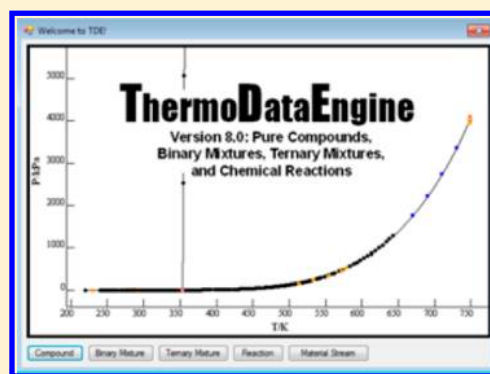


ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 9. Extensible Thermodynamic Constraints for Pure Compounds and New Model Developments

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ABSTRACT: ThermoData Engine (TDE) is the first full-scale software implementation of the dynamic data evaluation concept, as reported in this journal. The present article describes the background and implementation for new additions in latest release of TDE. Advances are in the areas of program architecture and quality improvement for automatic property evaluations, particularly for pure compounds. It is shown that selection of appropriate program architecture supports improvement of the quality of the on-demand property evaluations through application of a readily extensible collection of constraints. The basis and implementation for other enhancements to TDE are described briefly. Other enhancements include the following: (1) implementation of model-validity enforcement for specific equations that can provide unphysical results if unconstrained, (2) newly refined group-contribution parameters for estimation of enthalpies of formation for pure compounds containing carbon, hydrogen, and oxygen, (3) implementation of an enhanced group-contribution method (NIST-Modified UNIFAC) in TDE for improved estimation of phase-equilibrium properties for binary mixtures, (4) tools for mutual validation of ideal-gas properties derived through statistical calculations and those derived independently through combination of experimental thermodynamic results, (5) improvements in program reliability and function that stem directly from the recent redesign of the TRC-SOURCE Data Archival System for experimental property values, and (6) implementation of the Peng–Robinson equation of state for binary mixtures, which allows for critical evaluation of mixtures involving supercritical components. Planned future developments are summarized.



■ INTRODUCTION

As described in the earlier eight articles of this series,^{1–8} the *NIST ThermoData Engine* (TDE) software was developed at the National Institute of Standards and Technology (NIST) and is the first full-scale implementation of the concept of dynamic data evaluation for thermophysical properties,^{9,10} and TDE is the core component in implementation of the concept of *Global Information Systems in Science* for the field of thermodynamics.¹¹ Implementation requires the combination of large electronic databases, storing essentially all relevant experimental information known to date with metadata and uncertainties, with expert-system software, designed to automatically generate recommended property values based on available experimental and predicted data. This combination of tools allows production of critically evaluated data on demand. As discussed recently,^{12,13} rapid development of new chemical processes, compound types, and measurement efficiencies, plus greater globalization of scientific research, has overwhelmed the slow and labor-intensive traditional methods of critical data evaluation, and has created the environment in which a dynamic and responsive approach is essential.

TDE has evolved extensively from its first release, which was limited to thermophysical properties of pure compounds.¹⁴ Subsequent extensions have been implemented for on-demand generation of equations of state (EOS),¹⁵ dynamic web-based updates of local data resources¹⁵ through the TRC-SOURCE data storage system,¹⁶ support for properties of binary mixtures for both single-phase properties and phase equilibria, including vapor–liquid equilibrium (VLE), liquid–liquid equilibrium (LLE), and solid–liquid equilibrium (SLE),¹⁷ properties of chemical reactions,¹⁸ experiment planning and product design tools,¹⁹ as well as dynamic web-based dissemination of properties of pure components through the *NIST Web Thermo Tables*,²⁰ evaluation of properties of ternary mixtures, including VLE and LLE generated through on-demand evaluation of the binary subsystems,²¹ and most recently, properties of material streams with any number of components, plus tools for solvent design.²²

TDE is used in a broad variety of applications, including product and process design,^{12,23} data product development,⁶ data quality assurance,²⁴ and validation of new experimental

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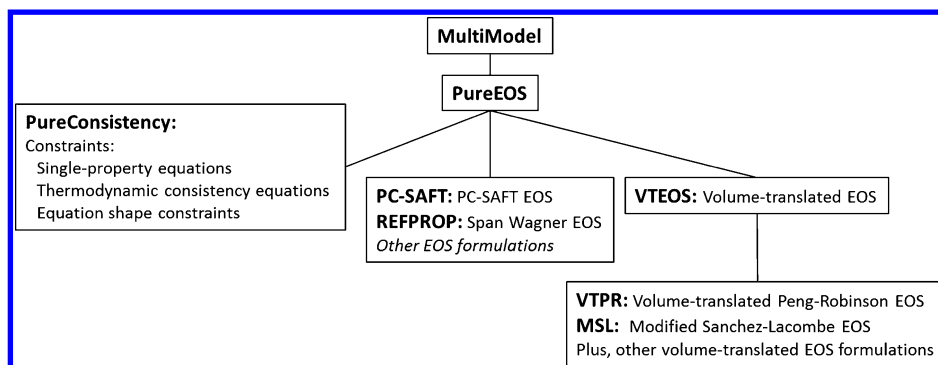


Figure 1. Hierarchy of classes (shown in boldface type) used for implementation of multiproperty thermodynamic-consistency enforcement in TDE. The text is provided to elucidate the abbreviations used as class names.

data in advance of publication.^{13,25} Recent additions include a vapor–liquid equilibrium (VLE) data modeling test for assessment of mixtures, involving supercritical components, that complements consistency tests implemented previously for low-pressure/subcritical VLE data,^{19,26} as well as addition of the NIST-KT-UNIFAC group-contribution prediction method²⁷ for VLE data with automatic decomposition of molecular structures into KT-UNIFAC groups and subgroups.²⁸

The present article describes the background and implementation for new additions in the latest release of TDE (version 8, released in 2013).²⁹ Unlike the descriptions for all previous versions of TDE,^{1–8} the advances described here, generally, do not involve evaluations for new properties or chemical system types not previously addressed. Instead, the advances are in the areas of program architecture and quality improvement for automatic property evaluations, particularly for pure compounds. It will be shown how selection of appropriate program architecture supports improvement of the quality of the on-demand property evaluations through application of a readily extensible collection of constraints. The basis and implementation for other enhancements to TDE are described briefly. These include the following: (1) implementation of model-validity enforcement for specific equations that can provide unphysical results if unconstrained, (2) newly refined group-contribution parameters for estimation of enthalpies of formation for pure compounds containing carbon, hydrogen, and oxygen, (3) implementation of an enhanced group-contribution method (NIST-Modified UNIFAC) in TDE for improved estimation of phase-equilibrium properties for binary mixtures, (4) tools for mutual validation of ideal-gas properties derived through statistical calculations (based on molecular structure, vibrational spectra, and quantum computational methods) and those derived independently through combination of experimental results (i.e., heat capacities, phase-boundary pressures, densities, and enthalpies of vaporization and sublimation), (5) improvements in program reliability and function that stem directly from the recent redesign³⁰ of the TRC-SOURCE Data Archival System for experimental property values, and (6) implementation of the Peng–Robinson equation of state for binary mixtures. This last enhancement allows for creation of models for mixtures involving supercritical components, which was not possible previously in TDE.³

■ SCOPE

Compound types within the scope of TDE remain unchanged since its initial release in 2004.^{1,14} Thermodynamic and

transport properties are considered primarily for 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.

■ SOFTWARE ARCHITECTURE FOR ENFORCEMENT OF THERMODYNAMIC CONSISTENCY FOR PURE COMPOUNDS

The approach used in TDE for evaluation of thermodynamic properties for most compounds involves separate equations for each property with some enforcement of thermodynamic consistency through application of specific constraints.¹ Although a single high-precision equation of state (EOS) can be used to represent all thermodynamic properties for a particular compound, there are relatively few compounds (~100) for which this approach is entirely successful. Simple equations of state, such as the various forms of the Peng–Robinson equation,^{31,2} are useful for rough approximations but do a relatively poor job of representing high-quality experimental data for many properties. Conversely, there is rarely adequate experimental data available for the range of properties needed to allow a reliable fit of more complex equations, such as those of Span and Wagner.³²

In the initial development of TDE, six consistency constraints were used: (1) the *Vapor-pressure Constraint* to constrain extrapolations to low temperatures using liquid–gas heat-capacity differences, (2) *Condensed-State phase Boundary Convergence* to ensure that equations describing condensed-state phase boundaries (crystal–liquid and crystal–crystal) converged at the triple point; (3) *Vapor and Sublimation Pressure Convergence* to ensure that vapor-pressure and sublimation curves converged at triple points; (4) *Saturation Density Consistency at T_c* to ensure that the saturated density of the liquid and vapor converged at the critical temperature T_c ; (5) *Gas phase Density Consistency* to ensure that low densities calculated with the virial equation were consistent with saturation densities near T_c ; and (6) enforced consistency of the saturated gas density with enthalpies of vaporization derived from vapor pressures through application of the Clapeyron equation. The most important problem with this approach was that the constraints were not applied simultaneously, resulting in some properties not being optimized in subsequent constraint applications. To overcome this problem, and to allow for ready addition of new constraints, a new program class was added to the software architecture.

The new program class (PureConsistency) is based on the EOS class (PureEOS) developed for fitting of various equations

of state implemented in TDE for pure compounds. The PureConsistency class includes equations for calculation of different properties and a parameter pool. The position of PureConsistency in the hierarchy of classes is shown in Figure 1. The objective function of this class is the sum of three types of contributions: (1) the summed objective functions for the separate properties, (2) contributions to represent deviations from thermodynamic consistency requirements, and (3) contributions to represent deviations of equations from a valid shape. The three contribution types to the objective function for this class are also shown in Figure 1.

The MultiModel class, which is a parent class of the PureConsistency class, includes methods for (a) equation fitting, (b) rejection of data that are of poor quality or erroneous, and (c) covariance calculation. The Simplex method³³ is used for all model fitting associated with consistency enforcement. Additional details of the MultiModel class were described previously.² A key feature of the MultiModel class is the ability to judge relative data quality between properties. As described earlier,² the covariance-based uncertainty is calculated for each data point, and then relative curve deviations are calculated as ratios of curve deviations to covariance-based uncertainties. The relative deviations can then be directly compared for different properties. The relative deviations take into account the data density and local data quality because regions of state variables poorly populated with data are associated with higher uncertainties for calculated values.

As described in the first paper of this series,¹ properties for pure components are evaluated as a series of "blocks" that include, (1) phase-diagram properties (phase transition temperatures and enthalpies, phase-boundary pressures, and critical temperatures), (2) volumetric properties, (3) energy-related properties, and (4) transport properties. The initial evaluations are followed by interblock consistency enforcement. Depending on progress within the property evaluation algorithm, the PureConsistency class can involve different sets of properties and constraints. Fitting of the combined properties and constraints is done by the methods and tools designed for multiproperty equation and EOS fitting.²

Only thermodynamic properties are involved in consistency enforcement in TDE at this time, and transport properties are not considered. In theory, all thermodynamic properties can be involved in consistency enforcement. In practice, the pure-compound properties that are involved within the PureConsistency class are vapor and sublimation pressures, single-phase and saturation gas and liquid densities, heat capacities for all phases, and enthalpies of vaporization and sublimation. Property values used in consistency enforcement, but not revised, are critical parameters (temperature, pressure, and density), triple-point temperatures, and crystal-to-crystal and crystal-to-liquid phase transition enthalpies. Constraints may be classified as *model-validity* constraints for single-properties (Waring constraint, compressibility factor Z constraint, second virial constraint, saturation Z_{sat} constraint), *property-connection* constraints (virial-to-saturation constraint), or *thermodynamic-consistency* constraints (triple-point pressure constraint, transition enthalpy constraint, vaporization/sublimation enthalpy constraint, and heat capacity difference constraint).

Each constraint is described below together with the mathematical formulation of the contribution to objective function of the PureConsistency class. Graphical representations are given, where practical. For the thermodynamic-

consistency constraints, the equation to be satisfied is given. The fitting weight assigned to each constraint is one, unless stated otherwise. Units used in all equations are those used in TDE: temperature, K; pressure, kPa; molar volume, $\text{m}^3\cdot\text{mol}^{-1}$; specific density, $\text{kg}\cdot\text{m}^{-3}$; enthalpy, $\text{kJ}\cdot\text{mol}^{-1}$; and heat capacity, $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

■ THERMODYNAMIC CONSISTENCY REQUIREMENTS AND EQUATION CONSTRAINTS FOR PROPERTIES OF PURE COMPOUNDS

The nine thermodynamic consistency requirements and equation constraints used presently in TDE are described in the following paragraphs. Graphical representations are provided, where possible. The six constraints included in the first release of TDE are included here in the revised and extended form within the nine sections.

Waring Constraint (1). This constraint^{34,35} helps to ensure a valid shape for the vapor-pressure equation. The Waring function is

$$W = RT^2 \ln(p)/dT \quad (1)$$

where T is temperature, p is the vapor pressure, and R is the gas constant. Requirements for W are that it must be positive, have a positive second derivative with respect to temperature, and have a minimum in the range $(0.85 \pm 0.05)T_c$.³⁴ The precise location of the minimum depends on the chemical nature of the compound.³⁵ The contribution to the objective function is Q^2 where

$$Q = \int_{T_{\min}}^{T_{\max}} (1000F)^2 dT \quad (2)$$

and

$$F = (d^2W/dT^2) - d^2W/dT^2/2 \quad (3)$$

which is the second derivative of the Waring function with respect to temperature, if less than zero, and is, otherwise, constrained to zero. T_{\min} and T_{\max} represent the bounds of the temperature range for which the vapor-pressure equation is defined, and the integration is approximated by summation with a step of 1 K. High-accuracy evaluation of Q is not required, so the integral is evaluated with the well-known trapezoidal rule. Integrals involved in evaluation of the contribution to the objective function for other constraints are approximated in the same way. Graphical representations are given in Figure 2 of invalid (upper plot) and valid (lower plot) Waring curves. The upper plot was generated in the initial stages of evaluation for 2-nitrophenol. A valid shape was obtained, once a better approximation for the critical temperature was determined by TDE. Only the final plot is available to program users through the TDE navigation tree.¹ At present, only the shape of the curve is considered in application of this constraint. Future research is planned to investigate use of the location of the minimum as an additional constraint.

Second Virial Constraint (2). This constraint helps ensure a valid shape for the second virial coefficient B as a function of temperature T . This function must have a negative second derivative and positive first derivative over the entire temperature range, plus negative values as the limit of $T/K \rightarrow 0$ is approached. The contribution to the objective function Q^2 is calculated with

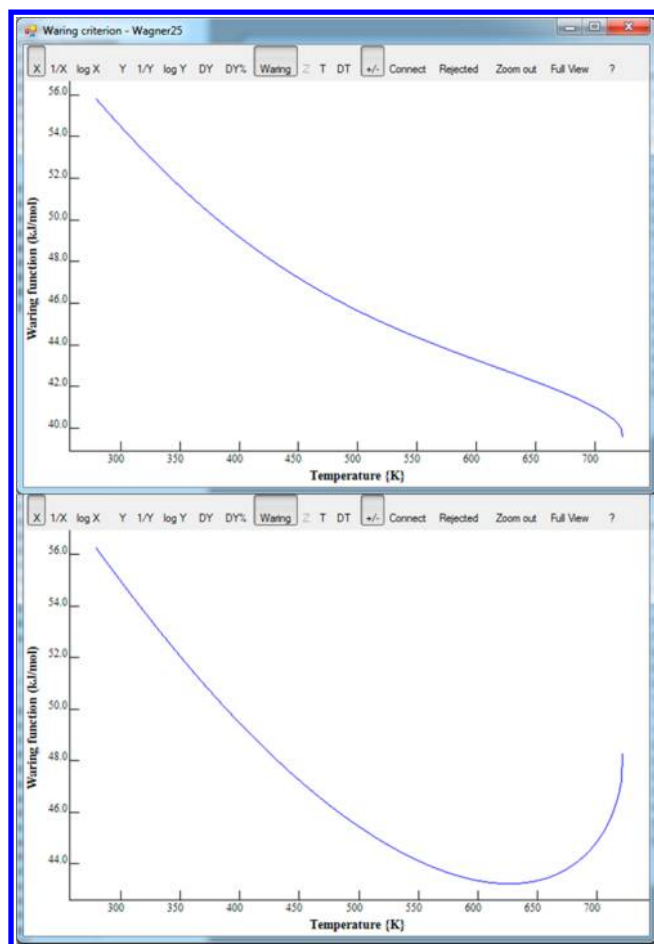


Figure 2. (upper) Waring curve that has an invalid shape. It was generated by TDE in the early stages of property evaluation for nitrobenzene. (lower) Valid curve for this compound obtained after complete evaluation by TDE.

$$Q = \int_{T_{\min}}^{T_{\max}} (10^6 F)^2 dT \quad (4)$$

where

$$F = (dB/dT) - dB/dT / 2 \quad (5)$$

which is the first derivative of the second virial coefficient with respect to temperature, if it is less than zero, and otherwise, it is zero. Presently, only the first derivative is constrained in TDE. T_{\min} and T_{\max} define the temperature range for the virial equation for the particular compound in TDE. Integration is approximated by summation with a step of 1 K. Graphical representations of valid and invalid curve shapes for this constraint are given in Figure 3. The plot of the second virial coefficient as a function of temperature is available to program users through the TDE navigation tree.¹

Compressibility Factor Z Constraint (3). This constraint helps to ensure a valid shape for the gas density as a function of temperature and pressure. The compressibility factor Z is defined as

$$Z = pV/RT \quad (6)$$

where p is pressure, V is molar volume, R is the gas constant, and T is temperature. For a subcritical gas, Z must be less than one and must increase with temperature with a negative second

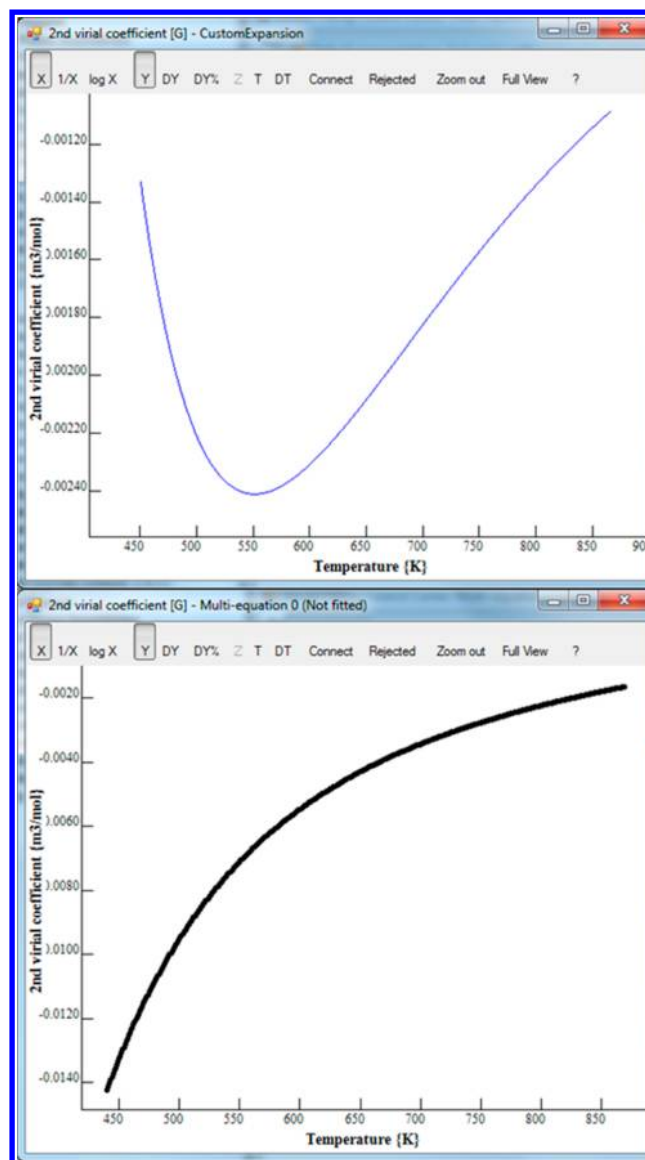


Figure 3. (upper) Invalid second-virial-coefficient curve for anthracene at low temperatures that was generated in an early stage of property evaluation by TDE. (lower) Valid evaluated shape for the same compound.

derivative with respect to temperature along isobars. The contribution to the objective function is Q^2 , where

$$Q = 0.01 \int_{p^0}^{p_{\max}} \int_{T_{\min}}^{T_{\max}} [(10^6 z_0)^2 + (1000 z_1)^2 + (1000 z_2)^2] dT dp \quad (7)$$

where z_0 is $(Z - 1)$ if $Z > 1$, and otherwise, it is zero. The pressure integral is over the range from $p^0 = 100$ kPa to p_{\max} , which is one-half of the highest pressure for which the equation for vapor pressure is valid. The temperature integral is over the valid range from T_{\min} to T_{\max} for the vapor-pressure equation. The term z_1 is the first derivative of Z with respect to temperature at fixed pressure p , if negative, and otherwise, it is zero. The term z_2 is the second derivative of Z with respect to temperature at fixed pressure p , if positive, and otherwise, it is zero. Integration is approximated by summation with a temperature step of 1 K and a pressure step of 100 kPa. An

equation for gas density that has a valid shape will have zero contribution to the objective function. Example plots of valid and invalid behavior are given in Figure 4.

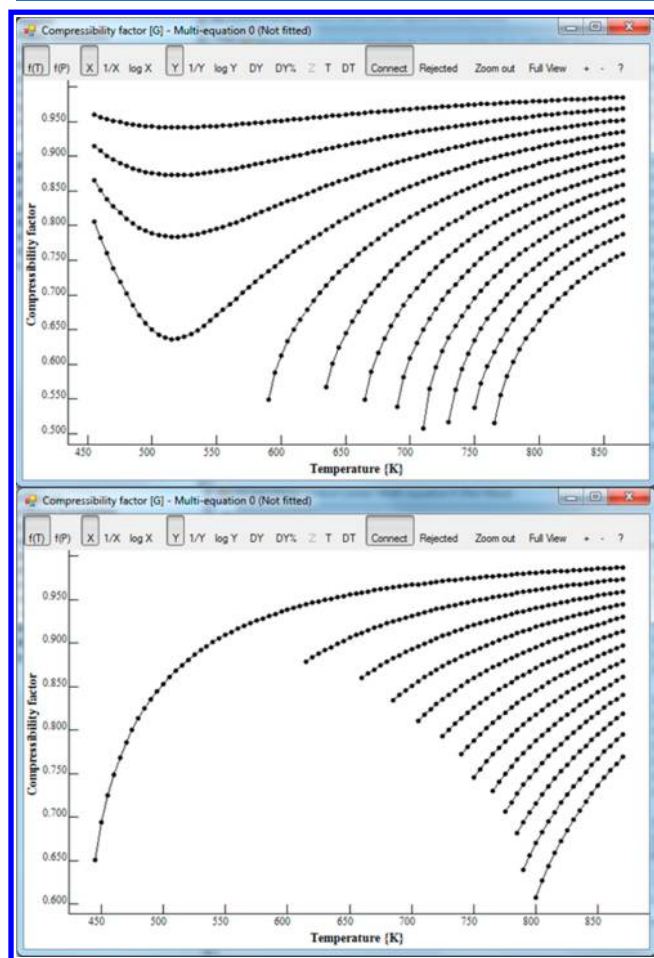


Figure 4. (upper) Invalid behavior of the compressibility factor at low temperatures for anthracene for several isobars. These curves were generated in an early stage of property evaluation by TDE. (lower) Valid evaluated shape for the same compound.

Saturation Z_{sat} Constraint (4). This constraint helps to ensure a valid shape for the compressibility factor of the saturated vapor over all temperatures. The compressibility factor of the vapor along the vapor–liquid phase-equilibrium line must be decreasing function of temperature with a negative second derivative. The contribution to the objective function Q^2 is calculated with

$$Q = \int_{T_{\min}}^{T_c} (1000z_1)^2 + (1000z_2)^2 dT \quad (8)$$

where T_c is the critical temperature and T_{\min} is the lowest temperature for the vapor-pressure and virial equations are valid. The term z_1 is the first derivative of Z_{sat} with respect to temperature if positive; otherwise, this contribution is zero. The term z_2 is the second derivative of Z_{sat} with respect to temperature if positive, and otherwise, it is also zero. This implies that a valid equation does not contribute to the objective function of the PureConsistency class. Again, integration is approximated by summation with temperature steps of 1 K. Plots showing valid and invalid behavior for Z_{sat} as a function of temperature are shown in Figure 5. This plot was

generated with an in-house version of TDE for the purpose of the constraint-functionality illustration and cannot be accessed in the public version.

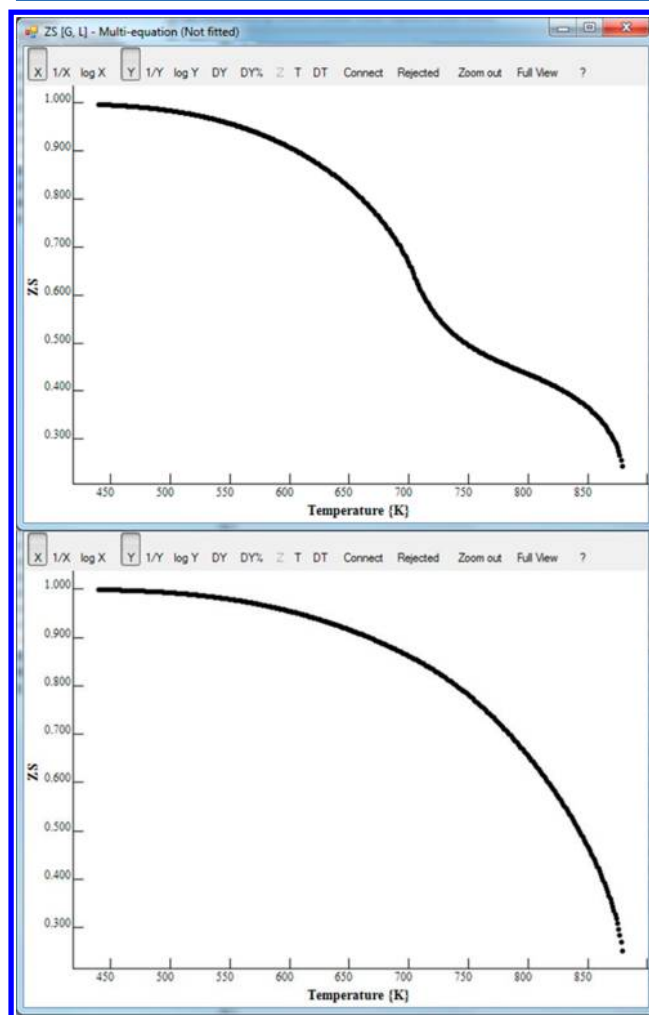


Figure 5. (upper) Invalid shape for the compressibility factor of the saturated gas for anthracene. The curve was generated in an early stage of property evaluation by TDE. (lower) Evaluated valid shape for the same compound.

Virial-to-Saturation Constraint (5). This constraint is a property-connection constraint. It is well-known that the virial equation does not represent densities well in the critical region ($T/T_c > 0.8$) when truncated at the third virial coefficient. To represent the saturated vapor density in the critical region, a separate equation with a mathematical form identical to that for saturated liquid density, but with different parameters, is used in TDE. These densities for the saturated vapor should seamlessly connect with those derived from the virial equation and vapor pressure at some temperature $T = T_{\text{conn}}$ below T_c . This means that the value of saturated vapor density and its first derivative with respect to temperature at T_{conn} should be indistinguishable in the two calculations. Any differences between the two calculations contribute to the objective function as Q^2 where

$$Q = \int_{T_{\text{conn}}-5}^{T_{\text{conn}}+5} \left(10^4 \frac{\rho_1 - \rho_2}{\rho_1 + \rho_2} \right)^2 dT \quad (9)$$

where ρ_1 and ρ_2 are values of saturated vapor density calculated by the two methods described above. Integration is approximated by summation with a step of 1 K. A plot demonstrating seamless connection between the two models for saturated vapor density is given in Figure 6. This plot was generated with an in-house development version of TDE and cannot be accessed in the public version.

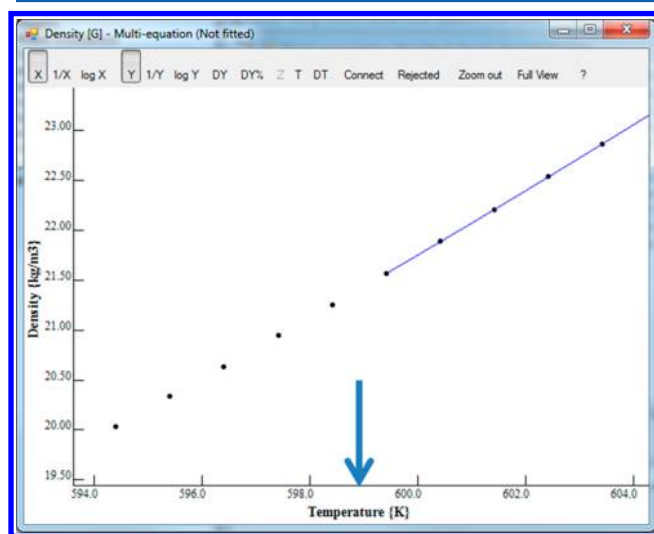


Figure 6. Seamless connection of two regions of saturated vapor density for naphthalene. The arrow indicates the temperature T equal to $0.8T_c$ where T_c is the critical temperature.

Triple-Point Pressure Constraint (6). This is a thermodynamic-consistency constraint that requires equality for the vapor and sublimation pressures at the crystal–liquid–gas triple point. Any deviation from equality contributes to the objective function. The contribution to the objective function Q^2 is calculated with

$$Q = \left\{ 1000 \frac{p_{\text{sat}}(l) - p_{\text{sat}}(\text{cr})}{p_{\text{sat}}(l) + p_{\text{sat}}(\text{cr})} \right\}^{\lg(2)} \quad (10)$$

where $p_{\text{sat}}(l)$ and $p_{\text{sat}}(\text{cr})$ are the vapor and sublimation pressures, respectively. The power $\lg(2)$ was found to be necessary to prevent excessive domination of this term in the objective function when the inequality is significant. For small pressure inconsistencies (less than $0.0001p$)

$$Q = 10^4 \frac{p_{\text{sat}}(l) - p_{\text{sat}}(\text{cr})}{p_{\text{sat}}(l) + p_{\text{sat}}(\text{cr})} \quad (11)$$

A plot demonstrating the consistency between saturation pressures for the liquid and crystal phases can be accessed by the user of TDE through the *Property Consistency* node of the program navigation tree.⁴

Transition Enthalpy Constraint (7). This is a thermodynamic-consistency constraint used to ensure that the difference between the enthalpy of sublimation $\Delta_{\text{cr}}^{\text{g}}H_m$ and enthalpy of vaporization $\Delta_{\text{l}}^{\text{g}}H_m$, both of which are derived typically from equations for phase-boundary pressures (see below), equals the enthalpy of fusion $\Delta_{\text{cr}}^{\text{l}}H_m$ at the crystal–liquid–gas triple point. The contribution to the objective function is Q^2 where

$$Q = 10\{\Delta_{\text{cr}}^{\text{l}}H_m - (\Delta_{\text{cr}}^{\text{g}}H_m - \Delta_{\text{l}}^{\text{g}}H_m)\} \quad (12)$$

The weight for this contribution is the reciprocal square of the uncertainty for the enthalpy of fusion evaluated from experimental measurements. In the absence of an evaluated virial equation for the gas, the saturated gas compressibility factor Z_{sat} is estimated as

$$Z_{\text{sat}} = Z_c + (1 - Z_c)\exp(-1 - 0.2\tau - 15\tau^2) \quad (13)$$

where Z_c is the estimated critical compressibility factor 0.27 and τ is the reduced temperature T/T_c . Z_c is not available at the early stages of evaluation and eq 13 is used. Once volumetric properties are evaluated, densities of the saturated gas and liquid can be used directly.

Vaporization Enthalpy Constraint (8). This is a thermodynamic-consistency constraint. The enthalpy of vaporization $\Delta_{\text{l}}^{\text{g}}H_m$ is expressed by a separate equation (the Watson equation) in TDE, and this must be consistent with the enthalpy of vaporization derived with the Clapeyron equation using the evaluated vapor-pressure curve and densities for the phases in equilibrium. The relevant equation is

$$\Delta_{\text{l}}^{\text{g}}H_m = (Z_{\text{gas}} - Z_{\text{liq}})RT^2 d \ln(p)/dT \quad (14)$$

where Z_{gas} and Z_{liq} are compressibility factors for the gas and liquid phase, respectively. The contribution to the objective function from this constraint Q^2 is calculated with

$$Q = \int_{T_{\text{min}}}^{T_c} \{\Delta_{\text{l}}^{\text{g}}H_m(1) - \Delta_{\text{l}}^{\text{g}}H_m(2)\}^2 dT \quad (15)$$

where $\Delta_{\text{l}}^{\text{g}}H_m(1)$ and $\Delta_{\text{l}}^{\text{g}}H_m(2)$ are the enthalpies of vaporization calculated with the Watson and Clapeyron equations, respectively. Integration is approximated by summation with the step of 1 K, and integration limits are defined by the validity ranges for the properties involved. An analogous constraint for sublimation enthalpy is also implemented in TDE.

Heat-Capacity Difference Constraint (9). This is a thermodynamic-consistency constraint in which the first derivative with respect to temperature of the enthalpy of vaporization derived with the Clapeyron equation (eq 14) should equal the heat-capacity difference between the gas and condensed phases in equilibrium. Heat capacities of all phases are expressed by separate equations. The contribution to the objective function Q^2 is calculated with

$$Q = \int_{T_{\text{min}}}^{T_{\text{max}}} \left[\frac{\Phi - \{C_{\text{sat},m}(\text{g}) - C_{\text{sat},m}(\text{l})\}}{u\{C_{\text{sat},m}(\text{g}) - C_{\text{sat},m}(\text{l})\}} \right]^2 dT \quad (16)$$

where T_{min} and T_{max} represent the temperature range for which all involved properties are available, Φ is the first derivative with respect to temperature of the enthalpy of vaporization derived with the Clapeyron equation, $C_{\text{sat},m}(\text{g})$ and $C_{\text{sat},m}(\text{l})$ are molar heat capacities at saturation pressure of the gas and liquid, respectively, and $u\{C_{\text{sat},m}(\text{g}) - C_{\text{sat},m}(\text{l})\}$ is the uncertainty of the difference in heat capacity. The integration is approximated adequately by summation with a step of 5 K. This constraint is difficult to satisfy precisely because of the involvement of the second order derivative of the vapor pressure. A corresponding constraint for sublimation pressure is calculated analogously.

Implementation of Consistency Enforcement in the Software Algorithm. The general algorithm for critical evaluation of thermophysical properties for pure compounds in TDE was described in the first article of this series.¹ A block representation of the algorithm is shown in Figure 7. Presently, there are three places in the algorithm where consistency

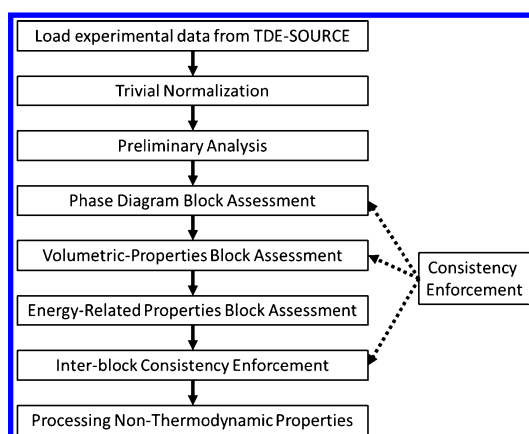


Figure 7. Major steps in dynamic critical evaluation of thermophysical properties for pure compounds by TDE are shown at the left side of the figure. Steps within which consistency enforcement is applied are indicated by the dotted arrows.

enforcement is invoked for pure compounds, and these are indicated in the figure. The first is in the *Phase Diagram Block Assessment* where vapor and sublimation pressures must be made consistent at the triple point. Consistency enforcement involves the vapor and sublimation pressures, the virial equation for the gas phase, the melting temperature or crystal–liquid–gas triple point, and the enthalpy of fusion. The Waring constraint (constraint 1, as numbered above) is the only model-validity constraint applied at this stage for many compounds. The triple point pressure constraint (constraint 6), the transition enthalpy constraint (constraint 7), and the heat-capacity difference constraint (constraint 9) are involved at this stage if the necessary auxiliary property values are available. Only the equations for vapor and sublimation pressure are adjusted at this point.

The second application of consistency enforcement is in the *Volumetric-Properties Block Assessment* where the equation for the saturated vapor density near the critical temperature must connect seamlessly with that derived with the virial and vapor-pressure equations, while giving saturated-gas compressibility factors that decrease smoothly with temperature. The process involves refinement of the virial equation for the gas and the equation for the saturated vapor density. The vapor-pressure equation is used in an auxiliary manner and is not adjusted. The property-connection constraint {(the virial-to-saturation constraint (constraint 5))} for seamless connection of the models for the saturated gas-phase densities at high and low temperatures is applied here. Model-validity constraints applied here are the second virial constraint (constraint 2), the compressibility factor Z constraint (constraint 3), and the saturation Z_{sat} constraint (constraint 4).

The third and last application of consistency enforcement is the final refinement of essentially all properties bound by strict thermodynamic relations. This stage is termed *Interblock Consistency Enforcement*. This final consistency enforcement involves all previous constraints, as well as the vaporization enthalpy constraint (constraint 8), which ensures that the equation for enthalpies of vaporization as a function of temperature (the Watson equation¹) is consistent with values derived with the Clapeyron equation (eq 14).

In summary, application of these constraints always provides improvement in the evaluated properties over that which would be obtained in their absence, while the degree of improvement

can vary substantially from compound to compound. Greatest improvement is often seen for those compounds for which the estimated uncertainties for experimental data are too small, which can lead to equation overfitting and unphysical behavior.

■ SPECIAL MODEL VALIDITY ENFORCEMENT FOR THE TAIT EQUATION FOR LIQUID DENSITIES OF PURE COMPOUNDS AND THE NON-RANDOM TWO-LIQUID (NRTL) ACTIVITY COEFFICIENT MODEL FOR BINARY MIXTURES

The mathematical relationships that form the basis of thermodynamics can restrict the range of possible values and the nature of dependencies on state variables (temperature, pressure, mixture composition) for certain properties. Unfortunately, some models that are commonly used to represent such properties do not inherently enforce those requirements. Fitting of models to experimental data with unknown or unreliable uncertainties may produce invalid equations that are “overfit” and can lead to predictions of unphysical behavior. The TDE software applies final validity tests to equations generated and rejects those that produce unphysical results. Nonetheless, it is preferable to produce a valid equation with reliable uncertainties through restricted optimization, rather than to reject the results entirely due to overfitting. Restricted optimization has been applied to two equations in the present version of TDE (version 8); the Tait equation for pure-compound single-phase liquid density and the NRTL³⁶ activity coefficient model for phase equilibrium of binary mixtures.

In the case of the Tait equation, the single-phase density of a liquid ρ is represented as

$$\rho = \rho_{\text{sat}} / [1 - c \ln\{(b + p)/(b + p_{\text{sat}})\}] \quad (17)$$

where ρ is the density of the liquid, ρ_{sat} is the density of the saturated liquid at pressure p_{sat} , and p is pressure. The parameters b and c are expressed as

$$b = \sum_{i=0}^{n_b-1} B_{(i+1)} t^i \quad \text{and} \quad c = \sum_{i=0}^{n_c-1} C_{(i+1)} t^i \quad (18)$$

where $t = (T - T_0)$ for temperature T and B , C , and T_0 are equation parameters that can change sign as temperature varies to create regions of unphysical density values.

The NRTL activity-coefficient model can predict the condition of two composition regions of liquid–liquid equilibrium at isothermal conditions for a binary system for certain combinations of fitted parameters. This prediction of “double LLE” is based on the existence of two concave regions in the calculated excess Gibbs energy against composition curve at isothermal conditions. Such behavior has never been observed experimentally and is unphysical. LLE is relatively insensitive to pressure changes, so that variable is not considered.

The Box method³⁷ is a well-known method for restricted optimization; however, we chose not to implement this alternative fitting method in TDE, but rather to apply similar restriction principles to the simplex method.³³ Valid, but not necessarily correct, initial approximations to the parameters are required; e.g., a nonrandomness parameter $k = 0.3$ for NRTL and $c_1 = c_2 = 0.001$ interaction parameters in the absence of LLE or $c_1 = c_2 = 2.0$ in the presence of LLE. (See ref 3, page 515, for complete definitions of parameters for the NRTL model in TDE). The initial value 0.001 for the interaction parameters is close to that for ideal mixing, which may be a

poor approximation for the final result; however, it scales quickly to a good approximation with the Simplex fitting method. When building the initial simplex, if any node falls outside of the validity region, it is replaced by the midpoint between that node and the initial approximation until valid. Similar adjustment is done to any trial node during optimization. Validity of the models (NRTL and Tait equation) is determined by scanning for invalid behavior over the temperature range for which they are defined. Invalid behavior is evidenced by negative b or c for the Tait equation, and more than one concave region of excess Gibbs energy over the full composition range at any isothermal condition for the NRTL equation.

NEW MODELS ADDED TO TDE

NIST-Modified UNIFAC. UNIFAC is a group-contribution method for the prediction of phase-equilibrium properties: VLE, LLE, and SLE. Original UNIFAC^{38,39} was implemented in version 3 of TDE,^{3,17} together with the introduction of critical evaluation for binary mixtures. In 2011, we described a new method for obtaining UNIFAC group interaction parameters²⁷ based on thermophysical property data evaluated with TDE (version 5),^{5,19} which included a quality assessment algorithm²⁶ for vapor–liquid equilibrium data. The most distinctive feature of this new approach was the use of experimental data with assessed quality, which allows regression without the need for labor-intensive manual prescreening. This approach also provides for simple, rapid, and continuous improvement of the interaction parameters and for extension of the parameter matrix, as new experimental data are published. The approach was used to derive group parameters for the KT-UNIFAC²⁸ formulation, within which temperature dependence of the parameters is represented by two terms, rather than one, as in original UNIFAC. The resulting parameterization was termed NIST-KT UNIFAC and was included for prediction of phase-equilibrium properties in TDE (version 6).^{7,21}

An enhancement of original UNIFAC is “Modified UNIFAC,” which was first developed by Weidlich and Gmehling in 1987.⁴⁰ Updates and extensions for the method have been published periodically by Gmehling and co-workers over the subsequent 20 years.^{41–44} The method involves an additional term for representation of the temperature dependence of the interaction parameters, and a special expression for the combinatorial term. Modified UNIFAC is used widely for prediction of phase equilibria; VLE, LLE, SLE of eutectic systems, azeotropic data, activity coefficients at infinite dilution, and excess enthalpies. The modified formulation was developed to provide a better description relative to original UNIFAC^{38,39} of the temperature dependence of the activity coefficients, and better predictions of phase equilibria in the dilute region and particularly for mixtures involving molecules of different size.^{40–44}

In analogy to the development of NIST-KT UNIFAC,²⁷ we have used the mathematical formulation of Modified UNIFAC^{40–44} together with the extensive experimental data collection in TRC-SOURCE and the evaluation tools of TDE to derive group parameters for the Modified UNIFAC framework. This parametrization is termed NIST-Modified UNIFAC and is included as a prediction tool for phase-equilibrium properties in TDE. A complete description of the development of NIST-Modified UNIFAC will be published separately.⁴⁵ Development of NIST-KT UNIFAC was made possible by development of a quality assessment algorithm for

VLE, and similar tools were developed for other types of phase equilibrium and properties in the development of NIST-Modified UNIFAC. These will also be described separately.⁴⁵ As with NIST-KT UNIFAC, a key feature of NIST-Modified UNIFAC is the evaluation of approximate uncertainties for all predictions. Uniform covariance levels were assigned to all interaction parameters and were adjusted to give uncertainties that were in accord with experimental uncertainties or curve deviations for more than half of the 13 000 mixtures tested. Individual adjustment of covariance values for each interacting pair of structural groups is planned in future research.

Peng–Robinson EOS. The first implementation of analyses for VLE of binary mixtures was provided in TDE version 3,¹⁷ which was released in 2008. At that time, systems that could be processed were limited to those involving subcritical components, and many important mixtures involving light components, such as carbon dioxide and methane, could not be accommodated. With the release of the current version of TDE (version 8), mixtures involving supercritical components can now be modeled through implementation of the original Peng–Robinson EOS³¹ with symmetrical mixing rule and no volume translation. This is the first EOS implemented in TDE for mixtures, and details of the implementation follow.

The Peng–Robinson EOS is used here in the form

$$p = \frac{RT}{V - b} - \frac{a}{V^2 + 2Vb - b^2} \quad (19)$$

where p is pressure, V is molar volume, R is the gas constant, T is temperature. The quantities a and b are mixture-specific functions of temperature and composition with the following mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (20)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad \text{with} \quad k_{ij} = k_{ji} (\text{symmetrical}) \quad (21)$$

$$b = \sum_i x_i b_i \quad (22)$$

Parameters a_i and b_i are specific for each component:

$$a_i = 0.45724(RT_c)^2 / p_{c,i} \left(1 + \kappa_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right)^2 \quad (23)$$

$$k_i = -0.26992\omega_i^2 + 1.54226\omega_i + 0.37464 \quad (24)$$

$$b_i = 0.0778(RT_c / p_{c,i}) \quad (25)$$

$T_{c,i}$, $p_{c,i}$, and ω_i are the critical temperature, critical pressure, and acentric factor, respectively, for component i .

Property calculations for the Peng–Robinson EOS have been implemented within the NIST REFPROP program.⁴⁶ Rather than reprogramming these calculations in TDE, the public dynamic link library (DLL) for REFPROP was used as an engine for calculations within a software code class compatible with TDE specifications. In order to decrease the processing time for calculations, required analytical derivatives of the Helmholtz energy were derived and implemented for inclusion in the REFPROP DLL. These derivations will be published separately.⁴⁷ As REFPROP does not presently support SLE and subcritical LLE calculations for mixtures, the required functions were implemented in the wrapping TDE class. The functions

are essentially the same as those used for activity coefficient models,³ but with pressure introduced as a variable. When subcritical LLE calculations are performed at gas saturation pressure, the pressure is evaluated in a few iterations starting from the sum of the vapor pressures of pure components. Pressure effects on SLE are not considered.

TDE interface provides a collection of convenient plots of phase equilibria modeled with the Peng–Robinson EOS, such as the VLE isotherm (Figure 8), VLE isopleths (Figure 9), and

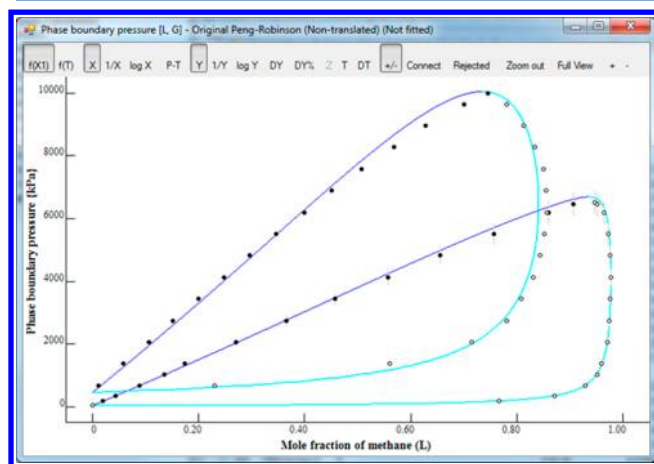


Figure 8. VLE isotherms for (methane + propane) at the temperatures $T/K = 213.72$ and 273.1 evaluated with the Peng–Robinson EOS. Filled circles are experimental values for the liquid phase and unfilled circles are experimental values for the gas phase. The lines were calculated with the fitted model. Dark blue lines represent the liquid phase, and light blue lines represent the gas phase. Experimental data were reported by Akers et al.⁴⁸ and by Wichterle and Kobayashi.⁴⁹

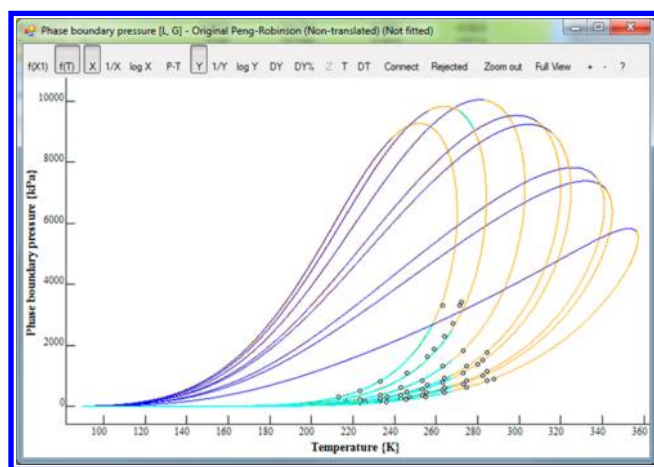


Figure 9. VLE isopleths for (methane + propane) evaluated with the Peng–Robinson EOS. Unfilled circles are experimental values for the gas phase reported by Rozhnov et al.⁵⁰ The lines were calculated with the fitted model. Dark blue lines represent the liquid phase, and light blue lines represent the gas phase. Orange lines were calculated with a density-based procedure established in the REFPROP program to close the loops without phase identification.

SLE/LLE diagram (Figure 10). The experimental data in Figure 8 were reported by Akers et al.⁴⁸ and Wichterle and Kobayashi,⁴⁹ while those in Figure 9 were reported by Rozhnov et al.⁵⁰ The orange lines in Figure 9 were calculated with a density-based procedure used in the REFPROP⁴⁶ software to connect the gas-phase and liquid-phase curves.

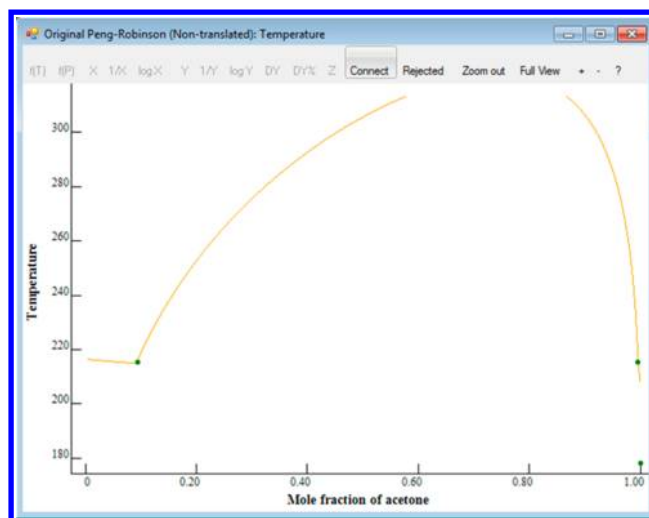


Figure 10. SLE and LLE calculated with the Peng–Robinson EOS for (acetone + octane). Green points are the eutectic (lower right) and monotectic (upper left and right) points. The orange color for the lines indicates that no experimental data are available at those conditions.

■ OTHER ADDITIONS TO TDE

Refined Benson-type Group-Contribution Parameters. Parameters used for prediction of enthalpies of formation in the liquid and gas states, plus enthalpies of vaporization at the temperature $T/K = 298.15$ for C–H–O compounds were recently refined.⁵¹ The updated parameters are now used in TDE. Three important aspects of the new parameters are the following: (1) they were derived with up-to-date and complete experimental data from TRC-SOURCE, (2) a new and unambiguous method was developed to account for 1,4- and 1,5- nonbonded interactions in place of the loosely defined “gauche” interactions used in the original formulation,⁵² and (3) the variance was evaluated for each group parameter, which allows estimation of uncertainties for the predicted values.

Validation of Ideal-Gas Entropies. The entropy for a compound in the ideal-gas state is required for calculation of real-gas or fluid entropy in the application of an EOS and is necessary for chemical equilibrium calculations in the gas phase. Ideal-gas entropies can be calculated with the methods of statistical physics based on molecular parameters⁵³ or by group contribution methods.⁴ TDE contains a large (2369 compounds) database of ideal-gas properties compiled by Frenkel et al.⁵³ or evaluated for the Web Thermo Tables⁵⁴ that are expressed in terms of the Wilhoit equation.⁵³ Entropies for the ideal gas are given at pressure $p/\text{kPa} = 100$ for a broad range of temperatures. Ideal-gas entropies can also be derived independently from experimental thermodynamic property data. One of the earliest examples is the famous work by W. F. Giauque on disorder of carbon monoxide in the solid state.⁵⁵ More recently, Chirico and co-workers have published a series of reports of high-quality determinations of ideal-gas entropies for a variety of molecule types based on thermodynamic property measurements (c.f., refs 56–58).

The two methods for derivation of ideal-gas entropies can be used to provide a valuable mutual validation for each. Inconsistencies can provide evidence of problems for either method, such as an incorrect vibrational assignment or incorrect accounting for internal rotations in the statistical method or undetected disorder in the solid state for the

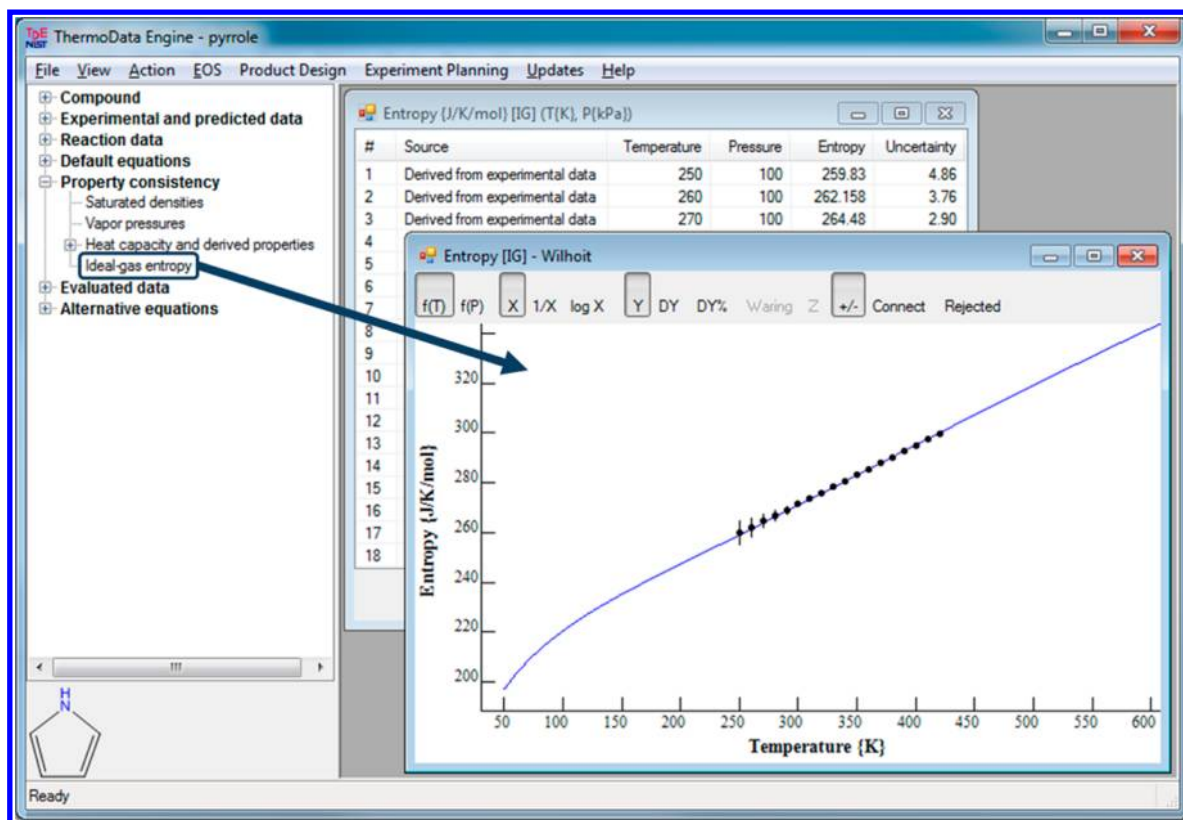


Figure 11. Ideal-gas entropy comparisons can be accessed by the user through the TDE navigation tree, as shown in the upper left. The graph provides a visual comparison of ideal-gas entropies derived from experimental thermodynamic data (black dots) and calculated by statistical methods (blue line).

experimental method. Many experimental thermodynamic properties must be combined to calculate ideal-gas entropies from thermodynamic property data, so a demonstrated consistency with values calculated statistically can provide validation of the properties involved, including heat capacities, vapor pressures, phase transition properties, enthalpies of vaporization and sublimation, saturation densities for the gas and liquid phase, and even critical properties. In view of these facts, TDE (version 8) includes the ability to compare experimental and statistical ideal-gas entropies where possible and gives the details of the calculations. At present, differences are demonstrated but not used for modification of the property-evaluation process. This is a subject for future work.

Ideal-gas entropies S° can be derived from experimental thermodynamic data based on the following relationship.

$$S^\circ = S(\text{condensed}) + \Delta_{\text{cr,l}}^{\text{g}} H_m / T + S^* + RT \ln(V^\circ / V_{\text{sat}}) \quad (26)$$

where T is temperature, $S(\text{condensed})$ is the entropy at temperature T for the crystal or liquid phase obtained by integration of experimental heat capacity from $T/K = 0$, $\Delta_{\text{cr,l}}^{\text{g}} H_m$ is the enthalpy of sublimation or vaporization at temperature T , S^* is the nonideality correction at density V_{sat} at temperature T , R is the gas constant, and V_{sat} and V° are the ideal-gas volumes at the saturated vapor pressure and the reference pressure $p^\circ / \text{kPa} = 100$, respectively. The equation for calculation of the nonideality correction S^* is given by Poling et al.⁵⁹

$$S^\circ - S^r = R\{(B + T \cdot dB/dT)/V + (C - TdC/dT)/2V^2 - \ln(Z)\} \quad (27)$$

where S^r is the entropy of the nonideal gas, B and C are the second and third virial coefficients, and Z is the compressibility factor.

The TDE interface provides tabulated ideal-gas entropies derived from experimental thermodynamic property data in the temperature range where all necessary properties are known without extrapolation. A plot of the experiment-based and statistics-based entropies can be accessed by the user through the Property Consistency node of the TDE navigation tree. An example of successful comparison is given in Figure 11 for pyrrole. At present, this type of comparison can be done in TDE for approximately 400 compounds. Such comparisons are essential for validation of results by computational chemistry methods, for which uncertainties are rarely reported or even considered.

Implementation of the New TRC-SOURCE Data Archival System. As described in the first article of this series, all property evaluations performed by the TDE expert system are based on three types of property data: (1) experimental data from the archival literature (stored in the TDE-SOURCE database distributed with the TDE software), (2) predicted data, and (3) user-supplied data.¹ The TDE-SOURCE database of experimental data is a subset of the TRC-SOURCE archive.

TRC SOURCE was recently completely redesigned and repopulated.³⁰ Several important new features for TRC-SOURCE directly affect the quality of TDE-SOURCE. All compounds in TRC-SOURCE are uniquely defined by their chemical structure, which eliminates problems of duplicate entry or ill-defined substances. Molecular structures are stored in TRC-SOURCE (and TDE-SOURCE) for all molecules with

experimental property data in the archive. This structural information is stored in MOL⁶⁰ format and can be parsed as needed for group definitions in property-prediction methods, structure search, and visual representation of compounds. Some tables and fields not essential for dynamic data evaluation (such as compiler and date of entry) are excluded in TDE-SOURCE, and some additional tables are included that index chemical families and data availability for compounds and mixtures, plus pre-evaluated property models for product design.

TRC-SOURCE now includes over 5 million numerical property values and their uncertainties on more than 22 000 pure compounds, 42 000 binary mixtures, 11 500 ternary mixtures, and 6000 reaction systems. At present, the rate of collection of numerical property values is near 0.5 million per year. It is estimated that TRC SOURCE contains approximately 80% of all available experimental thermodynamic property data for organic compounds.

CONCLUSIONS AND FUTURE DEVELOPMENT

The recent extensions of the NIST ThermoData Engine associated with version 8 are described in this article. These extensions include advanced program architecture and quality improvement for automatic property evaluations, particularly for pure compounds. Other enhancements include the following: (1) implementation of model-validity enforcement for specific equations that can provide unphysical results if unconstrained, (2) newly refined group-contribution parameters for estimation of enthalpies of formation for pure compounds containing carbon, hydrogen, and oxygen, (3) implementation of an enhanced group-contribution method (NIST-Modified UNIFAC) in TDE for improved estimation of phase-equilibrium properties for binary mixtures, (4) tools for mutual validation of ideal-gas properties derived through statistical calculations and those derived independently through combination of experimental thermodynamic results, (5) improvements in program reliability and function that stem directly from the recent redesign of the TRC-SOURCE database of experimental property values, and (6) implementation of the Peng–Robinson equation of state for binary mixtures, which allows for critical evaluation of mixtures involving supercritical components.

Future developments will be focused on implementation of additional EOS for properties of binary mixtures, as well as extension of the existing data evaluation infrastructure to properties of chemical species outside of organic compounds, such as metallic systems.

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Notes

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