

ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 4. Chemical Reactions

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ThermoData Engine (TDE) is the first full-scale software implementation of the dynamic data evaluation concept, as reported recently in this journal. This paper describes the first application of this concept to the evaluation of thermodynamic properties for chemical reactions. Reaction properties evaluated are the enthalpies, entropies, Gibbs energies, and thermodynamic equilibrium constants. Details of key considerations in the critical evaluation of enthalpies of formation and of standard entropies for organic compounds are discussed in relation to their application in the calculation of reaction properties. Extensions to the class structure of the program are described that allow close linkage between the derived reaction properties and the underlying pure-component properties. Derivation of pure-component enthalpies of formation and of standard entropies through the use of directly measured reaction properties (enthalpies of reaction and equilibrium constants) is described. Directions for future enhancements are outlined.

1. INTRODUCTION

As was discussed in the first three papers of this series,^{1–3} NIST *ThermoData Engine* (TDE) software represents the first full-scale implementation of the dynamic data evaluation concept for thermophysical properties.^{4,5} This concept requires large electronic databases capable of storing essentially all relevant experimental data known to date with detailed descriptions of metadata and uncertainties. The combination of these electronic databases with expert system software, designed to automatically generate recommended property values based on available experimental and predicted data, leads to the ability to produce critically evaluated data dynamically or ‘to order’.

The first version of TDE (version 1.0, released in 2004)⁶ focused on thermophysical properties of pure compounds. The second version (version 2.0, released in 2006)⁷ expanded the implementation of dynamic data evaluation to on-demand generation of equations-of-state (EOS). To adequately represent a range of data scenarios, four EOS of different complexity and precision were selected.² Also, a dynamically updated *TDE-SOURCE* data storage tool² was developed, in part, with the multitier Web–Oracle dissemination system⁸ recently established at NIST for several online products.^{9,10} As previously described,² experimental data used by TDE are extracted from the *TRC-SOURCE*¹¹ data storage system and distributed as a local database (*TDE-SOURCE*) with the program. *TRC-SOURCE* is maintained at NIST and is continuously populated with new experimental data (using guided data capture, GDC, software¹² developed at NIST). In order to more closely adhere to the requirements for dynamic data evaluation, TDE includes a mechanism for dynamically updating the local *TDE-SOURCE* based on additions and changes to *TRC-SOURCE* through a central server.

The third version of TDE (version 3.0, released in 2008)¹³ further expanded implementation of dynamic data evaluation to binary mixtures.³ This expansion progressed along two paths: (1) properties modeled individually (densities, surface tensions, critical temperatures, critical pressures, excess enthalpies, and transport properties, such as viscosity and thermal conductivity), and (2) properties modeled collectively (activity-coefficient models for phase equilibrium properties, including vapor–liquid (VLE), liquid–liquid (LLE), and solid–liquid (SLE) equilibria). In this development, many challenges were addressed related to enforcement of consistency among the phase equilibria properties, which are expressed in a broad variety of ways in the experimental literature as well as in the enforcement of consistency between properties of the pure components and binary mixtures. TDE 3.0 also included initial steps for implementation of dynamic data evaluation for chemical reactions. This earlier effort was limited to enthalpies of the formation reaction from the elements for compounds composed of carbon, hydrogen, nitrogen, and oxygen only.

TDE has proven to be a powerful software tool for thermophysical property data quality assurance,¹⁴ validation of new experimental data,¹⁵ and a variety of engineering applications, including chemical process design.¹⁶ It is also a critical component in implementation of the concept of global information systems in science and engineering with application to the field of thermodynamics.¹⁷

The present paper describes the further extension of TDE (version 4.0)¹⁸ in the implementation of the dynamic data evaluation concept for chemical reactions, including processing for both change-of-state and chemical equilibrium information. As an essential part of this development, the scope of properties for pure compounds evaluated by TDE was expanded to include enthalpies of formation for sulfur-containing and halogenated compounds, plus the integrated thermodynamic functions (entropy and enthalpy) for all

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phases. The evaluation and display of these properties is described. Finally, the first implementation of quantitative structure–property relationship (QSPR) prediction methods in TDE (for critical properties of pure compounds) is described.

2. SCOPE

A chemical reaction is defined through specification of the chemical species (participants) involved in the reaction, the stoichiometric coefficients (positive for products and negative for reactants), and the phase for each participant. Properties of chemical reactions evaluated within TDE 4.0 are the standard enthalpy of reaction $\Delta_r H^\circ$, standard entropy of reaction $\Delta_r S^\circ$, standard Gibbs energy of reaction $\Delta_r G^\circ$, and the thermodynamic equilibrium constant K° . Compounds composed of C, H, N, O, F, Cl, Br, I, and S are considered. Application of prediction methods allows evaluation for essentially all organic compounds, including hypothetical structures. For all evaluated properties, reaction participants are in their pure compound standard states; pure crystal, pure liquid, and ideal-gas state at the standard pressure $p^\circ = 10^5$ Pa.

3. GENERAL ALGORITHM

All properties for reactions (hydrogenations, isomerizations, esterifications, etc.) evaluated by TDE 4.0 are based upon the properties of the pure reactants and products. Although enthalpies of reaction and equilibrium constants can be measured directly, these are relatively rare in the literature and are used primarily as checks on the reaction properties derived from the pure participant properties. The exception to this is the measurement of enthalpies of combustion $\Delta_c H$ with oxygen from which enthalpies of formation $\Delta_f H$ have been derived for thousands of compounds. (Numerous examples of published reports can be found in well-known compilations.)¹⁹ The formation reaction is handled as a special case within TDE with $\Delta_f H$ considered a pure compound property, as described in the previous article in this series.³ Consequently, the enthalpies of combustion that underlie most of the $\Delta_f H$ values are also associated with the pure compounds. Enthalpies of combustion and enthalpies of formation for pure compounds are discussed in more detail later in this article.

Reaction properties are calculated by TDE through application of the following thermodynamic relations:

$$\Delta_r H^\circ(T) = \sum c_i \times \Delta_f H^\circ_i(T) \quad (1)$$

where $\Delta_r H^\circ$ is the standard enthalpy of the reaction at temperature T , $\Delta_f H^\circ_i$ is the enthalpy of formation of the i^{th} participant at temperature T , and c_i is the stoichiometric coefficients for the chemical reaction. Similarly:

$$\Delta_r S^\circ(T) = \sum c_i \times S^\circ_i(T) \quad (2)$$

where $\Delta_r S^\circ$ is the standard entropy of the reaction at temperature T , S°_i is the absolute entropy of the i^{th} participant at temperature T , and c_i is the stoichiometric coefficients with the usual convention; negative values for reactants and positive values for products. The standard Gibbs energy of reaction $\Delta_r G^\circ$ is calculated from these quantities with the equation:

$$\Delta_r G^\circ(T) = \Delta_r H^\circ(T) - T \times \Delta_r S^\circ(T) \quad (3)$$

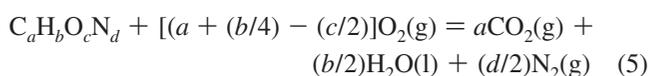
The thermodynamic equilibrium constant K° is related directly to $\Delta_r G^\circ$:

$$K^\circ = \exp(-\Delta_r G^\circ(T)/R \times T) \quad (4)$$

where R is the gas constant.

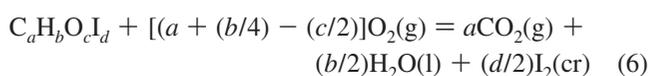
4. ENTHALPIES OF FORMATION FOR REACTION PROPERTY CALCULATIONS

Experimental Origins of $\Delta_f H^\circ$ for Organic Compounds. Enthalpies of formation for organic compounds are most commonly derived from experimental enthalpies of combustion determined at or near the temperature $T = 298.15$ K, as noted earlier. The combustion reaction for compounds composed of C, H, N, and O can be written as the following general equation:



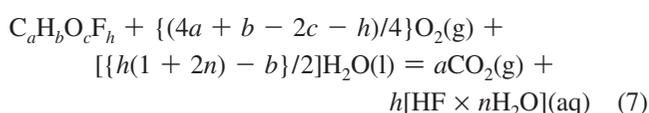
In the case of nitrogen-containing compounds, nitric acid is a possible product of the combustion reaction and must be determined by analysis of the solution after combustion.^{19a} This allows calculation of the enthalpy of reaction for the idealized combustion reaction (eq 4). The enthalpy of formation is then derived from the enthalpy of combustion through application of Hess's Law with recommended values for $\Delta_f H^\circ$ of $CO_2(g) - (393.51 \pm 0.13)$ and $H_2O(l) - (285.830 \pm 0.042)$ kJ·mol⁻¹ assigned by CODATA.²⁰ Evaluation of enthalpies of formation by TDE for compounds composed of C, H, N, and O was described previously.³

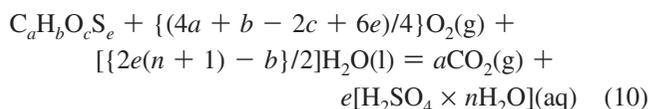
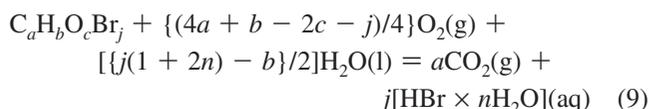
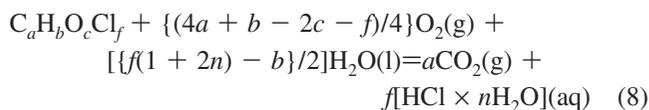
Evaluation of enthalpies of formation by TDE is now extended to include sulfur-containing and halogenated compounds (F, Cl, Br, and I). The combustion reaction for iodine-containing compounds is relatively simple with elemental iodine formed in its standard state $I_2(cr)$. The combustion reaction is analogous to reaction 4:



and derivation of $\Delta_f H^\circ$ requires only $\Delta_f H^\circ$ for $CO_2(g)$ and $H_2O(l)$.

For many years, reliable combustion calorimetric results for compounds containing F, Br, Cl, and S could not be determined, due to problems associated with obtaining a well characterized product slate from the combustion reaction. This difficulty was overcome with the development of the rotating bomb calorimeter in the mid-1950s.²¹ The rotation of the bomb allowed rapid dissolution of the combustion products, yielding acid solutions that could be readily analyzed. A series of chemical problems were also solved in the mid-1950s that allowed formation of simple acid solutions as products, rather than complex mixtures of gaseous elements, halocarbons, and acids.²² The combustion reactions for compounds containing F, Cl, Br, and S are as follows:





In the combustion of fluorine compounds, some $CF_4(g)$ can be formed and must be accounted for in the derivation of the enthalpy of combustion.²² In the case of Cl and Br compounds, arsenious oxide is added to the solution to reduce any elemental halogen, so that the overall reactions are given as above.²¹ Nonetheless, some authors historically reported combustion reactions for Br compounds with $Br_2(l)$ as a product, rather than hydrobromic acid, with appropriate use of Hess's law to adjust the measured enthalpy of combustion. Although some reporting standards were established concerning the concentrations of product acids (e.g., commonly $n = 600$ for HCl and $n = 115$ for H_2SO_4), these are not universally applied in the literature, and appropriate enthalpies of dilution^{23,24} must be used to adjust the results for nonstandard concentrations.

Many collections and databases of enthalpy-of-formation values exist in the scientific literature. The above discussion is provided to elucidate some of the common pitfalls that can be encountered in the creation and critical evaluation of such compilations. One key feature of the experimental data collection in *TDE-SOURCE* is that enthalpies of combustion for halogen and sulfur-containing compounds are not included (or are assigned very large uncertainties), if they were obtained prior to the advent of the rotating bomb calorimeter. When possible, the experimental enthalpies (preferably in units of energy per mass of compound combusted) for the well-defined combustion reactions (e.g., eqs 6 through 10) serve as the bases for the "experimental" enthalpies of formation used within TDE. Conversion of the combustion enthalpies to the enthalpies of formation is done in a consistent manner with use of best current values for quantities such as molar masses, $\Delta_f H^\circ$ values for common products and dilution enthalpies for acid solutions. Key values used in TDE for $HF(aq)$ were reported by Johnson et al.,²³ while those for $HCl(aq)$, $HBr(aq)$, and $H_2SO_4(aq)$ are those compiled by Glushko et al.²⁴ These values are fully consistent with the recommended CODATA key values of 1989.²⁰

Prior to the release of TDE 4.0, an extensive data collection and validation project was implemented for enthalpies of combustion reported in the literature. *TDE-SOURCE* currently contains such values for ~4000 reactions. Generally, enthalpies of formation are derived in the evaluation process by TDE. Some authors report only the derived $\Delta_f H^\circ$ and not the measured enthalpy of the combustion reaction. In these cases, the reported $\Delta_f H^\circ$ values are stored in *TDE-SOURCE* but only if the formation reaction is well-defined.

Prediction Methods for Enthalpies of Formation. It is clear that 4 000 compounds is a very small number in comparison to the infinite variety of organic compounds that

can be synthesized or imagined. A Benson-type second-order group-contribution method²⁵ is used in TDE to generate predicted enthalpies of formation for validation of experimental data and to provide values when experimental data are not available. The original formulation by Benson has been revised and extended.^{26,27} The original gauche interaction parameters²⁷ were replaced by Roganov et al.²⁸ with the parameters for 1,4 and 1,5 interactions. This replacement facilitates automated processing of molecular structures and yields results equivalent to those of the original approach.²⁷ Benson-type group parameters have been reported and revised by many researchers, resulting in considerable confusion in the literature. The definition of all chemical groups and numerical group values for all estimations made by TDE are included in the text output of the software. At this time, computational methods (i.e., ab initio and semiempirical methods; cf. methods described in the NIST Computational Chemistry Comparison and Benchmark Database²⁹) for prediction of enthalpies of formation are not implemented in TDE. These will be included in the future, once issues associated with reliable assignment of uncertainties are resolved.

Algorithm for Evaluation of $\Delta_f H^\circ$ with TDE. The procedures for the evaluation of $\Delta_f H^\circ$ for compounds containing C, H, N, and O were described in the previous article of this series.³ Extension of these procedures to include S-containing and halogenated compounds involves appropriate accounting for the enthalpies of dilution and formation for the product acid solution noted above. Otherwise, the general algorithm shown in Figure 15 of ref 3 remains the method used in TDE 4.0.

5. STANDARD ENTROPIES FOR REACTION PROPERTY CALCULATIONS

Experimental Origins of S° for Organic Compounds.

There are two common methods for the determination of standard entropies for organic compounds: statistical calculation of ideal-gas properties with assigned wavenumber values combined with structural parameters and barriers to internal molecular rotations,³⁰ and appropriate integration of heat capacities measured with adiabatic calorimetry for the stable condensed phases from near $T \rightarrow 0$ K to the temperature of interest.³¹ Each approach has strengths and weaknesses, as described below, and both are used in TDE 4.0.

Entropies for the ideal-gas state of a molecule can be calculated statistically with very small uncertainties ($u < 0.001 \times S^\circ$), particularly for small, rigid molecules, such as benzene, pyridine, quinoline, and their methyl-substituted derivatives (see ref 32 and refs therein). For the majority of molecules that are gases at room temperature and pressure, statistical calculation of the standard entropies is also the most reliable method. Uncertainties in such calculations increase rapidly for larger molecules due to problems associated with errors in vibrational assignments, quantification, and modeling of barriers to internal rotation, appropriate representation of moments of inertia for the overall molecule and in reduced moments of rotors, anharmonic vibrations, rotational–vibrational interactions, etc. TDE 4.0 includes a static database of calculated entropies for the ideal-gas state of ~2 500 compounds based on reliable evaluations by experts in the field.^{10,30} At present, all values in this database

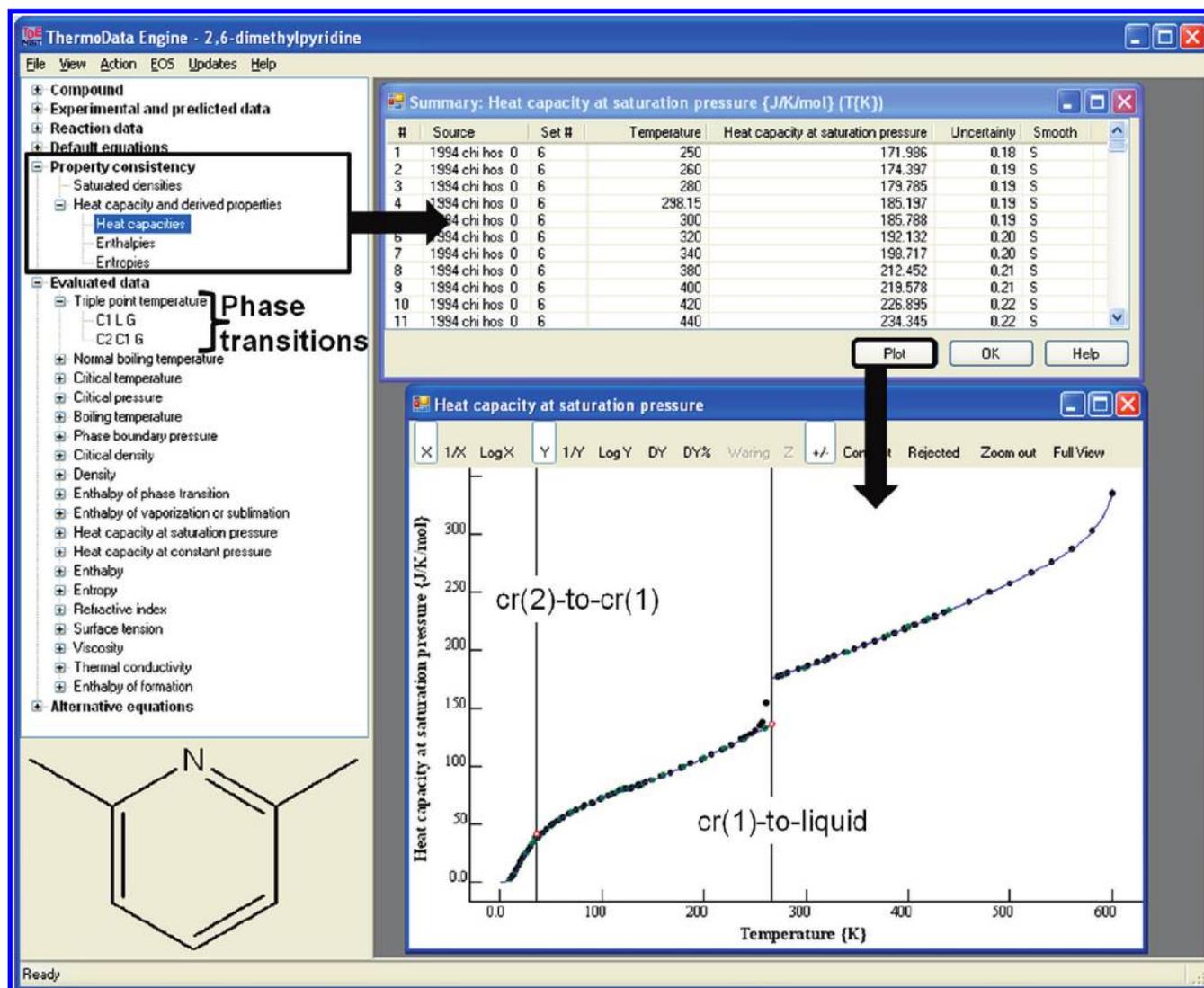


Figure 1. Plots of heat capacities (and derived integrated functions) that show the overall phase structure for pure compounds are available through the property consistency node on the navigation tree.

(heat capacities and derived enthalpies and standard entropies for the ideal-gas state) are assigned a standard uncertainty $u = 0.01 \times \theta$, where θ is the property value. Further refinement of these uncertainties is planned based on the computational uncertainty associated with each molecule. A first step in this refinement could be the assessment of each molecule for the presence of the problems noted above (anharmonic vibrations, hindered rotors, etc.) with some estimate of uncertainty associated with each. Quantification of uncertainties for ideal-gas entropies calculated with the methods of computational chemistry is a field in its infancy; however, progress has been made for rigid aromatic systems.^{32,33}

Entropies for condensed phases based upon measured heat capacities C_p from near $T \rightarrow 0$ K to temperature T , where T is typically near room temperature or moderately higher, first appeared in the literature in the 1920s, and such work continues today.³⁴ The relevant equation is

$$S^\circ(T) = \int (C_p/T)dT + \sum \Delta H_{\text{trs}}/T_{\text{trs}} \quad (11)$$

where the integration is over the temperature range for each stable phase, starting at $T \rightarrow 0$ K, and the summation is over all phase transitions with temperatures $T_{\text{trs}} \leq T$. Measurements must extend to $T < 20$ K to allow reliable extrapolation

of the measured heat capacities to $T \rightarrow 0$ K. In some early work, extrapolations from as high as $T = 90$ K were reported; however, these extrapolations are very unreliable, and such values are not included in *TDE-SOURCE*. In order to obtain valid entropies for the condensed phases, a sample must be cooled from room temperature to near $T \rightarrow 0$ K with complete conversion to the stable phase for all intervening phase transformations. Such conversions can be difficult to achieve for some compounds. For example, 1,1'-bicyclohexyl was shown to exhibit three phase transitions involving stable phases and two involving metastable phases, all within a range of only ~ 20 K.³⁵ Furthermore, there is no absolute method to determine that full conversion has been achieved. Close consistency between entropies derived based on the calorimetric measurements with those based on statistical calculations and on assigned spectra (i.e., agreement within $0.002 \times S^\circ$ for the ideal-gas state) is good evidence that complete transformations have been achieved, but this type of analysis is possible for very few (~ 100) molecules. (See ref 36 and refs therein for examples.) An additional problem is the possible presence of metastable phases and glassy crystals that have "frozen in" disorder. If these problems occur, then the derived standard entropies will be low by an indeterminate amount relative to a true value. The above

discussion is provided to show that considerable care is necessary in the experimental determination and the critical evaluation of such measurements.

Standard Entropy S° Values in TDE-SOURCE. Heat capacities in the regions of phase transitions and in other anomalies are often affected by premelting and other effects. During traditional data processing (i.e., as commonly reported with experimental results in the literature), the observed heat capacities are split into an idealized pure-phase heat capacities and an excess contributing to the enthalpy of a phase transition(s). This splitting is nontrivial and can be based on an estimated background or “lattice” heat capacity or derived with a particular thermodynamic model, such as those for fractional melting involving solid-insoluble³⁷ or solid-soluble³⁸ impurities. Smoothed heat capacities and enthalpies of phase transitions resulting from such processing must also be consistent with measured enthalpy increments spanning the temperature region of the phase transformation(s). Because of these complexities, heat capacities of condensed phases are preprocessed by experts and stored in TDE-SOURCE as smoothed data sets, together with smoothed derived standard entropies S° . TDE-SOURCE contains entropies derived from low-temperature heat capacity studies for the condensed states for ~ 700 individual compounds. In total, including duplicate studies for a particular compound, there are $\sim 1\,650$ such studies represented in TDE-SOURCE. Each literature source was reviewed by experts at NIST, and standard uncertainties u were assigned to the properties θ (heat capacities and standard entropies) in the range of $0.0005 \times \theta$ to $0.05 \times \theta$ based on the assessed quality of the work.

Property representations (equations and plots) in TDE are done for each phase or phase boundary (such as values on the liquid–gas saturation line). In order to provide the user with easy visualization of the phase structure for the condensed phases, a new plotting feature was added to the TDE interface. Once evaluation for a pure compound is complete, plots of heat capacities (and the derived integrated functions) that show the overall phase structure are available through the property consistency node on the navigation tree, as shown in Figure 1. The evaluated temperatures of the phase transitions T_{trs} (i.e., the triple-point temperatures) are available within the evaluated data node of the navigation tree. The vertical lines in the plot of heat capacity against temperature (lower right of Figure 1) represent the locations of the phase transitions. The curve represents the evaluation results by TDE, and the dots represent literature property values, both experimental and smoothed. The experimental and smoothed values are differentiated by color within the software. All numerical values can be accessed through the interface, as shown in Figure 1, and described previously.¹

Prediction Method for Standard Entropies. The prediction of standard entropies for all phases in TDE is based on the Benson group-contribution method for the ideal-gas state S° (at the temperature $T = 298.15$ K and pressure $p^\circ = 10^5$ Pa), as described by Poling et al.³⁹ This method requires molecular connectivity information to determine the groups contributing to the property. In contrast to group-contribution predictions for enthalpies of formation, predictions of the standard entropies S° also require the molecular symmetry number and the number of optical isomers. The relevant equation is

$$S^\circ(T = 298.15\text{K}) = \sum S_i(T = 298.15\text{K}) - R \times \ln(\sigma) + R \times \ln(N) \quad (12)$$

where the summation is over the i groups that represent the molecule, S_i are the individual group parameters, σ is the symmetry number, and N is the number of chiral forms. The group parameters implemented in TDE 4.0 are those listed by Poling et al.³⁹

Automated Evaluation of the Symmetry Number. An algorithm was developed to automatically determine the symmetry number of a molecule based on the molecular connectivity. This symmetry reflects all physically possible rearrangements of the atoms in the molecule, including the overall molecular symmetry and internal rotation.

Figure 2 shows the general algorithm for the calculation of the symmetry number by TDE. The approach involves use of two representations of the molecule: the *target* and *test* structures. The first step is initialization of the symmetry number (step 1, Figure 2). The atoms of the target structure are enumerated in the connectivity table, and one is selected arbitrarily for the target structure (step 2, Figure 2). The first atom of the test structure is selected (step 3, Figure 2). Selection of the first test atom is arbitrary, but each atom is considered sequentially in the overall process. A function is then called to count indistinguishable structure matches between the target and test structures (step 4, Figure 2). The function assures counting of all possible permutations resulting in matching the test and target structures, and the number of matches is added to the cumulative symmetry number (step 5, Figure 2). Physically impossible permutations, such as rotations about a double bond or an inversion of tetrahedral carbon bonds, are detected and excluded from the total count automatically. If the current test atom is the last of the test structure, then the process is complete, and the total symmetry number is returned (Steps 6 and 7, Figure 2). Chiral atoms are detected as non-ring carbon atoms with four different substituents, and appropriate adjustments are made to the symmetry number for racemic mixtures. Chiral-

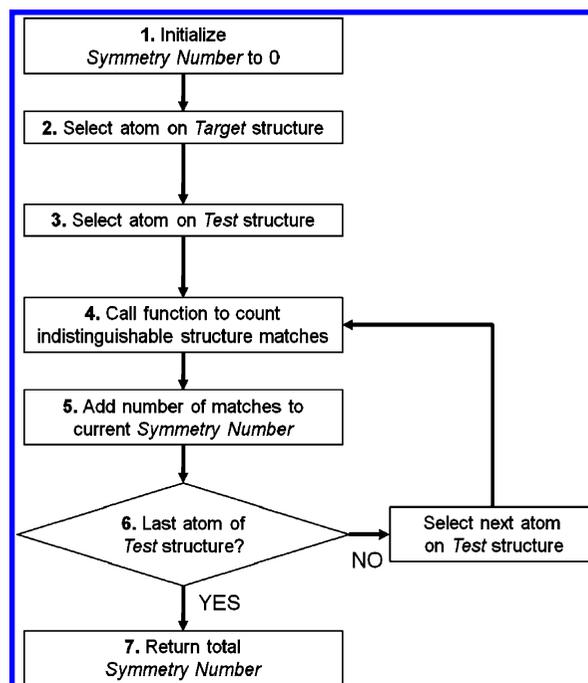


Figure 2. Steps in the general algorithm for the calculation of the symmetry number within TDE.

ity is not considered if the compound consists of only one stereoisomer.

The approach is consistent with the group parameters published by Poling et al.³⁹ Several methods for automated determination of symmetry have been published,^{40–42} however, none proved to be suitable for our needs. Limitations of these methods included the application to restricted compound types, the failure to consider internal rotations, and the need for three-dimensional structures, which would limit application to small and rigid molecules.

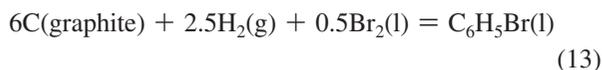
General Algorithm for Evaluation of S° with TDE. If smoothed heat-capacity data sets are available in *TDE-SOURCE* for the condensed phases, then they are selected by TDE and represented by splines. If smoothed data sets are available from multiple sources, then a preferred source is selected based on the assigned uncertainties, the temperature range, and the availability of transition enthalpies to higher temperature phases from the same source. If smoothed integrated entropies are not derived and the lowest temperature of the measurements is below $T = 20$ K, then the heat capacities are extrapolated to 0 K with a cubic function, and the standard entropy is derived based on the spline fit.

Heat capacities of the liquid are represented by an equation capable of describing the typical heat-capacity curve from the triple-point temperature T_{tp} to the critical region. The form of this equation, termed *CSExpansion* within the TDE software, is given in the Supporting Information of the first paper in this series.¹ Predicted values of liquid heat capacity are used, if necessary. In the absence of smoothed data sets, TDE fits polynomial equations to the experimental heat-capacity values with some criteria, such as the stipulation that the heat capacities increase with temperature for associating organic liquids (alcohols and carboxylic acids), and exhibits a positive second derivative of heat capacity with temperature for nonassociating liquids.

In the absence of a calorimetric basis for entropy calculation, condensed-state entropies are derived from values for the ideal-gas state, either based on the molecular partition function or the predicted, together with thermodynamic parameters of vaporization (sublimation), obtained as described in ref 1. A series of heat-capacity equations and of enthalpies of phase transitions is then used to calculate enthalpy and entropy differences between different temperatures needed for reaction data processing. Uncertainties are evaluated based on the rules of error propagation.

6. STANDARD STATES FOR FORMATION PROPERTIES IN TDE

A formation property for a compound is defined as the property of the reaction to form the compound from its constituent elements in their standard states. For example, the formation reaction for bromobenzene at the temperature $T = 298.15$ K and pressure $p^\circ = 10^5$ Pa is



Within the range of stability for organic compounds ($0 < T/\text{K} < 1500$), the phase associated with the standard state for some elements (Br, I, and S) is not constant, resulting in discontinuities in the enthalpy and entropy of formation at the phase-transition temperatures. Heat capacities and derived

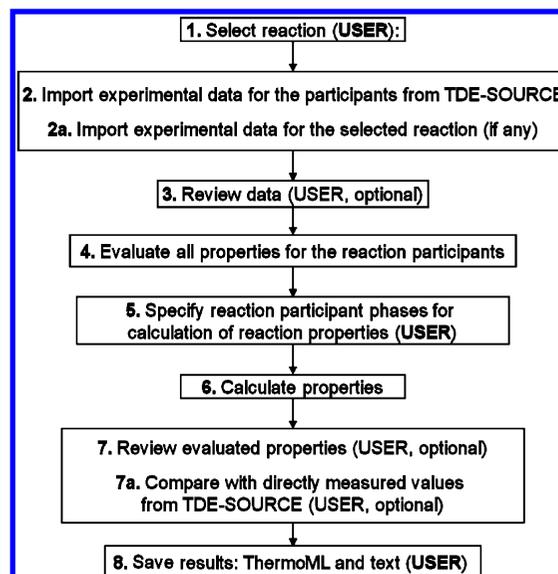


Figure 3. Steps in the evaluation of reaction properties in TDE. Actions by the user are required only for steps 1, 5, and 8.

enthalpies and entropies used in TDE for C(graphite), Br₂, I₂, and S, in their standard states, are the critically evaluated values from the NIST–JANAF *Thermochemical Tables*.⁴³ The phase sequence for the standard state of sulfur is particularly complex with four phase changes {cr(II)–cr(I), cr(I)–liquid, liquid–liquid λ transition, and liquid–gas} between $T \rightarrow 0$ K and $T = 900$ K. The standard state for H₂, N₂, O₂, F₂, and Cl₂ is the ideal gas at $p^\circ = 10^5$ Pa. Ideal-gas property values for these elements are based on published critical evaluations.³⁰ Some researchers have used S₂ in the ideal-gas state as the standard state for sulfur at all temperatures, as seen in refs 44 and 45. Such values are incompatible with those derived with TDE because of the difference in the standard states used. Verification that common standard states are used is essential when comparing formation properties from different sources.

7. ALGORITHM FOR REACTION PROPERTY EVALUATIONS WITH TDE

The essential steps in the evaluation of properties for reactions are shown in Figure 3. Step 1 is the specification of the reaction participants and stoichiometry. The participant phases are specified after the properties for each participant are evaluated. The identities and valid temperature ranges for the phases of the participants are determined by TDE during the processing, so these are known only at this later stage. The user can specify the reaction participants by any of three methods: (1) specification of each participant followed by manual or automated balancing of the stoichiometric coefficients, (2) specification of a single compound followed by automated completion of the formation reaction, and (3) specification of one or more reaction participants followed by selection from a list of reactions involving those participants for which data exist in *TDE-SOURCE*. Methods for selection of any pure compound within TDE, including drawing of two-dimensional structures, were described previously.^{1,2} A completed *reaction selection* form is shown in Figure 4. The buttons labeled *list reactions with data* and *auto-complete (formation)* are used for selection of specific reactions, as described above. The lower portion of the figure

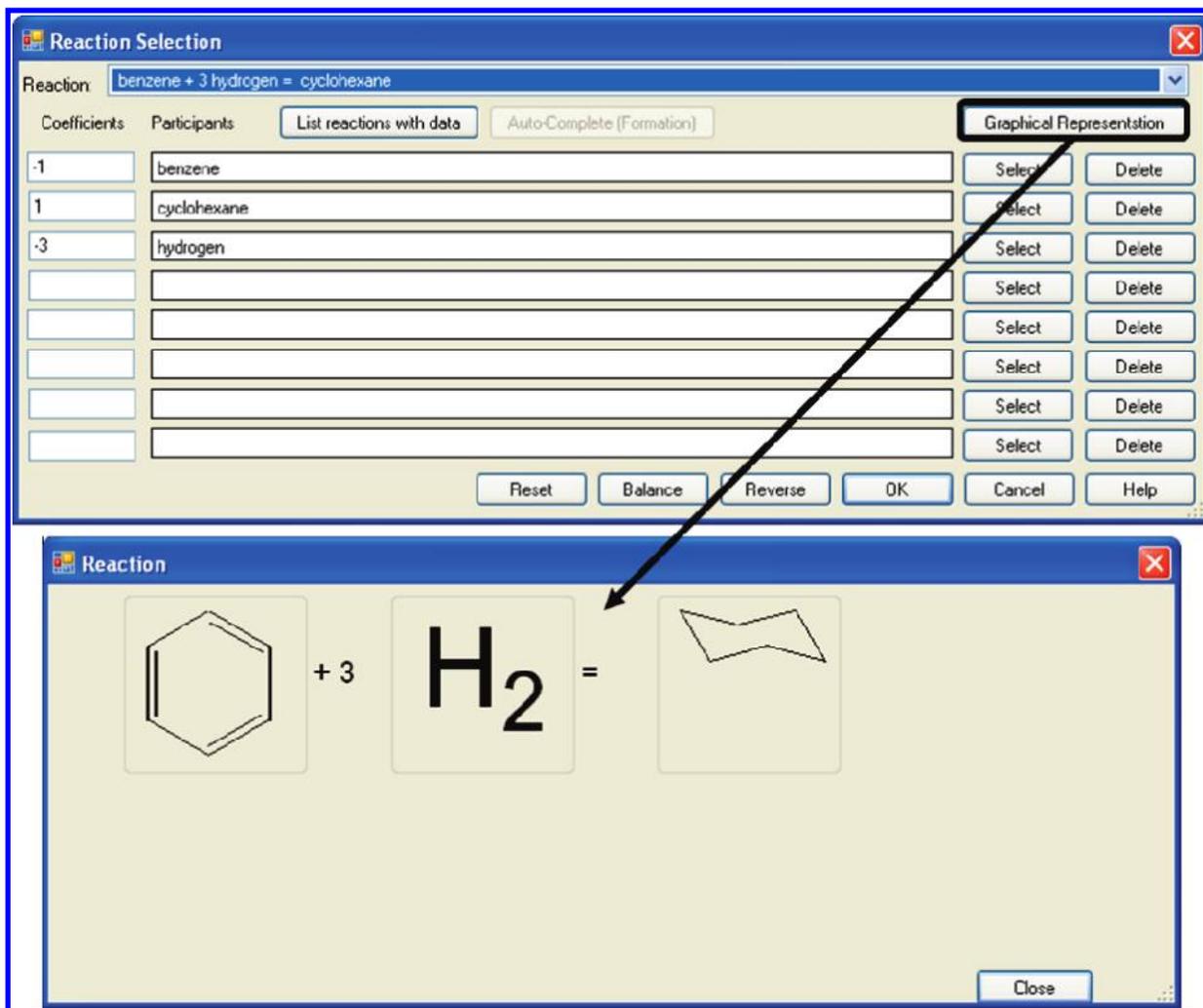


Figure 4. A completed reaction selection form in TDE (upper form), and a two-dimensional graphical representation of the reaction (lower form).

shows a graphical representation of the reaction, which can be accessed by the user through the button shown in the upper right of the form (Figure 4).

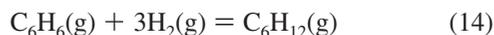
Once the reaction is specified, the software imports the experimental data for the participants, plus any directly measured experimental data for the reaction available in *TDE-SOURCE* (step 2, Figure 3). The user can review the available data and make manual additions and rejections (if desired), including addition of proprietary data for any property, as described earlier (step 3, Figure 3).¹ Next, TDE dynamically evaluates the properties of the reaction participants, including evaluation of the enthalpy of formation for each participant at the temperature $T = 298.15$ K (step 4, Figure 3). This is a conventional pure-component evaluation, as described earlier,^{1,2} with the exception of 70 compounds for which high-precision EOS are available from the NIST REFPROP Database.⁴⁶ These 70 compounds include common gaseous elements, such as oxygen, hydrogen, and nitrogen, as well as many common organics, such as methane, ethane, and benzene. The full list of 70 compounds is provided with the software. The REFPROP EOS are used for evaluation of all properties involving the liquid and gas, and the remaining properties (solid-state properties and absolute entropies) are evaluated by TDE. A similar procedure was described for components of mixtures³ and is used

to reduce the overall computation period for a particular reaction or mixture.

Immediately following the completion of the pure-component evaluations by TDE, the user is prompted to provide phase designations for the participants (step 5, Figure 3). The selected phases for calculation of reaction properties form is shown in Figure 5. Only phases for which the pure-component properties have been evaluated are provided in the list of choices, as shown in the figure for elemental hydrogen (Figure 5, upper). A completed form is shown in the lower portion of Figure 5. Next, TDE calculates the reaction properties (enthalpy, entropy, Gibbs energy, and thermodynamic equilibrium constant) for the temperature range of overlap for the selected phase combination (step 6, Figure 3). The user can review and plot the evaluated property values with access provided through the navigation tree, as shown in Figure 6. Many other features of the navigation tree were described in earlier articles on TDE.¹⁻³

Comparisons of TDE Evaluations with Literature Reaction Properties. If directly measured enthalpies or thermodynamic equilibrium constants are available in *TDE-SOURCE* for the selected reaction, then TDE provides a mechanism for comparisons with the critically evaluated values based on the reaction participant properties (step 7a, Figure 3). The comparisons can be explored through the TDE

navigation-tree node labeled consistency with participants, as shown in Figures 7 (enthalpy of reaction) and 8 (thermodynamic equilibrium constant). The particular examples chosen are for the hydrogenation of benzene to form cyclohexane with all participants in the ideal-gas state:



A key principle in the development of TDE is that all information is provided with full traceability to its source. In accord with this, the bibliographic information for the literature values is provided. Details of the access mechanism were published previously.¹

The final step in the evaluation process involves the saving of results in ThermoML⁴⁷ or in text (Step 8, Figure 3) formats. A mechanism is provided for the user to append comments that are stored with the text output.

Uncertainty Evaluations for Reaction Properties. Another key principle in the development of TDE is that the uncertainty (specifically, the combined expanded uncertainty with a level of confidence of 95%) is estimated for all evaluated properties. Uncertainties for reaction properties are derived from those of the participants based on the rules of error propagation. For the enthalpies of reaction $\Delta_r H$ and entropies of reaction $\Delta_r S$:

$$U_P = \left(\sum c_i^2 \times U_{P_i}^2 \right)^{0.5} \quad (15)$$

where U_P is the combined expanded uncertainty (with coverage factor $k \approx 2$) of the reaction property ($\Delta_r H$ or $\Delta_r S$), U_{P_i} represents the analogous values for the participant properties (enthalpies of formation $\Delta_f H$ or absolute entropies S°), and c_i is the stoichiometric coefficients for the reaction and the summation is taken over all reaction participants i . The uncertainty in temperature T is very small in comparison to that of the properties and, therefore, is not considered in the analysis.

The uncertainty U_G for the Gibbs energies of reaction $\Delta_r G$ at temperature T is

$$U_G = \{U_H^2 + (T \times U_S)^2\}^{0.5} \quad (16)$$

where U_H and U_S represent uncertainties of reaction enthalpies and entropies, respectively. Finally, the uncertainty for the thermodynamic equilibrium constant K is expressed in terms of its natural logarithm through the thermodynamic relationship:

$$U_{\ln(K)} = U_G / (R \times T) \quad (17)$$

Highly Polar Compounds. Properties for the gas phase of compounds that are well-known to dimerize (hydrogen

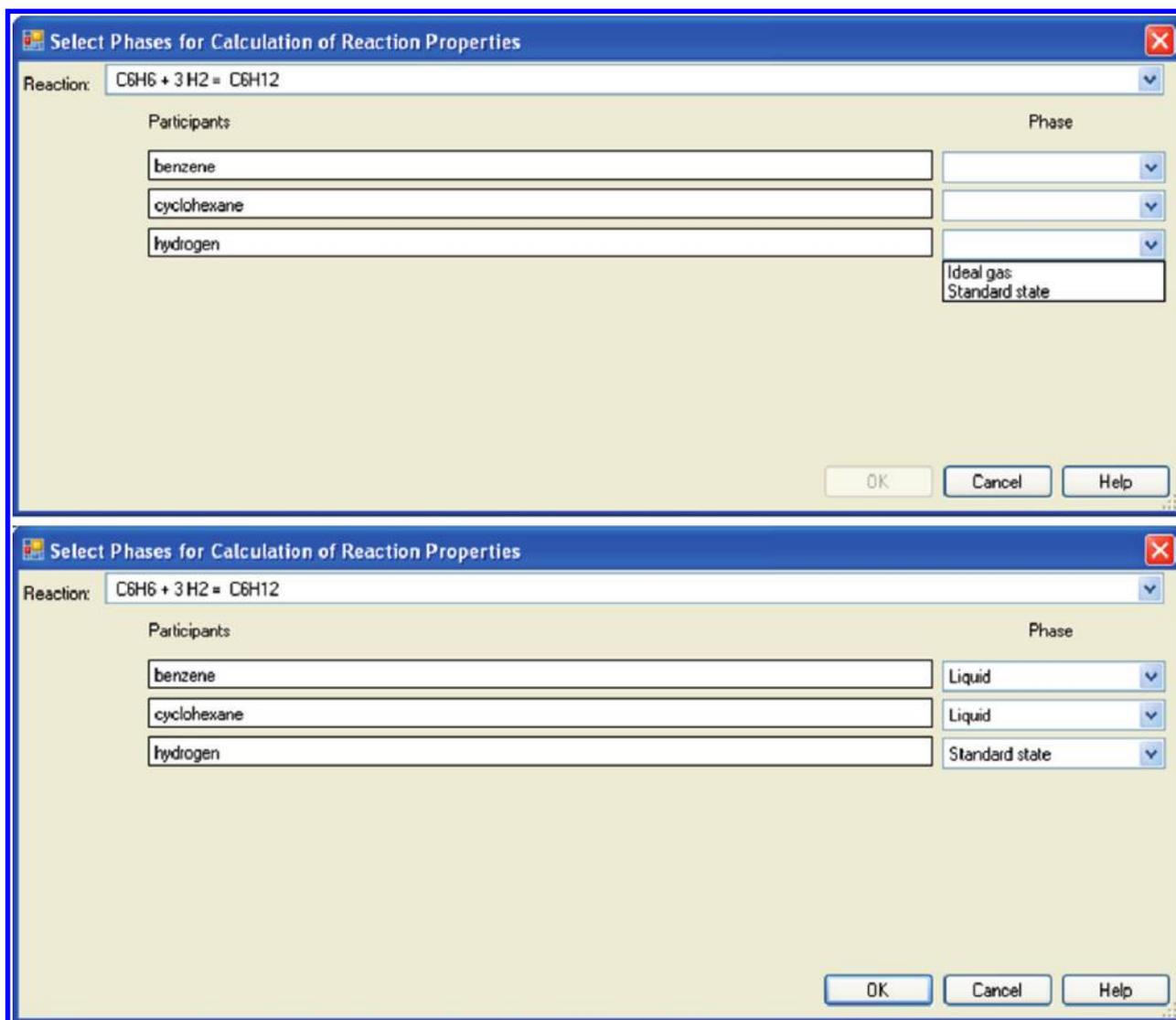


Figure 5. The select phases for calculation of reaction properties form in TDE.

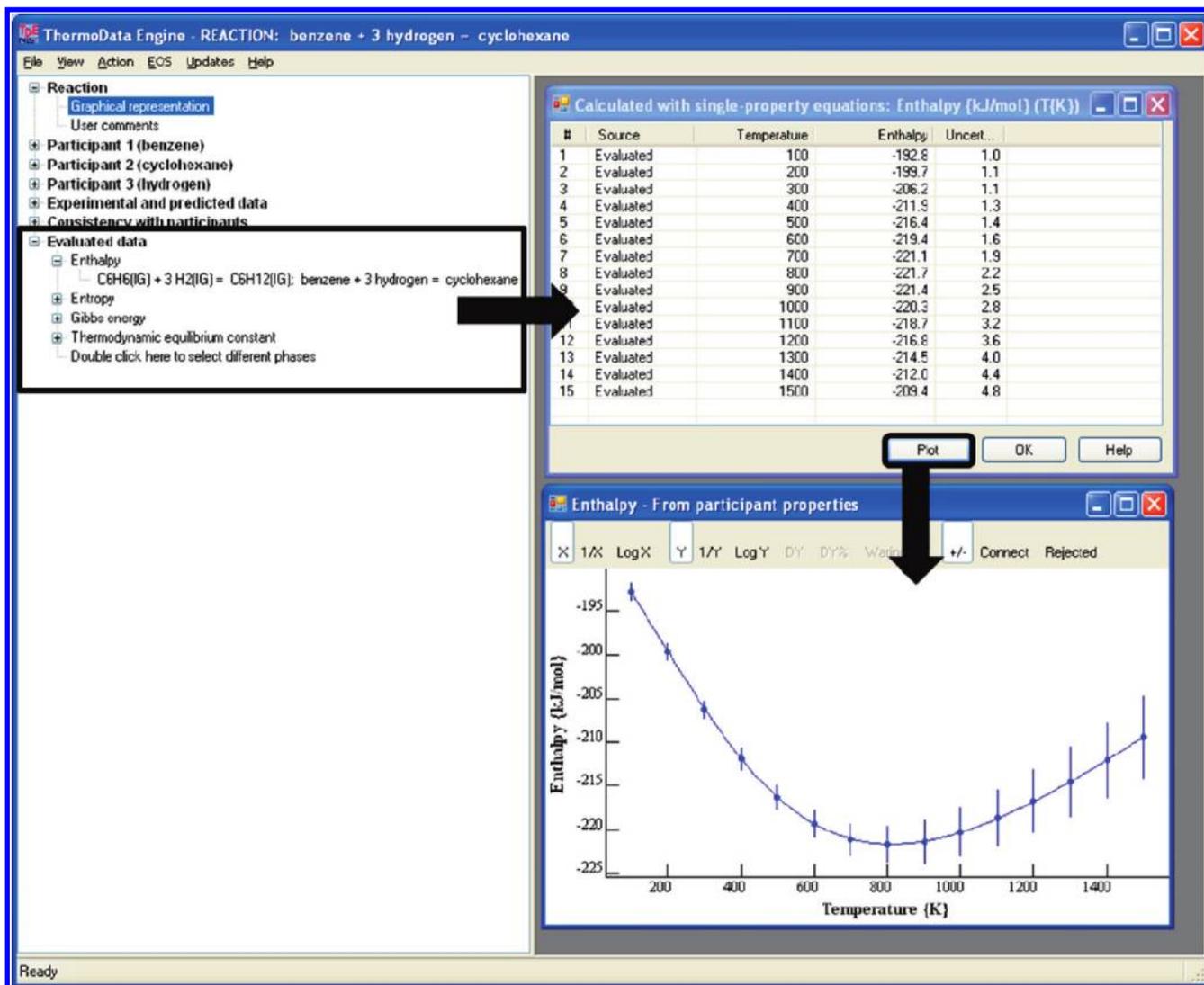


Figure 6. Access to tables and plots of results through the navigation tree in TDE.

fluoride and formic and acetic acids) are not presently considered in TDE. Implementation of special models for the gas phase is planned for future work. Alcohols and carboxylic acids are also considered to be highly associated with TDE. Equilibrium constants for the gas phase for these compounds at pressures $p > 0.1$ MPa are not considered at this time, unless they were explicitly converted to thermodynamic equilibrium constants by the authors of the original data.

8. DERIVATION OF $\Delta_f H^\circ$ AND S° FOR A PURE COMPOUND FROM REACTION DATA ($\Delta_r H^\circ$, K°)

The enthalpy of formation $\Delta_f H^\circ$ of a reaction participant can be derived from the enthalpy of reaction $\Delta_r H^\circ$, provided that the $\Delta_f H^\circ$ values for all other participants are known, either through experiment or prediction. Similarly, if values of the thermodynamic equilibrium constant K° are known for a reaction over a range of temperature, both the $\Delta_f H^\circ$ and entropy S° of a participant can be derived, provided that values for the other participants are known. The applicable thermodynamic relationship is

$$R \times \ln(K^\circ) = -\Delta_r G^\circ/T = \Delta_r S^\circ - \Delta_r H^\circ/T \quad (18)$$

where T is temperature and R is the gas constant. $\Delta_r S^\circ$ and $\Delta_r H^\circ$ can be calculated from the slope and intercept of a

plot of $R \times \ln(K^\circ)$ against $(1/T)$. More details are provided below in the discussion of the algorithm.

At the end of evaluation for a pure compound, TDE determines the availability of reaction data involving the compound (other than enthalpy of combustion, which is processed in the course of conventional evaluation) and, if available, enables evaluation for the reactions located. These evaluations require processing for all reaction participants and may take considerable time. Consequently, evaluation of the reaction data does not start automatically and must be initiated by the user. If $\Delta_f H^\circ$ and S° are not of interest to the user, then there is no need to initiate the additional data processing. The user is queried concerning evaluation of reaction properties only in cases where derived values may provide important new information, such as when no evaluation for $\Delta_f H^\circ$ or S° was possible or when either is based on prediction methods. Evaluated $\Delta_f H^\circ$ and S° values are based on the general priority sequence: direct experimental values ($\Delta_f H^\circ$ derived from combustion experiments or S° derived from low-temperature heat-capacity measurements) > derived values from reaction data using only experimental data for the other participants > predicted values for the compound using group-contribution or statistical methods > derived properties from reaction data involving

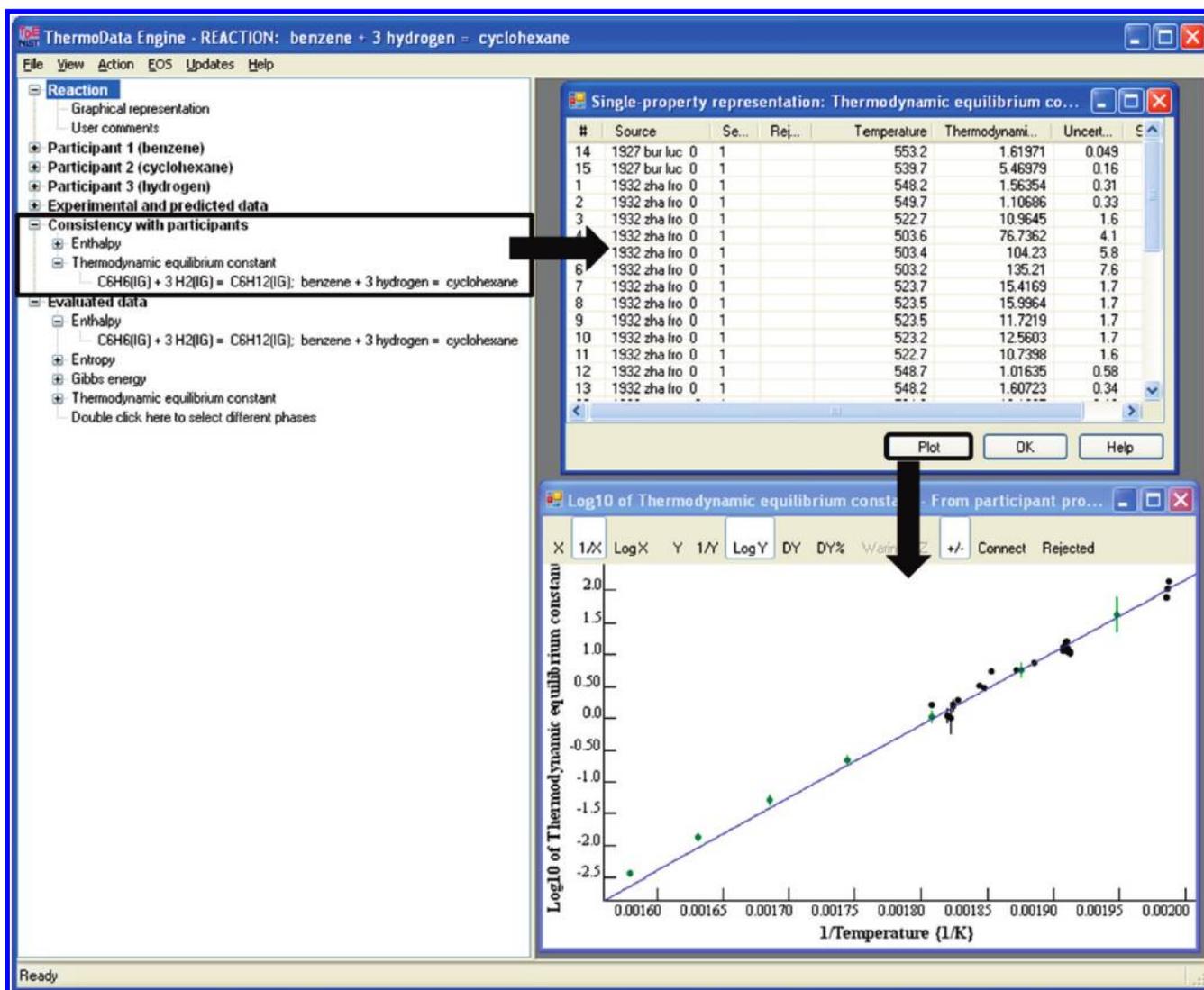


Figure 7. Comparison in TDE of evaluated thermodynamic equilibrium constants (the line in lower right graph) with literature data (dots). Literature values include experimental and smoothed data that are differentiated by color in the software.

predicted values for one or more participants. The final result in any particular case is based on the relative uncertainties for each $\Delta_f H^\circ$ and S° value.

Reaction Properties in TDE-SOURCE. Reaction properties are stored in the *TDE-SOURCE* experimental data archive in two tables: (1) state change data (generally, enthalpies and internal energies at one temperature and pressure), and (2) equilibrium data (equilibrium constants), which are often reported as functions of temperature. Two kinds of equilibrium constants are reported in the literature: (1) thermodynamic equilibrium constants K° derived from equilibrium compositions with adjustments for nonideality, and (2) apparent equilibrium constants K_x that are expressed in terms of pressures (K_p) or composition ratios (K_c) and that are calculated directly from the experimental observations. Over 8 000 distinct values of equilibrium constants for 1 400 reactions are stored in *TDE-SOURCE*. These data have been reviewed by experts and checked for consistency with experimental or predicted pure-compound data for the participants, where available.

Algorithm for Evaluation of $\Delta_f H^\circ$ and S° from Reaction Data in TDE. There are three subtasks in the derivation of pure-compound properties ($\Delta_f H^\circ$ and S°) from

reaction equilibrium data: (1) conversion, where necessary, of apparent equilibrium constants to thermodynamic equilibrium constants K° , (2) derivation of reaction enthalpies $\Delta_r H^\circ$ and entropies $\Delta_r S^\circ$ from the temperature dependence of K° values, and (3) derivation of $\Delta_f H^\circ$ and S° for the target compound from the $\Delta_r H^\circ$ and $\Delta_r S^\circ$ values. At this time, no adjustments for nonideality are made in TDE. Instead, it is assumed that $K_x = K^\circ$, except for data involving dimerized species (such as acetic acid) and most gas-phase reactions involving associating species (alcohols, acids, and primary amines) at pressures $p > 100$ kPa. These reaction types are excluded from consideration, unless the authors of the study explicitly demonstrated the equivalence of K_x and K° . K_x values for simple isomerization reactions are assumed equal to K° . Reactions involving associating species are considered only if the total number of associating sites ($-\text{OH}$, $-\text{OOH}$, and $-\text{NH}_2$) for the reactants and the products is the same. Apparent equilibrium constants are converted to thermodynamic constants based on the pure-compound standard states; pure crystal, pure liquid, and ideal gas at the standard pressure $p^\circ = 10^5$ Pa. An uncertainty contribution of 10% from each participant is added within TDE to compensate for the assumption that $K_x = K^\circ$.

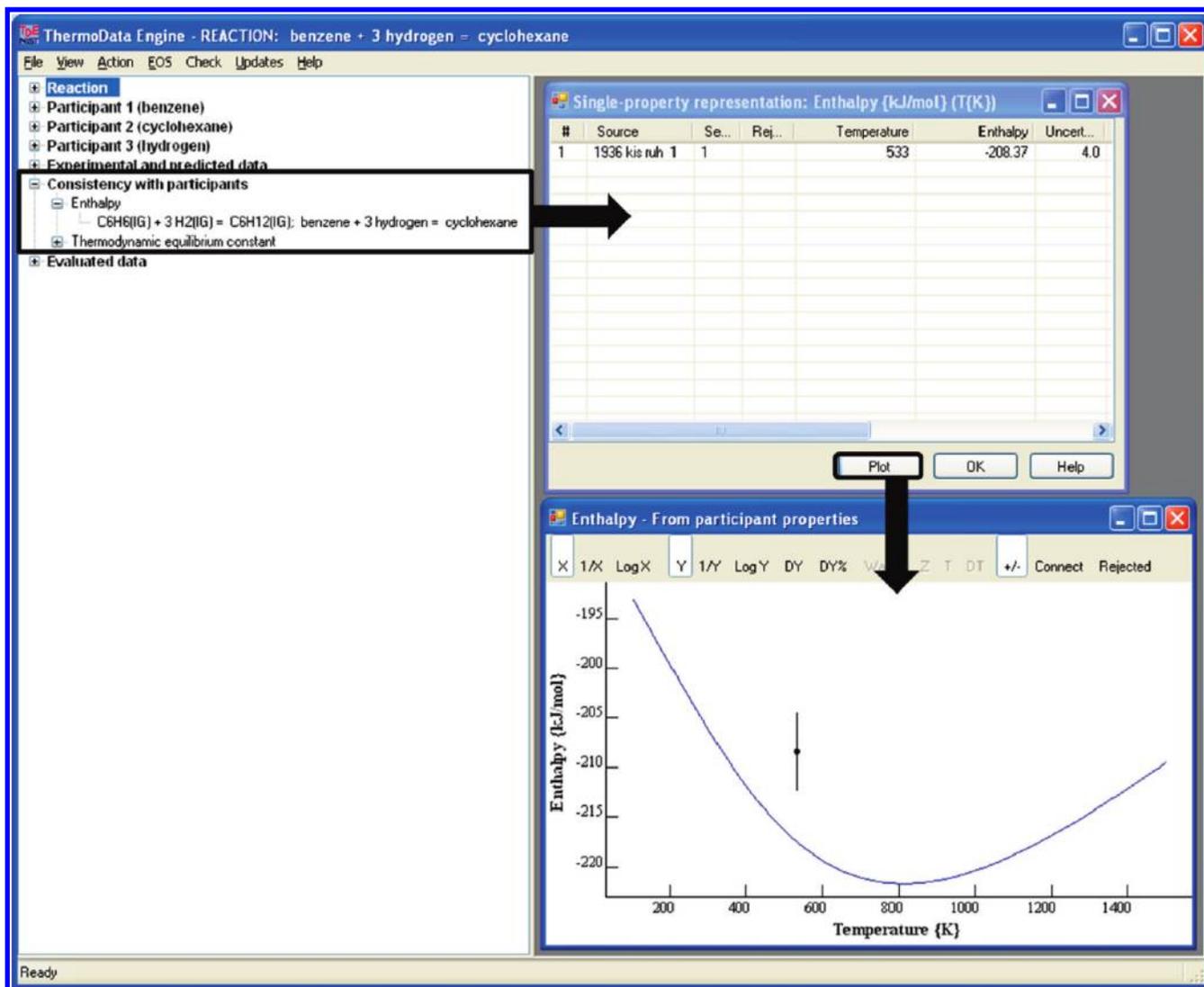


Figure 8. Comparison in TDE of evaluated enthalpy of reaction (the line in the lower right figure) with directly determined literature values. Here, a single literature value is shown with uncertainties.

The temperature dependence of the equilibrium constant is fitted by the equation:

$$R \times \ln(K^\circ) = A - B/T \quad (19)$$

where T is temperature, R is the gas constant, and A and B are equation parameters. Uncertainties for the parameters are derived from the covariance matrix, as described previously.¹ Equations involving more terms were tested and were shown to not improve the quality of the results. The derived enthalpy and entropy of the reaction ($\Delta_r H^\circ = B$ and $\Delta_r S^\circ = A$) are associated with the midpoint temperature $\langle T \rangle$ of the equilibrium constant measurements. Properties of one participant i are derived with the following equations:

$$\Delta_r H^\circ(\langle T \rangle) = \{ \Delta_r H^\circ(\langle T \rangle) - \sum c_j \times \Delta_r H^\circ(\langle T \rangle) \} / c_i \quad (20)$$

and

$$S^\circ(\langle T \rangle) = \{ \Delta_r S^\circ(\langle T \rangle) - \sum c_j \times S^\circ(\langle T \rangle) \} / c_i \quad (21)$$

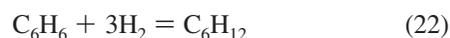
where the summations are over all participants other than participant i . Finally, the derived values of $\Delta_r H^\circ(\langle T \rangle)$ and

$S^\circ(\langle T \rangle)$ are adjusted to $T = 298.15$ K based on heat capacities and on enthalpies of phase transitions between $\langle T \rangle$ and $T = 298.15$ K that are evaluated by TDE.

Interface Features for Evaluation of $\Delta_r H^\circ$ and S° from Reaction Data. The only addition to the TDE interface for derivation of pure-compound properties from reaction data is a menu command to start the evaluation of reaction data. Reaction data and properties derived from reaction data are supported by the navigation tree together with all other properties for pure compounds.

9. SOFTWARE ARCHITECTURE

The previous articles in this series described pure-compound^{1,2} and binary-mixture objects.³ In the present paper, a third object is added: the chemical reaction. A chemical reaction object is defined within TDE by its reaction participants and its stoichiometric coefficients, for example, for the hydrogenation of benzene to form cyclohexane:



In addition, in order to define any reaction property, phases must be specified for each participant. In order to evaluate

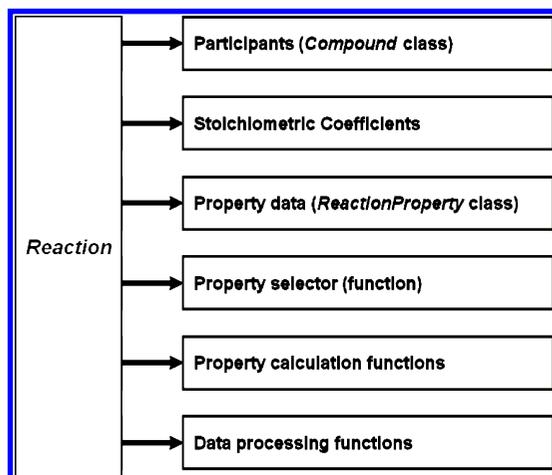


Figure 9. Architecture of the reaction class in TDE.

reaction properties, TDE makes use of numerous properties associated with the reaction participants (pure compounds). These requirements dictate the architecture of the reaction class (Figure 9), which contains the following: identification of the reaction (participants and stoichiometric coefficients), reaction property data (property data), all information about the participants (an instance of compound class for each participant), a function to recognize supported reaction properties (property selector), functions to calculate reaction property values at specified conditions, i.e., for specified temperatures and participant phases (property calculation functions), and evaluation of the participant properties that are the basis for calculation of reaction properties (data processing functions). Property data are supported by the reaction property class (Figure 9), which is an object that contains definitions of the property metadata and the numerical values of state variables, properties, and uncertainties. Metadata are phases for the reaction participants and definitions of the independent variables (temperature, composition, etc.). Reaction properties supported are the standard enthalpy, entropy, and Gibbs energy and the thermodynamic equilibrium constant.

10. OTHER NEW FUNCTIONALITIES IN TDE

Earlier versions of TDE (beginning with version 2)² included a static database of heat-capacity functions for the ideal-gas state based on statistical calculations, using assigned wavenumber values combined with structural parameters and barriers to internal molecular rotations.³⁰ In TDE 4.0, this database is expanded to include the integrated functions, the enthalpy, and the standard entropy.

Prior to TDE 4.0, all prediction methods used in TDE were based on a group-contribution and a corresponding-states method or a combination of both types.^{1–3} The quantitative structure–property relationship (QSPR) method is implemented for the first time in TDE 4.0 for prediction of critical temperature T_c and critical pressure p_c (with estimated uncertainties) for pure compounds based on three-dimensional molecular structure analyses. Critical temperatures used in the development of the QSPR method were based entirely on available direct measurements of this property; critical pressures were obtained from Wagner equation fits to all available vapor-pressure data, including direct measurements of the critical pressure. In performing the evaluations, the methods of robust regression

were used to eliminate the erroneous data. The resulting data set contained over 850 compounds. The obtained results indicate that the new correlations are competitive with the group-contribution methods implemented previously, both in terms of accuracy and scope of compound types. Details of the development of this QSPR method for T_c and p_c will be published separately.⁴⁸

11. CONCLUSIONS AND FUTURE DEVELOPMENT

The software framework of NIST ThermoData Engine (TDE) for the implementation of the dynamic data evaluation concept has been further expanded to provide capabilities for on-demand critical evaluation of thermochemical properties of chemical reactions. The application of QSPR methods based on three-dimensional molecular structures was incorporated in TDE for critical pressure and critical temperature predictions.

Plans for future development consist of deployment of the TDE framework for on-demand product design and strategic measurement planning as well as broadening the scope for binary mixtures beyond the current limit of two phases. Long-term plans involve implementation of the dynamic data evaluation concept to ternary mixtures.

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