ThermoML—An XML-Based Approach for Storage and Exchange of Experimental and Critically Evaluated Thermophysical and Thermochemical Property Data. 2. Uncertainties

Robert D. Chirico,* Michael Frenkel, and Vladimir V. Diky

Thermodynamics Research Center (TRC), Physical and Chemical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305-3328

Kenneth N. Marsh

Department of Chemical and Process Engineering, University of Canterbury, Private Bag 4800, Christchurch, New Zealand

Randolph C. Wilhoit

Texas Experimental Engineering Station, Texas A&M University System, College Station, Texas 77843

ThermoML is an XML-based approach for storage and exchange of experimental and critically evaluated thermophysical and thermochemical property data. Extensions to the ThermoML schema for the expression of uncertainties are described. Basic principles, scope, and description of all new structural elements are discussed. Representation of upper and lower limits for property values is also addressed. ThermoML covers essentially all experimentally determined thermodynamic and transport property data (more than 120 properties) for pure compounds, multicomponent mixtures, and chemical reactions (including change-of-state and equilibrium). Properties of polymers and radicals and some properties of ionic systems are not represented at present. The present role of ThermoML in global data submission and dissemination is discussed with particular emphasis on cooperation between major journals in the field and the Thermodynamics Research Center (TRC) at the National Institute of Standards and Technology. The text of several data files illustrating the expression of uncertainties in ThermoML format for pure compounds, mixtures, and chemical reactions are provided as Supporting Information, as well as the complete updated ThermoML schema text.

Background

The basic principles, scope, and description of all structural elements of ThermoML were discussed in the first paper1 in this series. ThermoML covers essentially all experimentally determined thermodynamic and transport property data (more than 120 properties) for pure compounds, multicomponent mixtures, and chemical reactions (including change-of-state and equilibrium) with a primary focus on molecular compounds. Properties of polymers and radicals and some properties of ionic systems are not represented at present. Expansion of ThermoML to cover these systems is under development. Representation of quantities for the expression of uncertainty was not considered in the first paper because the complex issues involved require extensive discussion. Extension of the ThermoML schema to include representation of these quantities is described here. A third paper in this series is planned for description of extensions to ThermoML for the representation of critically evaluated and predicted data.

The expression of uncertainty requires clear definition of a variety of quantities and terms. Definitions and descriptions of all quantities related to the expression of uncertainty in this paper conform to the Guide to the Expression of Uncertainty in Measurement, ISO (International Organization for Standardization), October, 1993.2 These ISO recommendations were adopted with minor editorial changes as the U.S. Guide to the Expression of Uncertainty in Measurement.3 Reference 2 is commonly referred to by its abbreviation; the GUM. Reference 3 is assumed equivalent to ref 2 and is referred to as the Guide in this paper. The historical development of these recommendations beginning in 1977 is described in the Guide. The recommendations have been summarized in Guidelines for the Evaluation and Expression of Uncertainty in NIST Measurement Results,4 which is available via free download from the Internet (http://physics.nist.gov/cuu/).

The definitions given in this paper are for the convenience of the reader and are not meant to modify in any way those given in the internationally accepted guides.2,3 In this paper, application of the recommendations given in the Guide to particular aspects of experimental thermodynamic property data will be discussed, and additions to the ThermoML schema will be described fully. The present paper describes uncertainty data structures primarily in application to thermodynamic data obtained experimentally. Many of the concepts described could also be applied to predicted and critically evaluated data, which will be the principal subject of the next paper in this series. The

* Corresponding author. Phone: (303)-497-4126. Fax: (303)-497-5044. E-mail: chirico@boulder.nist.gov.

10.1021/je034088i CCC: $25.00 © 2003 American Chemical Society Published on Web 06/26/2003
Table 1. Relationships between Quantities Used for the Expression of Uncertainty in ThermoML

<table>
<thead>
<tr>
<th>state functions (measurand, Y)</th>
<th>measurement result, y</th>
<th>standard uncertainty (1σ), u</th>
<th>coverage factor, k</th>
<th>expanded uncertainty, U</th>
<th>level of confidence, L (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>variable(s), Y_v</td>
<td>y_v</td>
<td>u_v = f(y_v, v_1, v_2, v_3, ...)</td>
<td>k_v</td>
<td>U_v = u_vk_v</td>
<td>L_v = f(k_v)</td>
</tr>
<tr>
<td>constraint(s), Y_c</td>
<td>y_c</td>
<td>u_c = f(c_1, c_2, c_3, ...)</td>
<td>k_c</td>
<td>U_c = uc_k_c</td>
<td>L_c = f(k_c)</td>
</tr>
<tr>
<td>property, Y_P</td>
<td>y_P</td>
<td>u_P = f(p_1, p_2, p_3, ...)</td>
<td>k_P</td>
<td>U_P = u_pk_P</td>
<td>L_P = f(k_P)</td>
</tr>
<tr>
<td>for properties Y_P (only)</td>
<td>measurement result, y</td>
<td>combined standard uncertainty (1σ), c</td>
<td>coverage factor</td>
<td>combined expanded uncertainty</td>
<td>combined level of confidence</td>
</tr>
<tr>
<td>property, Y_P</td>
<td>y_P</td>
<td>U_comb = f(u_P, U_c, U_v)</td>
<td>k_comb</td>
<td>U_comb = U_combk_P</td>
<td>L_comb = f(K_comb)</td>
</tr>
</tbody>
</table>

a All components of uncertainty are included except those of other state functions. b For many practical situations with assumed normal distributions, a coverage factor k near 2 corresponds to a level of confidence L near 95%. c Standard uncertainties of variables and constraints are propagated to the uncertainty of the property.

The complete ThermoML schema is available on the Internet (http://www.trc.nist.gov/ThermoML.xsd).

**Basic Principles and Definitions**

All definitions of quantities related to the expression of uncertainty are quoted or closely adapted from the Guide. Table 1 shows the general mathematical relationships between the quantities used for the expression of uncertainty, which are used explicitly in ThermoML. Uncertainties are represented for each state function is shown symbolically (\( Y = f(Y_1, Y_2, Y_3, ... \)).

The particular quantity subject to measurement is the measurand. The objective of a measurement is to determine the value of the measurand \( Y \). Within ThermoML, measurands are state functions (constraints, variables, and properties), as shown in column 1 of Table 1. The value of a measurand is by definition unknowable. Consequently, the meanings of the phrases “true value of the measurand” and “value of the measurand” are the same. The result of a measurement \( y \) is an estimate of the value of the measurand \( Y \) and is complete only when accompanied by a statement of the uncertainty of that estimate. The measurement result \( y \) for each state function is shown symbolically \( (y_c, y_v, y_P) \) in column 2 of Table 1.

The Guide establishes general rules for expression of uncertainty, which are designed to be applicable to a wide variety of applications and levels of accuracy “from the shop floor to fundamental research”. Consequently, some information in the Guide is not applicable to thermodynamic property measurements, such as discussions of uncertainties associated with incomplete definition of the measurand. All measurands specified within ThermoML are fully specified through their thermodynamic definitions. The use of the GDC (Guided Data Capture) software for data capture ensures full property specification through rigorous implementation of the Gibbs phase rule. The role of ThermoML and GDC in global data submission and dissemination is described later in this paper.

The Guide distinguishes between two uses of the word uncertainty, and this same distinction is used here. The word uncertainty means doubt, and therefore, in its broadest sense uncertainty of measurement means doubt about the validity of the result of a measurement. Because of the lack of different words for this general concept of uncertainty and the specific quantities that provide quantitative measures of the concept, for example, the standard deviation, it is necessary to use the word uncertainty in these two different senses. In the present paper, as in the Guide, the word uncertainty without adjectives refers to the general concept of uncertainty and to any or all quantitative measures of that concept. When a specific measure is intended, appropriate adjectives are used.

The formal definition of uncertainty listed in the International Vocabulary of Basic and General Terms in Metrology (commonly abbreviated VIM) and used by the Guide follows.

**Uncertainty (of measurement):** a parameter, associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

**Notes:**

1. The parameter may be, for example, a standard deviation (or a given multiple of it), or a half-width of an interval having a stated level of confidence.

2. Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterized by experimental standard deviations. The other components, which can also be characterized by standard deviations, are evaluated from assumed probability distributions based on experience or other information.

3. It is understood that the result of the measurement is the best estimate of the value of the measurand, and that all components of uncertainty, including those arising from systematic effects, such as components associated with corrections and reference standards, contribute to the dispersion.

This general definition of uncertainty of measurement is not associated with a numerical value. As noted earlier, numerical uncertainties will always include modifying words, such as standard uncertainty, expanded uncertainty, combined uncertainty, and so forth. It is very important to note that this definition includes all possible contributions to its value. It is therefore clearly distinguishable from other quantities, which are commonly reported (and defined later), such as repeatability, reproducibility, or deviations from a fitted curve. Such quantities may be components of an estimated uncertainty but can provide only lower limits for the uncertainty of measurement.

A second important point is expressed in note 2 (above), which describes how all uncertainties are expressed as standard deviations. These standard deviations can be derived from probability distributions based on (1) the statistical analysis of series of observations (designated Type A) or (2) other means (designated Type B). Because the uncertainty of measurement includes all sources of uncertainty, it is probable that components of Type A and Type B will be included in an uncertainty estimate.
by scientific judgment based on all of the available information regarding the variability of the quantity considered. To clarify the meaning of a Type B estimate, the Guide lists some items that might be included in that pool of information: (i) previous measurement data, (ii) experience with or general knowledge of the behavior and properties of relevant materials and instruments, (iii) manufacturers’ specifications, (iv) data provided in calibrations and other certificates, and (v) uncertainties assigned to reference data taken from handbooks.

To base the uncertainty of measurement entirely upon Type A evaluations, it would be necessary to include numerous repetitions of all steps leading to the measurement, including procurement and purification of samples, calibration of instruments, construction and operation of instruments and apparatus, and so forth. This is clearly not practical, particularly in the field of experimental thermodynamics. Consequently, estimates of uncertainties will almost always include some, if not primarily, Type B evaluations.

A third important aspect involves application of this definition in ThermoML. In ThermoML, uncertainties are represented for all thermodynamic state functions (i.e., variables, constraints, and properties) and not just for those designated as properties. This is reflected in Table 1 in that uncertainties for all state functions are represented. For many experiments, such as phase equilibrium studies, the identification of the terms variable and property with the measured temperatures, pressures, and phase compositions is arbitrary. Similarly, for a pure component, “vapor pressure data” might be considered saturation pressures at given temperatures or boiling temperatures at given pressures. The issue of propagation of uncertainties from variables and/or constraints to the designated property is discussed separately later in this paper.

The standard uncertainty differs from the more general term uncertainty of measurement in that the value of the uncertainty is expressed as a specified number of standard deviations (i.e., one).

**Standard Uncertainty u:** Uncertainty of the result of a measurement expressed as a standard deviation. This quantity $u$ is represented in column 3 of Table 1 as an expression

$$u_x = \sigma(x_1, x_2, x_3, \ldots)$$

where the $x$ symbols represent various uncertainty components that are appropriately weighted to estimate $u_x$. For example, the estimated uncertainty for a temperature value might be a function of the method and traceability of the sensor calibration, the instrument used to read its response, estimated gradients in the apparatus, effects of thermal inertia, and so forth. A well-designed experiment will improve the quality of these estimates, but some scientific judgment is always involved.

In a broader sense, $u_x$ could be considered a combined standard uncertainty (defined later) in that it “combines” uncertainties from various sources. In ThermoML, the term combined standard uncertainty is reserved for uncertainties derived by propagation of uncertainties in variables and constraints to those for the designated property. More detail is provided below.

As noted in a footnote of Table 1, the standard uncertainties associated with state functions are defined to be independent and do not include uncertainty components associated with propagation of uncertainty from one state function to another. For example, if the density of a single-component gas (the property) is reported as a function of temperature and pressure (the variables), it is important to avoid including the effect of uncertainty in temperature upon the uncertainty in the pressure. This is to avoid overestimation (or “double counting”) of uncertainties, when they are propagated to the designated property in a subsequent step.

In Table 1, the standard uncertainty is listed independently for the variables, the constraints, and the property. The appropriateness of this type of reporting can be shown using typical results for vapor–liquid equilibrium (VLE) experiments. In the reporting of VLE results, pressures $p$, temperatures $T$, and phase-composition values $x$, $y$, and $z$ are reported. Uncertainties associated with each quantity ($p$, $T$, $x$, $y$, and $z$) are often reported independently. In the case of overdetermined systems, all the data points are separated into data sets characterized with independent variables only. Furthermore, a “property” is often not specified explicitly because the designation is arbitrary. To accommodate this type of reporting, ThermoML includes representation of standard uncertainties for the variables, the constraints, and the property. A second uncertainty (the combined uncertainty) is defined only for the property and includes propagation of uncertainties from the variables and constraints to the property. The combined uncertainty is represented separately, as shown in the bottom of Table 1. Further discussion is given below with the definition of the combined standard uncertainty.

**Expanded Uncertainty $U$:** The quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand.

1. The fraction may be viewed as the coverage probability or level of confidence of the interval.
2. To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterized by a measurement result and its standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

**Coverage Factor $k$:** Numerical factor $k$ is a multiplier of the standard uncertainty in order to obtain an expanded uncertainty.

**NOTE:** A coverage factor $k$ is typically in the range 2 to 3.

The relationship between the standard uncertainty, the coverage factor, and the expanded uncertainty for the state functions in ThermoML is shown in the upper section of Table 1.

**Expanded uncertainty $U_x$:**

$$U_x = k\cdot u_x$$

Propagation of uncertainties from the variables and constraints to the property is not included in the expanded uncertainty $U_x$.

**Combined Standard Uncertainty $u_{\text{comb}}$:**

The standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities.

In ThermoML, the combined standard uncertainty $u_{\text{comb}}$ is included only for the quantity designated as the property.
The combined coverage factor \( k_{\text{comb}} \) and the combined expanded uncertainty \( U_{\text{comb}} \), which also apply only to the designated property, are defined through the equation

\[
U_{\text{comb}} = u_{\text{comb}} k_{\text{comb}}
\]

This relationship is also shown in the lower section of Table 1.

The final important term used in the expression of uncertainty in ThermoML is the Level of Confidence \( L \), which is represented as a percentage.

**Level of Confidence \( L \):** an estimate of the probability that the measurand is within a specified range \( y \pm U \).

[Note: In the Guide, the symbol \( p \) is used for Level of Confidence (or Coverage Probability). To avoid confusion with other terms such as property or pressure, the symbol \( L \) is used here. The term confidence interval is not used because in statistics it has a specific definition, which requires that all components of the uncertainty be obtained from Type A evaluations. As noted earlier, the results of experimental thermodynamic studies will very rarely meet this criterion.] The Guide includes an extensive discussion (Annex G) of the relationship between the level of confidence and the coverage factor. There is little value in repeating that discussion here, but a summary of several useful points follows.

Examples of the well-known correspondence between \( L \) and \( k \) for a normal distribution are given in Table 2. In general, to obtain the value of the coverage factor \( k \) that produces an interval corresponding to a specified level of confidence \( L \) requires detailed knowledge of the probability distribution characterizing the measurement results. However, as noted in the Guide (section G.6.6), for many practical measurements in a broad range of fields, some general approximations can be made. These emphasize the approximate nature of the uncertainty evaluation process and the impracticality of trying to distinguish between intervals having levels of confidence that differ by only a few percent. The following recommendations are given in the Guide: (i) adopt \( k = 2 \) and assume that \( U = 2u(y) \) defines an interval having a level of confidence of approximately 95%, (ii) or for more critical applications, adopt \( k = 3 \) and assume that \( U = 3u(y) \) defines an interval having a level of confidence of approximately 99%.

These practical suggestions should be of use to many authors reporting results of studies in experimental thermodynamics. Nonetheless, the coverage factor and level of confidence are represented separately in ThermoML to allow for those conditions that define an alternative mathematical relationship. It should be emphasized that the relationship between \( L \) and \( u \), shown in Table 2 is for an assumed normal distribution, and that for other types of distributions (rectangular, triangular, etc.) other relationships are obtained.

The following series of definitions describe terms that are commonly reported in the literature as reproducibilities, repeatabilities, or deviations from a fitted curve. These uncertainty-assessment components are referred to collectively in this paper as precisions. These represent components of an uncertainty assessment but do not meet the criteria for the uncertainty of measurement, which includes all sources of uncertainty. It was decided to include some precisions in ThermoML because certain of these quantities can be well defined and may be useful to data evaluators in subsequent assessments. The International Vocabulary of Basic and General Terms in Metrology (commonly abbreviated VIM) does not give a definition for precision because of the many definitions that exist for this word. This is consistent with the usage in this paper.

**Repeatability (of results of measurements) [VIM 3.6]:** Closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement.

**NOTES**
1. These conditions are called repeatability conditions.
2. Repeatability conditions include (i) the same measurement procedure, (ii) the same observer, (iii) the same measuring instrument used under the same conditions, (iv) the same location, and (v) repetition over a short period of time.
3. Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

Because repeatability can be expressed quantitatively, is readily defined, and is commonly reported in the thermodynamic literature, this quantity is represented in ThermoML. It must be recognized clearly by the user of this information that repeatability is only one component of many that can be used in estimating the broader uncertainty of measurement.

**Reproducibility (of results of measurements) [VIM 3.7]:** Closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement.

The definition of reproducibility includes an extensive list of what might be changed, including the principle of measurement, the method of measurement, the observer, the location, the reference standard, the measuring instrument, and so forth. To implement this definition in ThermoML, an extensive list of what was and what was not varied would be required. Consequently, representation of reproducibility is not included in ThermoML.

Several representations of precisions, which are not defined in the Guide, are included in ThermoML. These are included because they are commonly reported in the literature of experimental thermodynamics.

**Root-mean-square (rms) deviation from a fitted curve (for a data set):** A description of the fitted curve is included in ThermoML in addition to the numerical root-mean-square (rms) value. The deviation is represented in ThermoML for properties only and not for variables or constraints. This quantity is associated with entire data sets and is included in the numerical values (i.e., data points). In ThermoML, the rms deviation can be expressed as an absolute or relative value (percentage).

The value for the rms deviation from a fitted curve \( \delta_{\text{rms}} \) is defined by the following equation:

\[
\delta_{\text{rms}} = \left( \frac{1}{n} \sum (x_i - \text{x_{curve}})^2 \right)^{0.5}
\]

The summation is over all data points. The symbols in the equation represent the number of data points \( n \) and the deviation \( (x_i - \text{x_{curve}}) \) of data point \( i \) from the fitted curve.

**Deviation from a fitted curve (for each data point in a data set):** Again, a description of the fitted curve is...
included in ThermoML. The numerical value of the deviation from the curve for each data point of a data set is represented. Deviations are expressed in absolute terms only because relative (percentage) values can be derived readily.

**Device Specifications:** Device specifications from manufacturers or calibration certificates are often used and reported as part of an uncertainty assessment by experimentalists. The numerical value for this uncertainty component, level of confidence, and the information source should be specified. Elements corresponding to each are present in the extensions to ThermoML described in this paper.

Again, it must be recognized clearly by the user of this information that the repeatabilities, deviations from a fitted curve, and device specifications are components in an array of information that can be used in estimating the uncertainty of measurement.

**Precision:** As noted earlier, this term has numerous conflicting meanings, and it is not expressed quantitatively in the authoritative literature. This term is not represented in ThermoML.

**Accuracy (of Measurement)** [VIM 3.5]: Closeness of agreement between the result of a measurement and the measurand. "Accuracy is a qualitative concept." Accuracy cannot be represented quantitatively and is not represented in ThermoML.

When determination of a measurand is impossible, values that represent only an upper or lower limit are reported at times in the thermodynamic literature. For example, this may be due to sample decomposition or to a limited experimental range available with a particular apparatus. Such limiting values are related indirectly to uncertainties in that the sign of the deviation from the measurand is known without an estimate of its magnitude. Limiting values are represented in ThermoML for properties only and not for constraints or variables. Details of the quantities represented are described later.

**Implementation of Uncertainty Definitions in ThermoML**

The Guide provides specific recommendations for the reporting of uncertainties (Chapter 7: Reporting Uncertainty), which are accommodated fully in ThermoML. Specifically, section 7.2.3 of the Guide lists recommendations for reporting of the expanded uncertainty $U$. The recommendations are as follows:

1. Give a full description of how the measurand $Y$ is defined.
2. State the result of the measurement as $Y = y \pm u$ and give the units of $y$ and $u$.
3. Include the relative expanded uncertainty $U/|y|$, $|y| \neq 0$, when appropriate.
4. Give the value of $k$ used to obtain $U$ [or, for the convenience of the user, give both $k$ and $u$].
5. Give the approximate level of confidence associated with the interval $y \pm U$ and state how it was determined.
6. Give the information outlined in section 7.2.7 of the Guide or refer to a published document that contains it. (Note: section 7.2.7 makes specific recommendations related to reporting of the origins of all uncertainty estimates in the document text.)

Recommendation 1 was implemented previously in ThermoML through the definition of variables, constraints, and properties based on the established laws of phenomenological thermodynamics. The extensions to ThermoML that are the focus of this paper directly address recommendations 2–5. Although not included explicitly, the relative expanded uncertainty (item 3) can be derived simply from values that are represented. Recommendation 6 involves detailed reporting suggestions that would be impractical to implement fully in ThermoML. These include listing the source of all uncertainty estimates used to estimate any standard uncertainty and providing partial derivatives or "sensitivity coefficients" related to key uncertainty components. Nonetheless, in all cases a text schema element is provided, which can be used for descriptions of the uncertainty estimation methods.

**Schema Structure.** The modular schema structure of ThermoML was described in the first paper of this series. All new schema elements described here are extensions to ThermoML and do not modify the original structure in any way. ThermoML includes separate structures for the representation of variables, constraints, and properties. It will be seen that there is a one-to-one correspondence in elements for variables, constraints, and properties for representation of the uncertainty related quantities listed in the upper section of Table 1 (standard uncertainty, coverage factor, expanded uncertainty, and level of confidence). Some structural differences arise because constraints are defined once for a data set, while variables and properties are associated with individual numerical values or "data points." Uncertainty elements for properties also include separate elements related to propagated uncertainties from the variables and constraints to the property (i.e., the combined quantities shown in the lower section of Table 1).

**Units.** By design, there is only one unit selected for each property covered by ThermoML. This unit is SI-based; however, for a number of properties the selected unit is a multiple of the SI unit to ease interpretation of numerical values. Unit tagging is explicit in a ThermoML file as part of each property name, thus minimizing the possibility of unit misinterpretation. As a natural extension to this approach, the units for the uncertainty values are the same as those of the quantity whose uncertainty is being represented. Relative uncertainties are represented as percentages. These are indicated clearly in the element names and descriptions.

**Tagging.** All tagging related to uncertainty is based upon terminology described in the Guide. The names or "tags" for the elements of the schema include special characters related to the type of information to be stored. A name beginning with "e" designates an enumeration element (i.e., values selected from a predefined list), "s" designates a string element, and "n" specifies a numerical element (integer or floating). Elements identified by dotted boxes in a figure are optional, and those in solid-lined boxes are mandatory. Within ThermoML, all elements associated with the representation of uncertainty are optional. Complex elements illustrated without their internal structure are identified by "+1." Complex elements with internal structure displayed are identified with "−1." Multiple elements of the same type are identified by lower and upper limits listed below the relevant boxes in the figures. Within ThermoML, the only limits used are "0..∞" for optional elements and "1..∞" for mandatory elements. The "Choice" symbol, which appears as a switch (first seen in Figure 6), is used to designate elements that cannot be used simultaneously.

**Extensions to the ThermoML Schema**

ThermoML consists of four major blocks, which are shown in Figure 1 together with the new element Version
[complex]. The four major blocks were described previously.\textsuperscript{1} A new element \texttt{Version [complex]} is mandatory and provides for storage of the ThermoML version number. The subelements of \texttt{Version [complex]} are \texttt{nVersion-Major [numerical, integer]} and \texttt{nVersionMinor [numerical, integer]}. For example, if the version number of ThermoML were 2.1, the “major” element would store the value “2” and the “minor” element would store the value “1”.

The general locations of extensions described in this paper are indicated in Figure 1. Detailed schema figures (Figures 2–10) and the text of ThermoML were created with the software package XML SPY.\textsuperscript{7} (The trade name is provided only to specify the procedure adequately and does not imply endorsement by the National Institute of Standards and Technology. Similar products by other manufacturers may be found to work as well or better.) The four
major blocks are as follows:

1. Citation (description of the source of the data).
2. Compound (characterization of the chemical system).
   The description for every compound is linked to a description of the sample used in the measurements with indication of its initial purity, purification methods used, final purity, and the method used to determine it.
3. PureOrMixtureData (metadata and numerical data for a pure compound or multicomponent mixture).
4. ReactionData (metadata and numerical data for a chemical reaction with a change of state or in chemical equilibrium).

The extensions described in this paper are primarily in blocks 3 and 4, and they are associated with the numerical
values for the variables, constraints, and properties, as shown in Figure 1. Numerical values of uncertainty are not provided for compound purities (block 2), but an extension to allow specification of the number of digits is now added. The number of digits specified should correspond approximately to the number of significant digits, but there is no strict requirement for this correspondence. A comprehensive uncertainty-specification scheme for purities would add unjustifiable complexity to the schema.

The following sections describe details of the additions made to ThermoML for representation of uncertainties for state functions (variables, constraints, and properties). Many of the new schema elements for constraints, variables, and properties have common definitions. To avoid unnecessary repetition of definitions, the following discussion is separated into two sections. The first involves definitions for constraints, variables, and properties, and the second involves their precision location in the schema structure. All of the definitions apply to results for pure components, mixtures, and reactions. The elements for the representation of uncertainty are the same for blocks 3 and 4 (PureOrMixtureData and ReactionData). Extensions to ThermoML for the representation of uncertainties in blocks 3 and 4 differ only in terms of location.

### Definition and Structure of New Schema Elements

New schema elements are summarized in Tables 3 and 4. Table 3 lists all elements associated with the specification of defined uncertainties, while Table 4 lists all elements associated with the specification of defined precisions. This separation is done to emphasize the conceptual difference between these two types of quantities. Column 1 in Tables 3 and 4 indicates the element name used in ThermoML. Column 2 clarifies the meaning of the abbreviations used in column 1. Column 3 specifies the type of measurand to which the names apply. Columns 4 and 5 specify the general location of the element in the ThermoML schema terms of whether the element is associated with a “data set” or with each “data point.” In the following sections, each element is defined and some specific guidance related to its usage is given.

### ThermoML Elements for the Expression of Uncertainties

The elements listed in Table 3 are separated into those for representation of defined uncertainties, which are given for variables, constraints, and properties, and those for combined uncertainties, which are given for properties only. Elements for representation of the defined uncertainties are addressed first.

#### *Uncertainty [complex]*

This complex element includes the subelements associated with expression of the expanded uncertainty values \( U_x \) for variables, constraints, and properties. The symbol \( * \) indicates that this element is present in the schema for variables \((* = \text{Var})\), constraints \((* = \text{Constr})\), and properties \((* = \text{Prop})\). The subelements of *Uncertainty [complex] are described in the following paragraphs.

- **nUncertAssessNum [numerical, integer]**; the uncertainty assessment number
- **sUncertEvaluator [string]**; the uncertainty evaluator
- **nStdUncertValue [numerical, floating]**; standard uncertainty value \( u_x \)
- **AsymStdUncert [complex]**
  - **nUncertLevOfConfid [numerical, floating]**; level of confidence (%)
- **nCombStdUncertValue [numerical, floating]**; combined standard uncertainty value \( u_{comb} \)
- **AsymCombUncert [complex]**
  - **nCoverageFactor [numerical, floating]**; coverage factor \( k_{cov} \) to obtain \( U_x = k_{cov} u_x \)
- **sCombUncertEvalMethod [string]**; combined uncertainty evaluation method
- **nCombUncertLevOfConfid [numerical, floating]**; level of confidence (%) associated with \( U_{comb} \)
- **nUncertLevOfConfid [numerical, floating]**; level of confidence (%)
- **nCombUncertValue [numerical, floating]**; combined expanded uncertainty value \( U_{comb} \)
- **AsymCombUncert [complex]**
  - **nCoverageFactor [numerical, floating]**; coverage factor \( k_{cov} \) to obtain \( U_{comb} = k_{cov} U_{comb} \)
- **sCombUncertEvalMethod [string]**; combined uncertainty evaluation method
- **nStdUncertValue [numerical, floating]**; standard uncertainty value \( u_x \)
- **AsymStdUncert [complex]**
  - **nCoverageFactor [numerical, floating]**; coverage factor \( k_{cov} \) to obtain \( U_x = k_{cov} u_x \)
- **sStdUncertEvalMethod [string]**; standard uncertainty evaluation method
- **nUncertLevOfConfid [numerical, floating]**; level of confidence (%)
- **nUncertValue [numerical, floating]**; standard uncertainty value \( u_x \)
- **AsymUncert [complex]**
  - **nUncertLevOfConfid [numerical, floating]**; level of confidence (%)
- **nUncert [numerical, floating]**; standard uncertainty value \( u_x \)
- **AsymUncert [complex]**
sources of key information. In this way, this element can be used to accommodate item number 6 of the recom-

Table 4. Names and Locations of ThermoML Elements for the Expression of Precisions

<table>
<thead>
<tr>
<th>abbreviated element name</th>
<th>full element name</th>
<th>measurand type</th>
<th>location</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>n</em>Digits [numerical, integer]</td>
<td>number of digits</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>*Repeatability [complex]</td>
<td>repeatability</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sRepeatEvaluator [string]</td>
<td>repeatability evaluator</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>eRepeatMethod [enumeration]</td>
<td>repeatability method</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>sRepeatMethod [string]</td>
<td>repeatability method</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>nRepeatValue [numerical, floating]</td>
<td>repeatability value</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>nRepetitions [numerical, integer]</td>
<td>number of repetitions</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>*sDeviceSpec [complex]</td>
<td>device specification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sDeviceSpecEvaluator [string]</td>
<td>device specification evaluator</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>eDeviceSpecMethod [enumeration]</td>
<td>device specification method</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>sDeviceSpecMethod [string]</td>
<td>device specification method</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>nDeviceSpecValue [numerical, floating]</td>
<td>uncertainty based on device specification only</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>nDeviceSpecLevelOfConfid [numerical, floating]</td>
<td>level of confidence for nDeviceSpecValue</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>CurveDev [complex]</td>
<td>rms deviation from a fitted curve</td>
<td></td>
<td></td>
</tr>
<tr>
<td>nCurveDevAssessNum [numerical, integer]</td>
<td>fitted curve assessment number</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>sCurveDevEvaluator [string]</td>
<td>fitted curve evaluator</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>sCurveSpec [string]</td>
<td>fitted curve specification</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>nCurveRmsDevValue [numerical, floating]</td>
<td>fitted curve relative rms deviation value (%)</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>nCurveRmsRelativeDevValue [numerical, floating]</td>
<td>fitted curve relative rms deviation value</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>nCurveDevValue</td>
<td>deviations from the fitted curve</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>n*NegativeValue [numerical, floating]</td>
<td>is for storage of the Level of Confidence ( L_x ), associated with ( U_x ). The level of confidence is always expressed in ThermoML as a percentage.</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>CombinedUncertainty [complex]</td>
<td>This complex element includes the subelements associated with expression of the combined expanded uncertainty values ( U_{\text{comb}} ). The combined expanded uncertainty is stored for properties only and includes propagation of uncertainties in the variables and constraints to that of the property, as discussed earlier and as indicated in the lower section of Table 1. Nearly all subelements are analogous to those for *Uncertainty [complex]. One additional element provides an enumeration list for description of the method of assessment.</td>
<td>P, V, C</td>
<td>•</td>
</tr>
<tr>
<td>nCombUncertAssessNum [numerical, integer]</td>
<td>the combined uncertainty assessment number is an integer used to identify a particular assessment of the combined uncertainty. Its use is as described for nUncertAssessNum [numerical, integer].</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>sCombUncertEvaluator [string]</td>
<td>the combined uncertainty evaluator string is for identification of the individual or institution responsible for the assessment of the combined uncertainty.</td>
<td>P only</td>
<td>•</td>
</tr>
<tr>
<td>eCombUncertEvalMethod [enumeration]</td>
<td>provides an enumeration list for specification of the general method for evaluation of the combined uncertainty. The enumerations are (Propagation of estimated standard uncertainties, Comparison with reference property values). In the field of experimental thermodynamics, it is common to test the reliability of an apparatus through measurements performed on reference materials with property values having well-established uncertainties. This approach is an alternative to that of determining uncertainties for all possible components and propagating these to the uncertainty in the property. The source of the reference property values should be provided in the corresponding string element, which follows.</td>
<td>P only</td>
<td>•</td>
</tr>
</tbody>
</table>
| sCombUncertEvalMethod [string] | the combined uncertainty evaluation method element allows storage of descriptive information related to the uncertainty assess-
This element can be used to accommodate item number 6 of the recommendations for the reporting of uncertainties given in the Guide. In addition, this element can be used for storage of information about the source of reference property values if “Comparison with reference property values” is chosen in the eCombUncertEvalMethod [enumeration].

nCombStdUncertValue [numerical, floating] is used for storage of the combined standard uncertainty value $u_{comb}$ as defined earlier and shown in column 3 of the lower section of Table 1. The value $u_{comb}$ represents one standard deviation by definition.

AsymCombStdUncert [complex] is for storage of the combined standard uncertainty for an uncertainty that is asymmetrical about the property value. This element is included only for properties. The values spanned by the unsymmetrical range lie between $(y_p + u_{comb-})$ and $(y_p - u_{comb-})$, where $u_{comb-} = u_{comb-}$. Subelements of AsymCombStdUncert [complex] are nPositiveValue [numerical, floating] for storage of $u_{comb-}$ and nNegativeValue [numerical, floating] for storage of $u_{comb-}$.

nCombCoverageFactor [numerical, floating] stores the coverage factor $k_{comb}$ used to obtain $U_{comb} = k_{comb}U_{comb}$.

AsymCombExpandUncertValue [numerical, floating] stores the combined expanded uncertainty value $U_{comb}$.

AsymCombExpandUncert [complex] is for storage of the combined expanded uncertainty for an uncertainty that is asymmetrical about the property value. This element is included only for properties. The values spanned by the unsymmetrical range lie between $(y_p + u_{comb-})$ and $(y_p - u_{comb-})$, where $u_{comb-} = u_{comb-}$. Subelements of AsymCombExpandUncert [complex] are nPositiveValue [numerical, floating] for storage of $u_{comb-}$ and nNegativeValue [numerical, floating] for storage of $u_{comb-}$.

nCombUncertLevOfConfid [numerical, floating] stores the Level of Confidence $L_{comb}$ associated with $U_{comb}$. The level of confidence is stored as a percentage.

PropLimit [complex]

This complex element is a new subelement of PropertyValue [complex] and is for storage of property values reported as upper or lower limits for the measurand. This type of element is included for properties only and is not included for variables, constraints, or properties. The subelements of PropLimit [complex] are nPropUpperLimitValue [numerical, floating] and nPropLowerLimitValue [numerical, floating] for storage of either numerical limiting value, and nPropLimitDigits [numerical, integer] for storage of the number of digits in the value.

ThermoML Elements for the Expression of Precisions

The elements listed in Table 4 are for the expression of precisions. The measurand types to which these may be associated are listed in column 3 of Table 4. These quantities are completely independent of those specified in Table 3. The term combined is not used in these elements. This term is applicable only to uncertainties, which include contributions from all sources. With the exception of n*Values [numerical, integer] all of the following elements are optional in the schema, as is true for all elements associated with the specification of uncertainty. The general locations of the elements listed in Table 4 are indicated in columns 4 and 5. Detailed locations are provided later in this paper.

n*Values [numerical, integer]. Every numerical element in ThermoML has an element of this type associated with it for specification of the number of reported digits. The symbol * indicates that this element is present in the schema for many different quantities. The number of decimal places associated with uncertainties and precisions is assumed equal to the number specified for the relevant variable, constraint, or property. By design, the number of digits is not specified as the number of significant digits. There are numerous occasions in the reporting of experimental thermodynamic results when it is valuable to report additional digits to avoid round-off errors in subsequent calculations. If uncertainties are reported as recommended in the Guide, the number of significant digits can be determined from these.

*Repeatability [complex]

The numerical quantity, repeatability, was defined earlier. The symbol * indicates that this element is present in the schema for variables (* = Var), constraints (* = Constr), and properties (* = Prop). The following elements are used for specification of this quantity for variables, constraints, and properties.

sRepeatEvaluator [string]; the repeatability evaluator string is used to identify the individual or institution responsible for the assessment of the repeatability. In most cases, this will be the author of the original publication.

eRepeatMethod [enumeration] provides an enumeration list for specification of the statistical definition of the repeatability value. The four enumerations are (Standard deviation of a single value (biased), Standard deviation of a single value (unbiased), Standard deviation of the mean, and Other). These terms are defined in most common texts in the field of statistics (cf. ref 8). Selection of the enumeration “Other” should be accompanied by a description of the method in the string element sRepeatMethod [string].

The standard deviation of a single value (unbiased) $\sigma_{\text{unbiased}}$ for a series of observations with mean value $x$ is calculated with the following equation. The summation is over the number $n$ of observations.

$$\sigma_{\text{unbiased}} = [(n - 1)^{-1}\sum (x_i - \bar{x})^2]^{0.5}$$

(5)

The standard deviation of a single value (biased) $\sigma_{\text{biased}}$ is calculated with the equation

$$\sigma_{\text{biased}} = [n^{-1}\sum (x_i - \bar{x})^2]^{0.5}$$

(6)

The standard deviation of the mean $\sigma_{\text{mean}}$ is calculated with the equation

$$\sigma_{\text{mean}} = [(n(n - 1))^{-1}\sum (x_i - \bar{x})^2]^{0.5}$$

(7)

A discussion of the application of these formulas to particular experimental conditions is beyond the scope of this paper. The reader is referred to any common text in statistics for this information. Equation 7 is often applied in the analysis of results obtained with combustion bomb calorimetry.9

sRepeatMethod [string]; the repeatability assessment method can be used for storage of details related to the determination, such as the particular type of statistics used in determining the repeatability value. This element should always be used when “Other” is selected in eRepeatMethod [enumeration].

nRepeatValue [numerical, floating] is used for storage of the results of the repeatability value. The units match those of the quantity being repeated.

nRepetitions [numerical, integer] is used for storage of the number of measurement repetitions $n$ used in the calculation of the repeatability value.

*DeviceSpec [complex]
This complex element includes subelements for storage of components of uncertainty obtained as device specifications from manufacturers or certificates of calibration. The symbol * indicates that this element is present in the schema for variables (* = Var), constraints (* = Constr), and properties (* = Prop). These quantities are often used and reported as part of an uncertainty assessment by experimentalists, and they may be of value to subsequent data evaluators.

sDeviceSpecEvaluator [string]: the device specification evaluator string is used to identify the individual or institution responsible for assessment of the device specification. In most cases, this will be a manufacturing company or an institute or company providing calibration services.

eDeviceSpecMethod [enumeration]: provides an enumeration list for identification of the device specification method. The three enumerations are (Specified by the manufacturer, Calibrated by the experimentalist, Calibrated or certified by a third party). Details related to the specification can be described in sDeviceSpecMethod [string].

sDeviceSpecMethod [string]: this element is used for storage of details related to the enumeration selected in eDeviceSpecMethod [enumeration]. Details might include particulars of the calibration method, identities and sources of reference materials, literature references to exclude particulars of the calibration method, identities and sources of reference materials, literature references to standard values, and so forth.

nDeviceSpecValue [numerical, floating]: is used for storage of the numerical value of the uncertainty component arising from the device specification. The units match those of the state function being determined with the device.

nPurityMolDigs [numerical, integer], nPurityMassDigs [numerical, integer], nPurityVolDigs [numerical, integer], and nWaterMolPerCentDigs [numerical, integer], are indicated by arrows in the figure. New schema elements are indicated in all of the detailed schema figures (Figures 2–10).

CurveDev [complex]: This element allows storage of uncertainty information derived from fitting of curves to experimental property data. By definition, these quantities are associated with properties only. The information stored is the root-mean-square deviation of the experimental values from the fitted curve (for a data set) and the deviations from the fitted curve for each numerical value (i.e., for each data point), as indicated in Table 4.

nCurvRmsDevAssessNum [numerical, integer]: the deviation assessment number is an integer used to identify a particular assessment. Its use is as described for nUncertAssessNum [numerical, integer]. The assessment number is needed to allow storage of results for fits with various equations. Identification of the particular equation is stored in sCurvSpec [string], as described below.

sCurvDevEvaluator [string]: the curve deviation evaluator element is used to identify the individual or institution responsible for the assessment.

sCurvSpec [string]: the curve specification element is used for storage of text that describes the fitted curve. The description might include a particular equation name (e.g., Antoine or Wagner for vapor pressures), an equation form (e.g., \( C_{p,m} = a + bT \), for heat capacities of a liquid), or special conditions, such as specification of fixed parameters.

nCurvRmsDevValue [numerical, floating]: the curve rms deviation value is stored in this element and has the same units as the associated property. This value is associated with the data set as a whole. The numerical value \( \delta_{\text{rms}} \) is defined in eq 4.
are shown in Figures 6 and 7. Figure 7 shows those elements associated with the data set as a whole, while Figure 6 shows the elements associated with the individual numerical data points. The additional elements for properties associated with representation of combined uncertainties and deviations from fitted curves are apparent in the figures.

**Extensions to the “ReactionData” Block.** Extensions to this block are also shown separately for constraints, variables, and properties. Detailed locations for all of the new elements for the expression of uncertainties and precisions for constraints are shown in Figure 8. This is analogous to the structure shown in Figure 3 for the “PureOrMixtureData” block.

New elements for the expression of uncertainties and precisions for variables in the “ReactionData” block are shown in Figures 5 and 9. The schema structure for the representation of numerical values for variables is the same in the “PureOrMixtureData” block and the “ReactionData” block. Figure 9 shows those elements associated with the data set as a whole, while Figure 5 shows the elements associated with the individual numerical data points.

New elements for the expression of uncertainties and precisions for properties in the “ReactionData” block are shown in Figures 6 and 10. The structure of the schema for the representation of numerical values for properties is the same in the “PureOrMixtureData” block and the “ReactionData” block. Figure 10 shows those elements...
associated with the data set as a whole, while Figure 6 shows the elements associated with the individual numerical data points.

Example 1: A Comparison of the Expanded Uncertainty and the Combined Expanded Uncertainty

The distinctly different meanings of the expanded uncertainty and the combined expanded uncertainty can be demonstrated with the following vapor–liquid equilibrium data set for a binary mixture. The reported state functions are the pressure ($p = 101.3$ kPa), the composition of the liquid phase $x_1$ (the mole fraction of component 1), and the boiling temperature $T$ of the mixture. The experimental boiling temperatures are shown plotted as a function of the composition of the liquid phase in Figure 11 (upper graph).

The contributions to the uncertainties for each independent state function were analyzed by the authors, and the following values of the standard uncertainty $u$ were estimated: $u_T = 0.1$ K, $u_p = 0.1$ kPa, and $u_{x_1} = 0.005$. Normal distributions were assumed in each case, and a coverage factor $k = 2$ was used to estimate each expanded uncertainty: $U_T = 0.2$ K, $U_p = 0.2$ kPa, and $U_{x_1} = 0.010$.

The combined expanded uncertainty $U_{comb}$ can be calculated for any of the state functions, but it can be stored in ThermoML for only one: the designated property. In this example, the boiling temperature $T$ is selected as the property, and the combined expanded uncertainty is calculated by propagation of $U_T$ and $U_{x_1}$ to calculate $U_{comb}$.

Figure 11 (lower graph) shows the two types of uncertainties ($U_T$ and $U_{comb}$) associated with the temperature, as a function of $x_1$. $U_T$ is independent of the other state functions and is constant. For $x_1 > 0.5$, $U_T$ and $U_{comb}$ are nearly the same. For $x_1 < 0.5$, however, $U_{comb}$ increases rapidly (to a value approximately 10 times $U_T$) and passes through a maximum before approaching $U_T$ again near $x_1 = 0$. The contribution of $U_{x_1}$ to $U_{comb}$ [i.e., $U_{x_1}(dT/dx_1)_{p}$] is the primary source of the large values for $0 < x_1 < 0.5$. The contribution from $U_p$ is relatively small.

Example 2: Estimates of Combined Expanded Uncertainties

The estimation of uncertainties for experimental data is a key step in the data evaluation processes, which form the foundation for all recommended thermodynamic data. The NIST Thermodynamics Research Center (TRC) is one of the oldest data research centers in the United States, and for over 60 years has produced a great number of periodical compilations (the TRC Tables, International Data Series for mixtures, TRC Books of evaluated property data, etc.) that have become major sources of recommended data for scientific research and industrial process design.

The following paragraphs outline an approach for the estimation of combined standard uncertainties developed at TRC and used by the personnel of the TRC Data Entry Facility. This example is provided to reinforce the concept that all contributions to uncertainty should be considered in the estimation of uncertainty of measurement. The
estimates described are based on the information provided in a given document (e.g., a journal article, thesis, report, etc.) and do not involve comparisons with previously evaluated data. This is done so as not to bias the assessment. These estimates provide preliminary values, which are subject to further improvement based on the enforcement of single-property and multiple-property consistency requirements included in the TRC data quality-assurance program.¹³

Estimated uncertainties for experimental data have essentially two purposes: (1) to provide weighting factors needed to distinguish between duplicate determinations (i.e., relative uncertainties) and (2) to provide a basis for propagation of uncertainties to derived properties required for recommended values for chemical-process design, benchmark values for validation of results from ab initio or other computational methods, and numerous other applications (i.e., absolute uncertainties).

Estimation of uncertainties for experimental data is critical to a new approach for data evaluation that is under development at NIST. This approach, which is termed dynamic data evaluation (DDE), requires the development of large electronic databases capable of storing essentially all experimental data known to date with complete descriptions of the relevant metadata and uncertainties. The combination of these electronic databases with expert-system software leads to the ability to produce compilations of recommended values dynamically or “to order”. General descriptions of DDE have been published.¹⁴,¹⁵ As part of the DDE implementation, TRC has developed a general and consistent scheme for estimation of uncertainties for a wide variety of properties and experimental methods.

Although almost all publications of experimental data include some discussion or estimation of “uncertainties”, these are rarely done in the structured and defined way recommended by the Guide. Inconsistencies abound between different journals and publications, and conflicting interpretations and implementations of many terms such as precision, accuracy, systematic error, random error, and so forth are common. Consequently, most “uncertainties” reported in the literature cannot be used for weighting of data or error propagation, particularly if the reported uncertainties are combined from different sources.

The scheme developed by TRC for estimation of the combined standard uncertainty \( u_{comb} \) for a given property \( p \) as a function of constraints \( c \) and variables \( v \) is based upon a summation of terms:

\[
\begin{align*}
\sum_{i} \left( \frac{\partial f_{m}}{\partial c_i} \right)^2 + \sum_{i} \left( \frac{\partial f_{v}}{\partial v_i} \right)^2 \end{align*}
\]

This relationship involves two major contributions to \( u_{p} \): uncertainties associated with the experimental method, and those associated with the sample.

The term \( u_{method} \) is a default contribution to \( u_{p} \) and is based on the particular experimental method only. For example, a heat capacity \( C_{sat,m} \) determined with high-precision adiabatic calorimetry might have a default value for \( u_{method} \) of 0.002 \( C_{sat,m} \), while the same property determined with a differential-scanning calorimeter might have a default value 10 times larger. Some details related to particular methods are also considered, such as the method of calibration for a vibrating-tube densimeter or the failure to report degassing procedures for a static vapor-pressure measurement. These adjustments are indicated as \( u_{method-details} \). In eq 9 and can increase or decrease \( u_{p} \) on the basis of the value of \( f_{m} \), which is 1 or \( -1 \).

The term \( u_{sample} \) in eq 9 represents a default contribution to \( u_{p} \) related directly to the purity of the sample. Additional contributions to \( u_{p} \) related to the sample are indicated as \( u_{sample-details} \). In eq 9. The magnitude of \( u_{sample-details} \) is a function of several items, including the property, experimental method, special characteristics of the material (e.g., thermal stability or hygroscopicity), and the experimental conditions (e.g., pressure or temperature range). This formulation is required to take into account the fact that impurities do not affect all properties or experimental methods to the same extent. The value of \( f_{s} \) is 1 or \( -1 \).

Values for the standard uncertainties \( u_{c} \) and \( u_{v} \), and \( u_{p} \), if appropriate) are taken from the document, if provided and supported in the text. Default values are substituted for those not provided. Default values are based upon the general method used and are larger than those reported typically in the literature for the method. Incomplete reporting or the absence of information in the document is considered indicative of the general quality of the work. Consequently, results reported with incomplete uncertainty descriptions are given uncertainties at TRC larger than those with well-supported estimates.

If estimates of \( u_{comb} \) are provided in the document, these are checked against the estimates calculated with eq 8. Large discrepancies are reviewed carefully and can form the basis for modification of default values. Because various indicators of precision (repeatabilities, deviations from fitted curves, etc.) provide only a lower limit for any uncertainty estimate, these are considered only if larger than the default uncertainties for the particular variable, constraint, or property. As a final step, the estimated combined standard uncertainty \( u_{comb} \) is multiplied by a coverage factor \( k_{comb} \) to estimate the combined expanded uncertainty \( U_{comb} \) corresponding to a level of confidence of approximately 95%. For most cases, \( k_{comb} = 2 \); however, other values are used, if required to obtain the desired level of confidence. The \( U_{comb} \) values are stored together with the property values \( p_{f} \) and required metadata in the TRC SOURCE Data System.¹⁸

This approach to the estimation of combined standard uncertainties provides the basis for consistent evaluations of the numerous data types encountered by TRC as part of its thermodynamic data evaluation projects. This brief overview demonstrates that even approximate estimates of \( U_{comb} \) require careful consideration of a wide variety of contributions to the uncertainty.

Use Cases and ThermoML Schema Text

Examples illustrating the format of the data files created with the ThermoML formats for pure compound or mixture data sets,¹⁹ as well as for chemical reactions,²⁰ are included as Supporting Information. The examples are based upon experimental studies published in the peer-reviewed literature.
Schema Validation

The developed schema was validated extensively with data records in SOURCE.10 Validation covered essentially all properties within the scope of ThermoML, including pure compounds, multicomponent mixtures, and chemical reactions. In addition, the validation process included data files submitted to TRC by authors of articles submitted through the Editorial Board of the Journal of Chemical & Engineering Data, as well as data files submitted to TRC by its data collection contractors.

Role of ThermoML in Global Data Submission and Dissemination

The role of ThermoML in global submission and dissemination of experimental thermodynamic property data was described.1 Guided Data Capture (GDC) software was developed at TRC for mass-scale abstraction from the literature of experimental thermophysical and thermochemical property data. This software is freely available for download from the Internet.19

Following the peer-review process, authors are requested by the journal editors to download and use the GDC software to capture the experimental property data that has been accepted for publication. The output of the GDC software is an electronic data file (plain text file), which is submitted directly to TRC. The electronic data files are converted into ThermoML format with software (Trans-Thermo) developed at TRC. Upon release of the manuscript for publication, the ThermoML files are posted on the public-domain TRC Web site with unrestricted public access. This procedure has been established formally by the Journal of Chemical & Engineering Data.20 Expansion of this operation to other journals in the field is under discussion.

Version 1 of the GDC software included very limited tools for the specification and capture of uncertainty information. This software is now being expanded to include a more comprehensive representation of uncertainty based on the definitions and structures described here. The new version (Version 2) will also be available for free download from the Internet.19 After release of this new version of GDC, posted ThermoML files will include uncertainty estimates provided by the article authors. Version 2 will implement tools for generation of ThermoML files upon completion of the data-capture process.

Acknowledgment

The authors express their appreciation to the following people for their valuable advice in the development of the extensions to the ThermoML format described in this paper: Drs. J. W. Magee, R. A. Perkins, D. G. Friend, and W. M. Haynes (NIST, Boulder, CO); Drs. S. E. Stein, T. C. Allison, and P. Linstrom (NIST, Gaithersburg, MD); Our special thanks to Dr. G. J. Rosasco for his support and help in coordination of the project. The authors also wish to express their appreciation to Dr. D. L. Embry (DIPPR, ConocoPhillips, Ponca City, OK); Dr. T. L. Teague (DIPPR, ePlantData, Inc., Houston, TX); Dr. P. R. Franschke (NIST, Boulder, CO); S. Frenkel (NIST, Boulder, CO), for their valuable cooperation in development of the ThermoML format, and Drs. W. A. Wakeham (University of Southampton, U. K.), J. H. Dymond (University of Glasgow, U. K.), and A. R. H. Goodwin (Schlumberger-Doll Research, Ridgefield, CT) for valuable discussions concerning global data submission and dissemination.

Supporting Information Available: Examples are provided illustrating the use of ThermoML for representation of experimental data with uncertainties for pure compounds, mixtures, and chemical reactions. The complete current text of the ThermoML schema is included also as Supporting Information and is available on the Web (http://www.trc.nist.gov/ThermoML.xsd) or through direct request to the authors. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(2) Guide to the Expression of Uncertainty in Measurement (International Organization for Standardization, Geneva, Switzerland, 1993). This Guide was prepared by ISO Technical Advisory Group 4 (TAG 4), Working Group 3 (WG 3). ISO/TAG 4 has as its sponsors the BIPM, IEC, IFCC, (International Federation of Clinical Chemistry), ISO, IUPAC (International Union of Pure and Applied Chemistry), IUPAP (International Union of Pure and Applied Physics), and OIML. Although the individual members of WG 3 were nominated by the BIPM, IEC, ISO, or OIML, the Guide is published by ISO in the name of all seven organizations.
(6) International Vocabulary of Basic and General Terms in Metrology, 2nd ed. (International Organization for Standardization, Geneva, Switzerland, 1993). This document (abbreviated VIM) was prepared by ISO Technical Advisory Group 4 (TAG 4), Working Group 1 (WG 1). ISO/TAG 4 has as its sponsors the BIPM, IEC, IFCC, International Federation of Clinical Chemistry, ISO, IUPAC (International Union of Pure and Applied Chemistry), IUPAP (International Union of Pure and Applied Physics), and OIML. The individual members of WG 1 were nominated by BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, or OIML, and the document is published by ISO in the name of all seven organizations.

Received for review May 6, 2003. Accepted May 8, 2003.
JE034088I