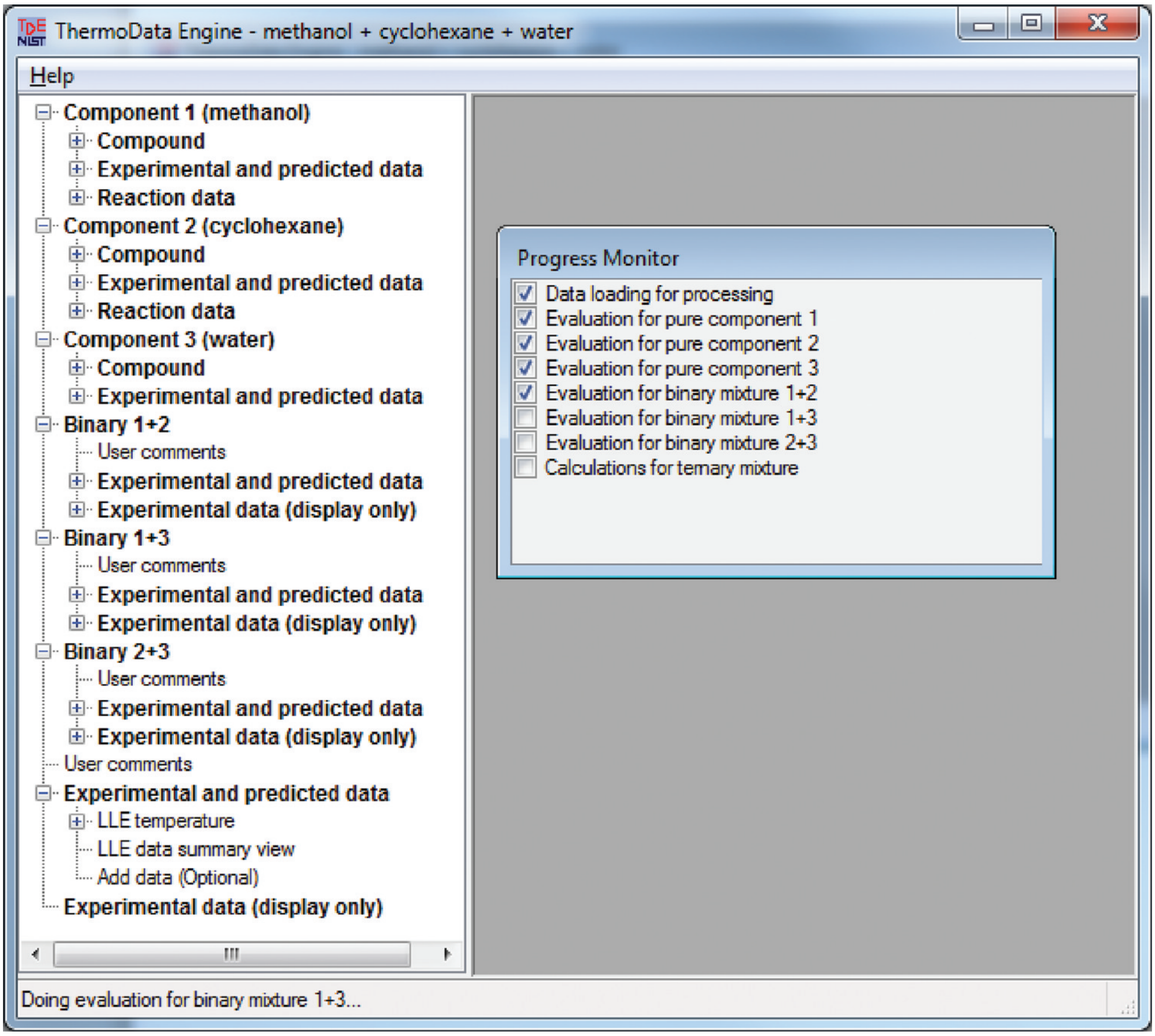
Progress Monitor. The first release of TDE involved evaluation of the properties for single pure components only.[1] Processing for calculation of properties for ternary mixtures involves evaluations for three pure components and the three binary subsystems, plus creation of the ternary models. This large number of evaluations can take several minutes to complete on modern computers, so it is important that the user be kept informed of progress. The TDE progress monitor form is shown in Figure 9. The check boxes are marked as each major step in the evaluation process is completed. The form also serves as a reminder to the user concerning the overall complexity of the process and the availability of access to the experimental data and evaluated results at all steps. Full traceability for all results, including the underlying experimental data, remains a core feature of TDE.

Graphical Representation of $p-T-x_1-x_2-y_1-y_2$ Data. Representation of ternary VLE compositions in the liquid and gas phase ("tie-line" data) is displayed in triangular plots. A typical graph is shown in Figure 10, where the lines connect the compositions of the phases in equilibrium (i.e, those that are "tied"). The experimental data plotted in Figure 10 are isobaric ($p = 101.3$ kPa) results for temperatures T in the range $\{330 < (T/\mathrm{K}) < 350\}$ reported by Amer et al.[27] Reported $p-T-x_1-x_2$ ("bubble point") or $p-T-y_1-y_2$ ("dew point") data can also be shown on such a plot as single points without ties. Access to numerical values and literature data sources is available through interactive features of the plot, as described in the first article of this series.[1]

Graphical Comparison of Experimental and Calculated Gas-Phase Compositions. Gas-phase compositions calculated with TDE (based on the combined results for the binary subsystems) may be compared readily with available experimental data from the literature. Display in TDE of calculated and experimental gas-phase compositions for the system (acetone + methanol + ethanol) is shown in Figure 11. Green lines connect the experimental liquid and gas compositions, and blue lines connect the experimental and calculated gas compositions.

Graphical Representation of Ternary LLE (Binodal Curve and Tie-Line Data). Binodal curve and tie-line data are clearly distinguished in graphical representation of ternary LLE in TDE. An example is shown in Figure 12, where experimental binodal and tie-line compositions are shown. The lines connect compositions for the tie-line data for liquid phases in mutual equilibrium.

Graphical Comparison of Experimental and Calculated LLE Compositions. Graphical comparison of calculated and experimental LLE results for a ternary system is shown in Figure 13. The experimental tie-line data were reported by Gramajo de Doz et al.[28] and Plackov and Stern.[29] Green lines connect compositions



- ☑ Data loading for processing
- ☑ Evaluation for pure component 1
- ☑ Evaluation for pure component 2
- ☑ Evaluation for pure component 3
- ☑ Evaluation for binary mixture 1+2
- ☐ Evaluation for binary mixture 1+3
- ☐ Evaluation for binary mixture 2+3
- ☐ Calculations for ternary mixture

Doing evaluation for binary mixture 1+3...

Figure 9. Screenshot of the TDE progress monitor.

determined experimentally for the liquid phases in mutual equilibrium (tie lines), and blue lines represent the calculated binodal curves and tie lines. Consistency of slopes for the calculated and experimental tie-lines is a useful visual indicator of good model quality. In this case, two of the binary subsystems show phase separation, and the method depicted in Figure 5 was used to provide initial approximations for the phase compositions prior to refinement.

OTHER ADDITIONS TO TDE

Beyond implementation of dynamic data evaluation for ternary mixtures, which is the main focus of the new version of TDE (version 6), there are three other major enhancements incorporated: (1) addition of the NIST-KT-UNIFAC prediction method[23] for VLE data, which was developed based on data quality factors described previously[22] and automatic decomposition of molecular structures into KT-UNIFAC groups and subgroups[24] (see Algorithm Section, step 1); (2) addition of a data quality test for VLE data at high pressures (see Algorithm Section, step 4; mathematical details are provided in Appendix B); and (3) improved representation of viscosities for mixtures. Indeed, to avoid calculation of unphysical negative values, the formulation for viscosity of a mixture η fitted by the Redlich–Kister equation reported earlier[3] is now changed to a logarithmic representation. Details are provided in Appendix A.

UNCERTAINTY EVALUATIONS

Uncertainties for ternary properties represented by single property equations are calculated with the covariance matrix method, as described in the first article of this series.[1] Contributions from pure components and excess property are considered:

$$u(\Psi)^2 = \sum_{i=1}^{3}\left\{u(\Psi_i)\frac{\partial \Psi}{\partial \Psi_i}\right\}^2 + \{u(\Psi_{\mathrm{ex}})\}^2 \qquad (3)$$

where $u(\Psi_i)$ is the uncertainty for the pure component property, $\partial\Psi/\partial\Psi_i$ is the partial derivative of the mixture property with respect to the pure component property, and $u(\Psi_{\mathrm{ex}})$ is the uncertainty contribution to the mixture property propagated from the excess property:

$$u(\Psi_{\mathrm{ex}})^2 = \mathbf{D}^{\mathrm{T}}\mathbf{C}\mathbf{D} \qquad (4)$$

where **C** is the covariance matrix consisting of three blocks of binary-parameter covariance, **D** is a vector of partial derivatives of the mixture property with respect to the binary parameters, and $\mathbf{D}^{\mathrm{T}}$ is transposed **D**. There is no covariance between the binary

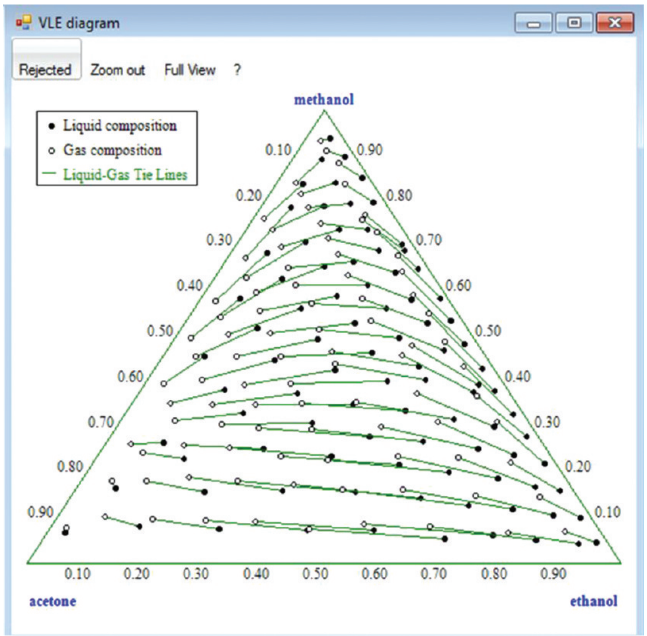


Figure 10. An example of graphical representation of $p-T-x_1-x_2-y_1-y_2$ data in TDE: ●, liquid composition; ○, gas composition, and lines connect results for phases in mutual equilibrium. The experimental data shown were reported by Amer et al.[27] for the system (methanol + ethanol + acetone).

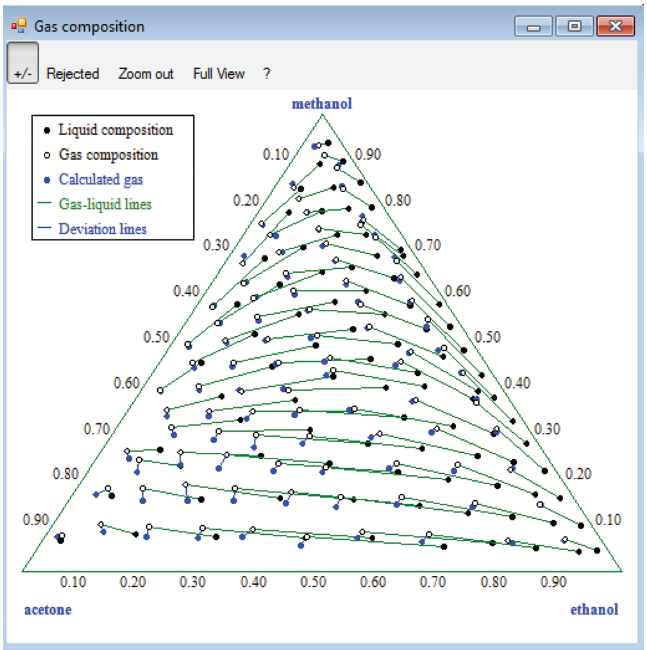


Figure 11. Display of calculated and experimental VLE gas-phase compositions in TDE. Results are shown for the system (acetone + methanol + ethanol). Black filled circles, experimental liquid compositions; white filled circles, experimental gas compositions; blue filled circles, calculated gas compositions; green lines connect the experimental liquid and gas compositions; and blue lines connect the experimental and calculated gas compositions. The experimental data were reported by Amer et al.[27]

pairs, and the method does not consider possible errors caused by not accounting for higher-order (ternary and greater) interactions.

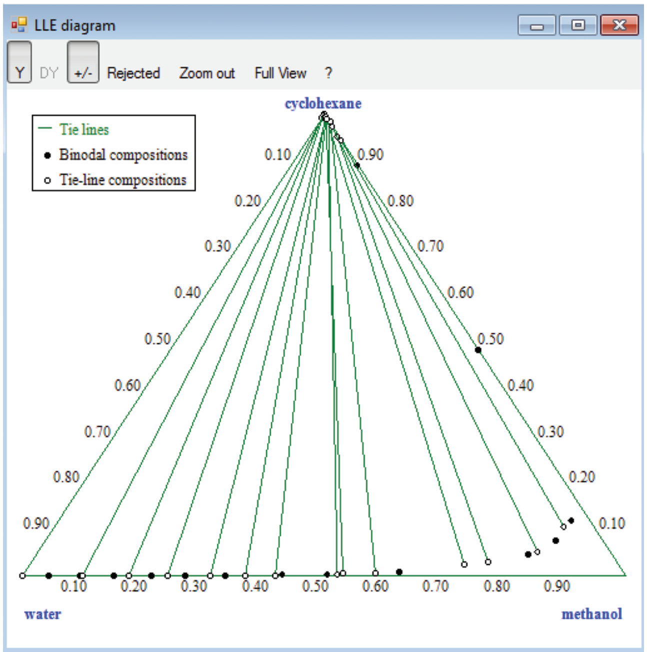


Figure 12. Display of binodal and tie-line ternary LLE compositions in TDE. Results are shown for the system (methanol + water + cyclohexane). Experimental binodal and tie-line data are those of Gramajo de Doz et al.[28] and Plackov and Stern:[29] ●, binodal compositions; and ○, tie-line data. The lines connect compositions for the liquid phases in mutual equilibrium ("tied" values).

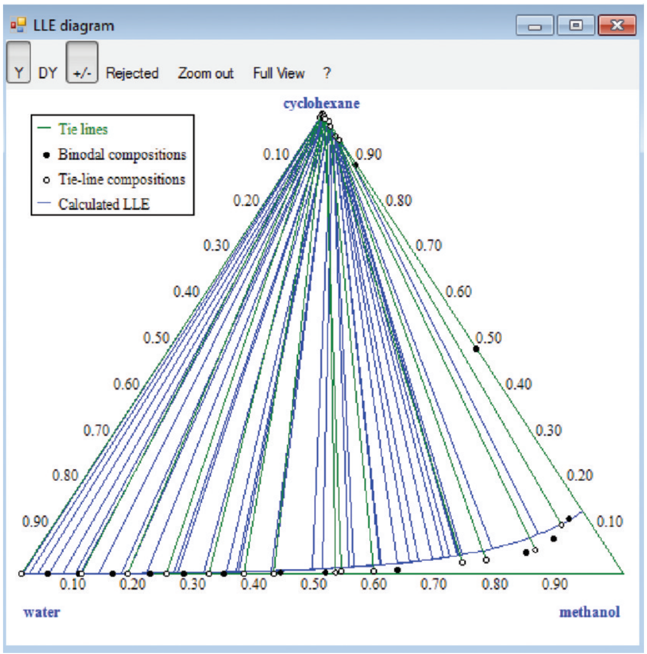


Figure 13. Graphical comparison of experimental and calculated LLE compositions for ternary systems in TDE. Results are shown for the system (methanol + water + cyclohexane), and the experimental binodal and tie-line data are those of Gramajo de Doz et al.[28] and Plackov and Stern:[29] ●, binodal compositions; and ○, tie-line data. Green lines connect compositions determined experimentally for the liquid phases in mutual equilibrium (tie lines), and blue lines represent the calculated binodal curves and tie lines.

Although successful for single property equations, the method involving the covariance matrix yielded unreasonable uncertainties for properties derived from AC models. While this problem requires additional research (planned for the next version of TDE), an alternative approach was developed here. First, property uncertainties are calculated for binary mixtures containing the components in the same proportion as in the ternary mixtures. Then, they are multiplied by fractions of the corresponding binary pairs in the ternary mixtures and combined to give an uncertainty estimate $u(\Psi)$ for the ternary property:

$$u(\Psi)^2 = \sum_{i=1}^{3} \sum_{j \neq i} \{(x_i + x_j) \cdot u(\Psi_{ij})\}^2 \tag{5}$$

where x_i and x_j are mole fractions of components i and j in the ternary mixture, and $u(\Psi_{ij})$ is the uncertainty of the property for the corresponding binary mixture with the components in the same proportion as in the ternary mixture.

CONCLUSIONS AND FUTURE DEVELOPMENT

The algorithm for extension of dynamic data evaluation for ternary mixtures has been developed and implemented in the newest version of the NIST ThermoData Engine software (version 6).[21] Other important enhancements are the addition of the NIST-KT-UNIFAC prediction method, the incorporation of a data quality test for VLE data at high pressures, and the improved representation of viscosities for mixtures.

Future plans include propagation of combined expanded uncertainties from the properties of pure compounds and mixtures to those of process streams and development of algorithms for thermodynamic analysis of solubility and extraction options in chemical process design.

APPENDIX A: MATHEMATICAL FORMULATION OF MODELS FOR TERNARY CHEMICAL SYSTEMS

Data evaluation for a ternary mixture includes evaluation for three pure components and three binary mixtures. Two types of binary models are used to calculate properties of ternary mixtures. The Redlich−Kister equation is used to fit excess volume, excess enthalpy, viscosity, thermal conductivity, surface tension, and index of refraction for single phase (liquid or gas) systems. The form Ψ^{ex} used for excess volume and excess enthalpy is

$$\Psi^{\text{ex}} = \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \tag{A1}$$

where a_{ijk} are binary parameters for components i and j. Bulk properties Z (except viscosity and density) are calculated as

$$Z = \sum_{i=1}^{3} x_i \cdot Z_i + \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \tag{A2}$$

Density ρ is calculated as

$$\begin{aligned} \rho = \sum_{i=1}^{3} x_i \cdot M_i / V_m; \; V_m = \sum_{i=1}^{3} x_i \cdot M_i / \rho_i \\ + \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \end{aligned} \tag{A3}$$

where M_i is the molar mass of component i. Viscosity η is calculated as

$$\ln(\eta/\eta^\circ) = \sum_{i=1}^{3} x_i \cdot \ln(\eta_i/\eta^\circ) + \left\{ \frac{1}{2} \sum_{i=1}^{3} \sum_{j=1}^{3} \sum_{k=0}^{nTerms} a_{ijk} \cdot x_i \cdot x_j \cdot (x_i - x_j)^k \right\} \tag{A4}$$

where η° is 1 Pa·s.

AC models for ternary mixtures were implemented in accordance with the methods described by Novak.[30]

NRTL Model.

$$\ln(\gamma_{\text{i}}) = \frac{\sum_{j=1}^{3} x_j \cdot \tau_{ji} \cdot G_{ji}}{\sum_{k=1}^{3} x_k \cdot G_{ki}} + \sum_{j=1}^{3} \frac{x_j \cdot G_{ij}}{\sum_{k=1}^{3} x_k \cdot G_{kj}} \cdot \left(\tau_{ji} - \frac{\sum_{m=1}^{3} x_m \cdot \tau_{mj} \cdot G_{mj}}{\sum_{k=1}^{3} x_k \cdot G_{kj}} \right) \tag{A5}$$

where $G_{ji} = \exp(-\alpha_{ij} \cdot \tau_{ij})$ and α_{ij} and τ_{ij} are binary NRTL parameters at a given temperature. Parameter τ_{12} is binary parameter c_1, τ_{21} is binary parameter c_2, α_{12} and α_{21} are binary parameter k for a mixture of components 1 and 2, $\tau_{ii} = 0$, and $\alpha_{ii} = 0$. The binary parameters c_1, c_2, and k were defined previously.[3]

UNIQUAC Model.

$$\begin{aligned} \ln(\gamma_i) = \ln\left(\frac{\Phi_i}{x_i}\right) + 10 q_i \ln\left(\frac{\Theta_i}{\Phi_i}\right) - q_i \ln t_i \\ - q_i \sum_{j=1}^{3} \frac{\Theta_j \tau_{ij}}{t_j} + l_i + q_i - \frac{\Phi_i}{x_i} \sum_{j=1}^{3} x_j l_j \end{aligned} \tag{A6}$$

where

$$\Theta_i = \frac{x_i q_i}{\sum_{j=1}^{3} x_j q_j}; \; \Phi_i = \frac{x_i r_i}{\sum_{j=1}^{3} x_j r_j}; \; l_i = 5(r_i - q_i) + 1 - r_i; \; t_i = \sum_{j=1}^{3} \Theta_j \tau_{ji} \tag{A7}$$

and τ_{12} is binary parameter t_{12}, τ_{21} is binary parameter t_{21} for a mixture of components 1 and 2 at temperature T, r_i is parameter r for component i, q_i is parameter q for component i, and $\tau_{ii} = 1$. The binary parameters t_{12} and t_{21} and the pure component parameters r and q were defined previously.[3]

Wilson Model.

$$\ln(\gamma_i) = 1 - \ln\left(\sum_{j=1}^{3} A_{ij} \cdot x_j\right) - \sum_{j=1}^{3} \frac{A_{ji} \cdot x_j}{\sum_{k=1}^{3} A_{jk} \cdot x_k} \tag{A8}$$

where A_{12} is binary parameter a_2, A_{21} is binary parameter a_1 for a mixture of components 1 and 2, and $A_{ii} = 1$. Definitions of the binary parameters were given previously.[3]

Van Laar.

$$\ln(\gamma_i) = A_i \cdot (1 - z_i)^2 \cdot \left[1 + 2 \cdot z_i \cdot \left(\frac{A_i \cdot B_i}{|A_i \cdot B_i| - 1} \right) \right] \tag{A9}$$

where

$$z_i = \frac{|A_i| \cdot x_i}{|A_i| \cdot x_i + |B_i| \cdot (1 - x_i)}; \; A_i = \frac{\sum_{j=1}^{3} x_j \cdot A_{ij}}{(1 - x_i)}; \; B_i = \frac{\sum_{j=1}^{3} x_j \cdot A_{ji}}{(1 - x_i)} \tag{A10}$$

where A_{12} is binary parameter a_1, A_{21} is binary parameter a_2 for a mixture of components 1 and 2, and $A_{ii} = 0$. The binary parameters were defined previously.[3]

Redlich–Kister.

$$\ln(\gamma_\mathrm{i}) = \sum_{j=1}^{3}\left[\sum_{n=1}^{N} x_j A_{ijn}(x_i - x_j)^{n-2}(nx_i - x_j)\right.$$

$$\left. - \frac{1}{2}\sum_{k=1}^{3}\sum_{n=1}^{N} x_j x_k A_{jkn}(x_j - x_k)^{n-2}[(2n-1)x_j - x_k]\right] \qquad (A11)$$

where N is number of terms and A_{ijk} is binary parameter a_k for components $(i + j)$.[3]

UNIFAC.

$$\ln \gamma_i = \ln(\gamma_{i,c}) + \sum_{j=1}^{N} n_{i,j}\{\ln(\gamma_j^{Group}) - \ln(\gamma_{i,j})\} \qquad (A12)$$

where

$$\ln(\gamma_{i,c}) = \ln\left(\frac{\phi_i}{x_i}\right) + 5 \cdot q_i \cdot \ln\left(\frac{\theta_i}{\phi_i}\right) + l_i - \left(\frac{\phi_i}{x_i}\right) \cdot \sum_{k=1}^{3} x_k l_k \qquad (A13)$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^{3} x_j q_j};\ \phi_i = \frac{x_i r_i}{\sum_{j=1}^{3} x_j r_j};\ l_i = 5(r_i - q_i) + 1 - r_i \qquad (A14)$$

$$\ln(\gamma_{j,k}) = Q_{\mathrm{type}(k)} \cdot \left[1 - \sum_{i=1}^{N} \theta_{j,i} \cdot \psi_{ki} / \sum_{m=1}^{N} \theta_{j,m} \cdot \psi_{mi} - \ln \sum_{i=1}^{N} \theta_{j,i} \cdot \psi_{ki}\right] \qquad (A15)$$

$$\ln(\gamma_k^{Group}) = Q_{\mathrm{type}(k)} \cdot \left[1 - \sum_{i=1}^{N} \theta_{M,i} \cdot \psi_{ki} / \sum_{m=1}^{N} \theta_{M,m} \cdot \psi_{mi} - \ln \sum_{i=1}^{N} \theta_{M,i} \cdot \psi_{ki}\right] \qquad (A16)$$

$$x_{i,j} = \frac{n_{j,i}}{\sum_{m=1}^{N} n_{m,i}};\ \theta_{i,j} = \frac{x_{i,j} \cdot Q_{\mathrm{type}(j)}}{\sum_{m=1}^{N} x_{i,m} \cdot Q_{\mathrm{type}(m)}} \qquad (A17)$$

$$x_{M,i} = \frac{\sum_{m=1}^{3} x_m n_{m,i}}{\sum_{k=1}^{N}\sum_{m=1}^{3} x_m n_{m,k}};\ \theta_{M,i} = \frac{x_{M,i} \cdot Q_{\mathrm{type}(i)}}{\sum_{j=1}^{N} x_{M,j} \cdot Q_{\mathrm{type}(j)}} \qquad (A18)$$

where $n_{i,j}$ is the number of groups of type j in the molecule of component i, and N is the number of distinct types of structural groups in the mixture.

$$\psi_{ij} = \exp[-B\{\mathrm{MainGroup}(i), \mathrm{MainGroup}(j)\}/T] \qquad (A19)$$

for original UNIFAC,[3] and

$$\psi_{ij} = \exp[-(A\{\mathrm{MainGroup}(i), \mathrm{MainGroup}(j)\}$$

$$+ B\{\mathrm{MainGroup}(i), \mathrm{MainGroup}(j)\}/T)] \qquad (A20)$$

for NIST-KT-UNIFAC,[23] where $A(i,j)$ and $B(i,j)$ are the interaction parameters between groups i and j. $Q_{\mathrm{type}(k)}$ is the UNIFAC parameter q for structural group k. The quantities q and r for each component are calculated as the sum of q and r contributions for all structural groups.

APPENDIX B: NEW EOS CONSISTENCY TEST FOR BINARY HIGH-PRESSURE (P > 1 MPA) VLE DATA SETS

Several methods have been suggested in the literature for a consistency test of VLE data set at high pressure. Won and Prausnitz[31] proposed an extension of Barker's method, but an appropriate equation of state (EOS) model was not available at that time and an AC model with an unsymmetrical convention was used. Jackson and Wilsak[32] applied a differential test and the van Ness test and concluded that such tests can be applied only when data are far from critical conditions. Valderrama and Alvarez[33] and Trejos et al.[34] suggested an extension of the Gibbs–Duhem equation for the gas phase. However, the calculation involves the ratio of two small numbers (compressibility factor $Z - 1$ and the logarithm of the fugacity) at low pressure, which often results in poor test results for VLE of good quality data at low pressures.

A new high-pressure test for isothermal T–p–x–y data sets has been developed for use in the present version of TDE. It is based on an extension of Barker's method at high pressure with the use of the Peng–Robinson EOS, the Mathias–Copeman function,[35] and the universal mixing rule (UMR) suggested by Voutsas et al.[36]

$$p = \frac{RT}{V - b} - \frac{a}{V(V + b) - b(V - b)} \qquad (B1)$$

The UMR mixing rule can be expressed as

$$a = \frac{1}{A}\frac{G_{\mathrm{AC}}^{\mathrm{E,SG}} + G_{\mathrm{AC}}^{\mathrm{E,res}}}{RT} + \sum_i x_i a_i \qquad (B2)$$

where $A = 0.53$ and a_i is based on properties of the pure components:

$$a_i = 0.45724\frac{(RT_\mathrm{c})^2}{p_\mathrm{c}} f(T) \qquad (B3)$$

where R is the gas constant, T_c and p_c are the critical temperature and critical pressure, respectively, and $f(T)$ is the Mathias–Copeman function:

$$f(T) = [1 + c_1(1 - \sqrt{T_r}) + c_2(1 - \sqrt{T_r})^2$$

$$+ c_3(1 - \sqrt{T_r})^3]^2 \qquad (B4)$$

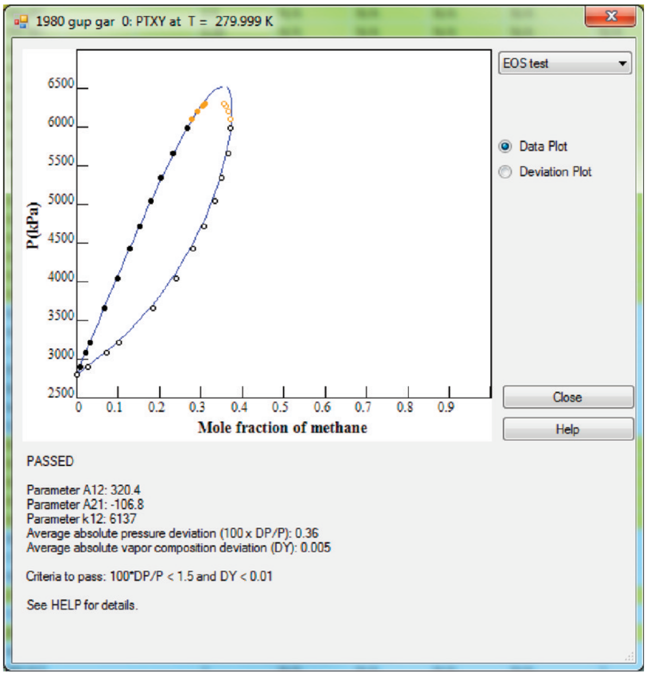
The parameters c_i are derived with vapor pressures for the pure components. The parameter b is also calculated with properties of the pure components.

$$b = \sum_i \sum_j x_i x_j b_{ij};\ b_{ij} = \left(\frac{b_i^{1/s} + b_j^{1/s}}{2}\right)^s \qquad (B5)$$

where

$$b_\mathrm{i} = 0.0778RT_\mathrm{c}/p_\mathrm{c} \qquad (B6)$$

and $s = 2$. The terms $G_{\mathrm{AC}}^{\mathrm{E,SG}}$ and $G_{\mathrm{AC}}^{\mathrm{E,res}}$ represent, respectively, the Staverman–Guggenheim term and residual term in the



```
PASSED

Parameter A12: 320.4
Parameter A21: -106.8
Parameter k12: 6137
Average absolute pressure deviation (100 x DP/P): 0.36
Average absolute vapor composition deviation (DY): 0.005

Criteria to pass: 100*DP/P < 1.5 and DY < 0.01

See HELP for details.
```

Figure B1. Program screenshot of results for the EOS consistency test for binary high pressure (p > 1 MPa). The experimental data are those reported by Gupta et al.[40] for the system (methane + ethane): ●, experimental bubble-point pressures; and ○, experimental dew-point pressures. The curve represents the fitted model. The experimental data near the critical conditions (shown in gray) were not considered in evaluation of the data set quality, as described in the text.

UNIQUAC[37] or UNIFAC[38] AC model.

$$\frac{G_{\mathrm{AC}}^{\mathrm{E,\,SG}}}{RT} = \frac{z}{2}\left(q_1 x_1 \ln\frac{\Phi_1}{x_1} + q_2 x_2 \ln\frac{\Phi_2}{x_2}\right) \tag{B7}$$

where

$$\Phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2};\ \Phi_2 = \frac{x_2 r_2}{x_1 r_1 + x_2 r_2} \tag{B8}$$

$$\frac{G_{\mathrm{AC}}^{\mathrm{E,\,res}}}{RT} = -q_1 x_1 \ln(\theta_1 + \theta_2 \tau_{21}) - q_2 x_2 \ln(\theta_2 + \theta_1 \tau_{12}) \tag{B9}$$

where

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2};\ \theta_2 = \frac{x_2 q_2}{x_1 q_1 + x_2 q_2} \tag{B10}$$

and

$$\tau_{12} = \exp(-\varepsilon_{12}/RT);\ \tau_{21} = \exp(-\varepsilon_{21}/RT) \tag{B11}$$

Volume parameters (r_1 and r_2) and surface area parameters (q_1 and q_2) are required as pure component properties and are calculated with the method of Bondi.[39] Note that the Flory–Huggins terms in the AC expressions are removed due to overlap with the cubic EOS terms, as indicated by Voutas et al.[36] For a given $T-p-x-y$ data set at isothermal condition, two binary interaction parameters (ε_{12} and ε_{21} in eq B11) are fitted, and bubble-pressure calculation results are compared with the experimental data.

This test is now added to the previously implemented consistency tests, as described earlier in the text. The test is called automatically by TDE for all isothermal binary VLE data sets with pressures p > 1 MPa. The numerical test results are similar to those for the van Ness test: average percent deviation of vapor pressure and average absolute deviation of the gas composition. As it is known that EOS may not be adequate in the critical regions, data in the vicinity of a binary critical point (pressure or temperature maximum for a supercritical data set) are excluded from deviation accounting. The pass/fail thresholds are chosen to be $0.015 \cdot p$ for vapor pressure p and 0.01 mol fraction for vapor composition y. If the test is passed, its contribution to the overall quality factor is 1, otherwise

$$q_{\mathrm{EOS}} = 3/(\Delta p + 100 \cdot \Delta y) \tag{B12}$$

where Δp is the average percent pressure deviation and Δy is the average gas composition deviation. Numerical and graphical test results are available to the user. A representative result for the system (methane + ethane)[40] is shown in Figure B1. Due to the inadequacy of the EOS in the critical region, experimental data near the mixture critical conditions (shown in gray in Figure B1) are excluded from calculation of the pressure and gas composition deviations.

AUTHOR INFORMATION

Corresponding Author

*E-mail: frenkel@boulder.nist.gov.

Notes

[§]Guest Researcher at the National Institute of Standards and Technology 2009–2011.

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