

ThermoML: an XML-Based Approach for Storage and Exchange of Experimental and Critically Evaluated Thermophysical and Thermochemical Property Data. 5. Speciation and Complex Equilibria

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ThermoML is an XML-based approach for storage and exchange of measured and critically evaluated thermophysical and thermochemical property data. Extensions to the ThermoML schema for the representation of speciation and complex equilibria are described. The text of ThermoML (xml) is provided to illustrate application of the new extensions. These are provided as Supporting Information together with the complete updated ThermoML schema.

Background

This is the fifth paper in the series describing ThermoML, an XML-based approach for storage and exchange of thermo-physical and thermochemical property data.^{1–4} The principles, scope, and description of the basic structural elements of ThermoML were discussed in the first paper in this series.¹ The scope of ThermoML spans 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). Representation of quantities for the expression of uncertainty was discussed in the second paper of the series.² In the third paper, the expansion of ThermoML to include critically evaluated and predicted data was discussed, as well as equations for data representation. These three papers collectively report the development of ThermoML, which was authorized by the International Union of Pure and Applied Chemistry (IUPAC) within project 2002-055-3-024 “XML-based IUPAC Standard for Experimental and Critically Evaluated Thermodynamic Property Data Storage and Capture.”⁵ Meta- and numerical data infrastructure reported in these papers served as the foundation for recommendations establishing ThermoML as the IUPAC standard for thermophysical property data communications.⁶ The complete schema for the IUPAC ThermoML standard is available on the Internet.⁷

ThermoML has proven to be a critical component in the development of one of the first global data delivery processes,⁸ now endorsed by five major journals in the field.⁹ ThermoML is used extensively by scientists, engineers, and informatics experts worldwide. Based on the feedback we obtained after the release of ThermoML as an IUPAC standard, another project was initiated as IUPAC project 2007-039-1-024, entitled “Extension of ThermoML - the IUPAC Standard for Thermodynamic Data Communications.”¹⁰ The purpose of this project was to broaden the scope of ThermoML and support storage and exchange of thermodynamic property data for the following: (1) biomaterials and (2) speciation and complex equilibria in aqueous and non-aqueous solvents. Recently, the extensions of ThermoML for thermophysical and thermochemical properties of biomaterials were described.⁴ These focused on properties of enzyme-catalyzed reactions, molecular association determined with titration calorimetry, biothermodynamic properties determined with differential scanning calorimetry (DSC), and solubilities in complex media. This article describes specific extensions of ThermoML to speciation and complex equilibria.

Scope of Extensions for Speciation and Complex Equilibria

The primary goal of this work is to ensure that thermodynamic property data associated with chemical speciation and complex equilibria can be represented within the ThermoML schema. In particular, a series of extensive reviews of the thermodynamic properties for compounds and complexes of selected metals have been considered.¹¹ These reviews were completed under the auspices of the Organization for Economic Co-operation and Development (OECD)¹² Nuclear Energy Agency. Extensions necessary to adequately represent the information within ThermoML in these and

related literature documents include additional properties, reaction specification details, reaction types, experimental methods, crystal phase specification details, and numerical representations. These may be classified into two broad categories: (1) those that require additional structural elements to be added to ThermoML and (2) those that require extensions to existing enumeration lists that are used for such items as common reaction types (e.g., hydrogenation or combustion with oxygen) or common experimental methods (e.g., static bomb calorimetry). The ThermoML schema was expanded to represent properties of ions and reactions involving ions at the time of publication of the ThermoML IUPAC standard in 2006.⁶ Consequently, most of the schema elements necessary for representation of speciation and complex equilibria were included at that time. New elements and other extensions needed for a more complete representation of chemical speciation and complex equilibria are described in this manuscript. Examples (*Use Cases*), illustrating these new features are provided as ThermoML files in the Supporting Information.

Conventions for Names of Elements in the ThermoML Schema

The names (or *tags*) include special leading characters that indicate the nature of the information to be stored. A name beginning with “e” indicates an enumeration element (with values selected from a predefined list), “s” designates string elements (text strings), “n” specifies numerical elements (integer or floating), “yr” designates elements characterizing the year, “date” specifies date elements, and “url” indicates elements specifying addresses on the World Wide Web. Elements shown as dotted boxes in the figures are optional, while those shown as solid-lined boxes are mandatory. A complex element is an element that includes subelements. Complex elements illustrated without their internal structure are identified by “+” at the right-hand edge of the box. Multiple elements of the same type are often needed within the schema to specify, for example, multiple authors for a given citation or multiple property values for a given data type. These multiple elements are identified in the figures by lower and upper limits listed below the relevant boxes. The limits used for repeated elements are “0..∞” for optional elements and “1..∞” for mandatory elements. A switch symbol in a figure indicates that only one of the subelements can be selected. An element can have *attributes* associated that provide additional information regarding the contents.

General Implementation of Structural Elements Related to Speciation and Complex Equilibria in ThermoML

ThermoML consists of four major blocks that are represented in Figure 1 together with the element **Version** [complex], which specifies the ThermoML version number. All elements of the four major blocks (prior to the current extensions and those for biomaterials⁴) were described previously.⁶ The four major blocks are

- (1) *Citation* (description of the data source)
- (2) *Compound* (characterization of the chemical system)
- (3) *PureOrMixtureData* (meta- and numerical data for a pure compound or multicomponent mixture)
- (4) *ReactionData* (meta- and numerical data for a chemical reaction with a change of state or in chemical equilibrium)

Extensions described here are within the *PureOrMixtureData* and *ReactionData* blocks only. In all figures, the extensions are

† “ThermoML” is the reserved namespace for the XML-based IUPAC standard for experimental and critically evaluated thermodynamic property data storage and capture (<http://www.iupac.org/namespaces/ThermoML/>).
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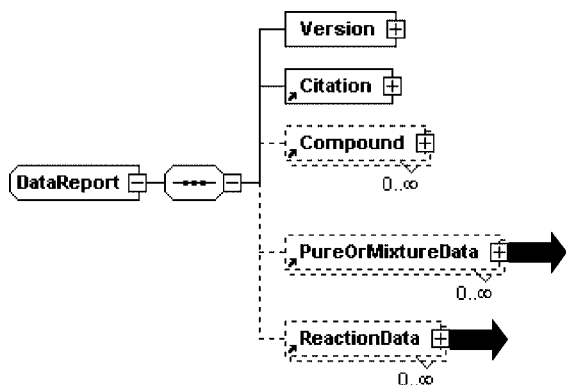


Figure 1. Major components of ThermoML. The arrows indicate the locations of extensions to the schema.

indicated with arrows: those that point to the right indicate extensions within the subelements of the complex element, and arrows pointing to the left indicate specific additions to the schema. Detailed schema figures and the text of ThermoML were created with the software package XML SPY.¹³ (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.)

New Structural Elements for Speciation and Complex Equilibria

Crystal Phase Specification Details. The element **eCrystalLatticeType** [enumeration] (cubic, tetragonal, hexagonal, rhombohedral, orthorhombic, monoclinic, triclinic) was included in the original formulation of the ThermoML standard.⁶ Many compounds have names of various types (geologic, colloquial, pharmaceutical, etc.) for specific crystalline forms, such as the “stishovite” form of SiO₂.¹⁴ Also, standard states for elements often include crystal specifications, such as “Cu(cr, cubic)” for copper, “Pu(cr, monoclinic)” for plutonium, and “C(cr, graphite)” for carbon.^{11k} It is not possible to enumerate a complete list of these common names, so the element **sPhaseDescription** [string] has been added.

Specification of the crystal lattice type can be necessary within many aspects of the representation of a property. Consequently, the new element **sPhaseDescription** [string] has been added in six locations within the ThermoML schema. Additions within the *PureOrMixtureProperty* block are shown in Figures 2 to 5. In the *ReactionData* block (Figure 6), the element **sPhaseDescription** [string] is a subelement of the **Participant** [complex] element (Figure 7) and the **Variable** [complex] element (Figure 8).

Application of **sPhaseDescription** [string] is demonstrated in *Use Case 1* in the Supporting Information, where the

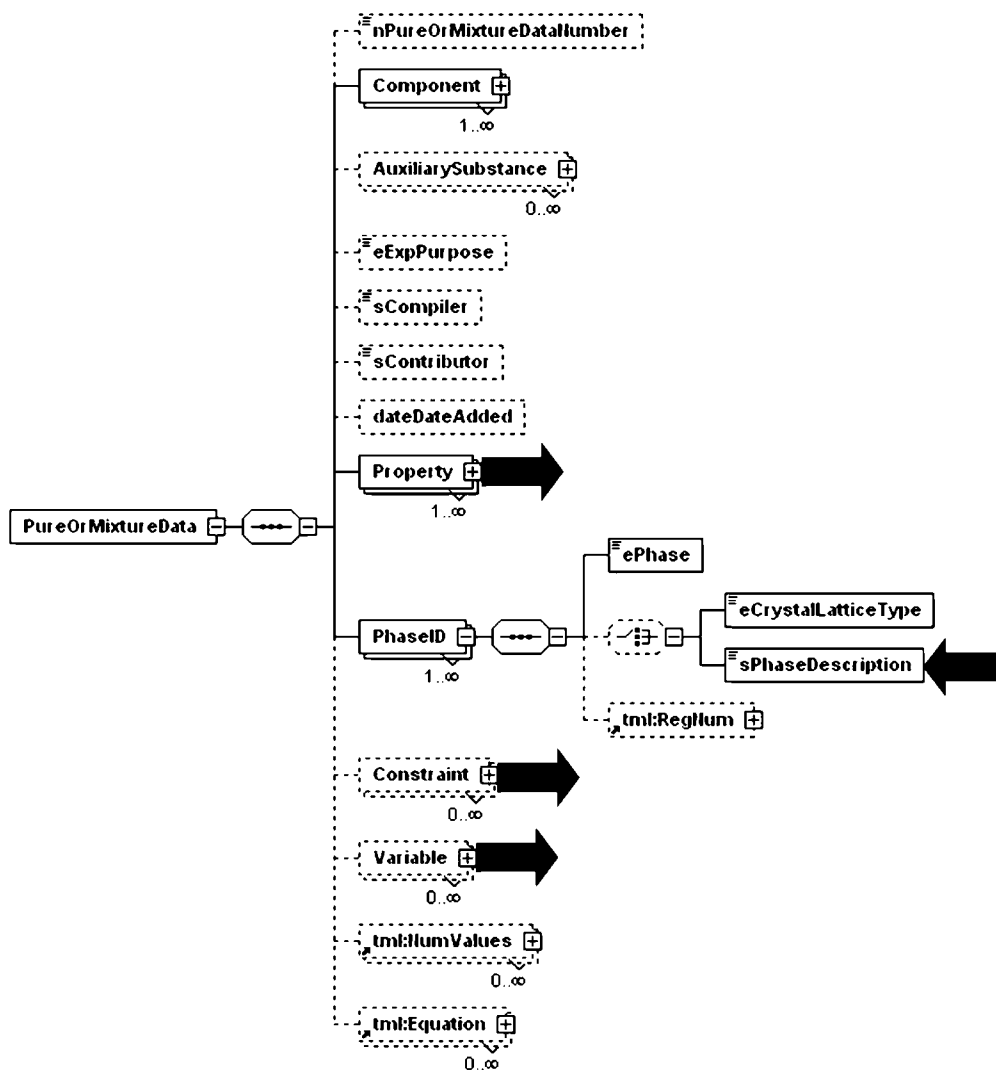


Figure 2. Structure of the *PureOrMixtureData* block. The arrows indicate the locations of extensions to the scheme for special crystal phase specifications; **sPhaseDescription** [string].

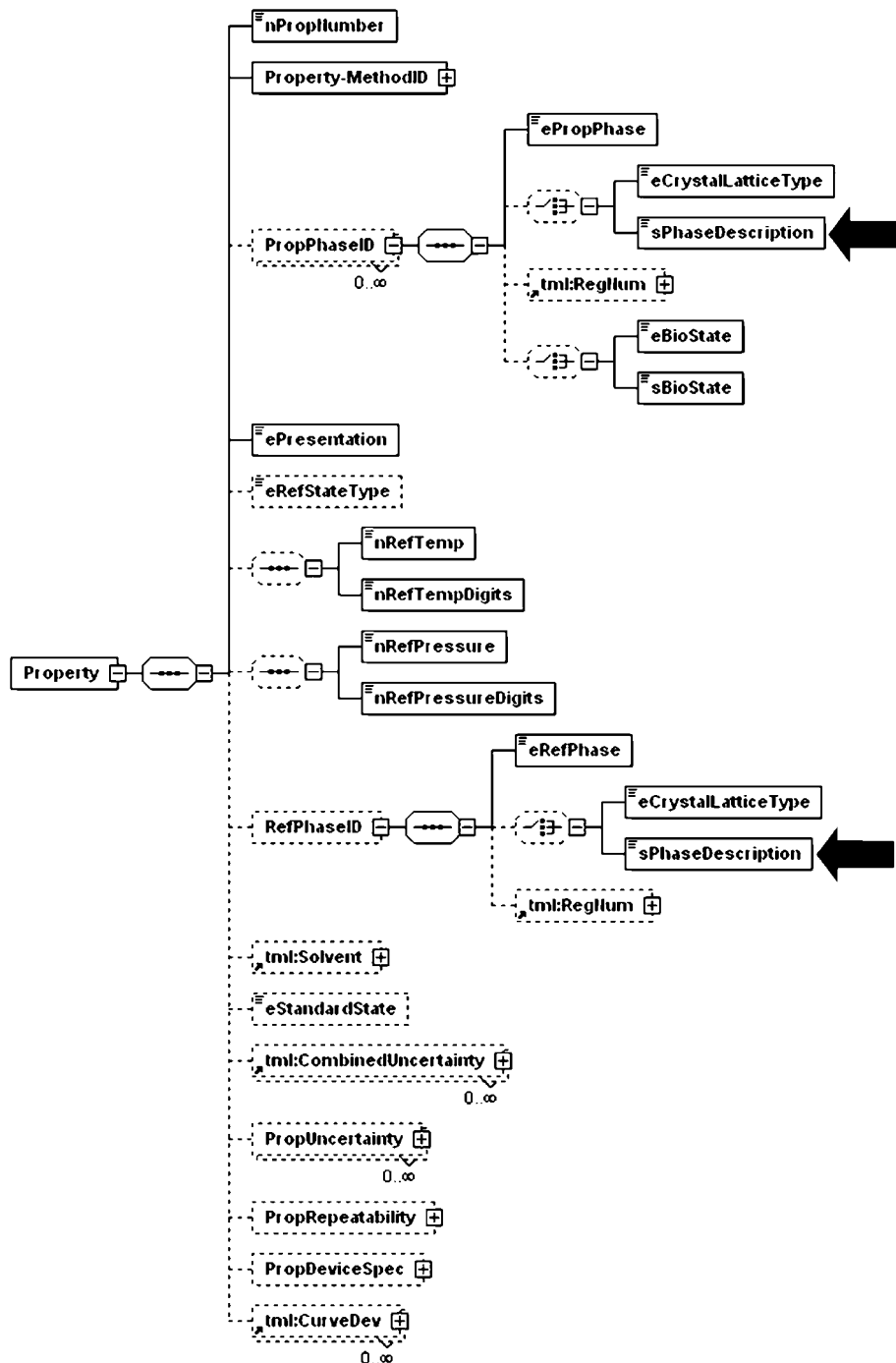
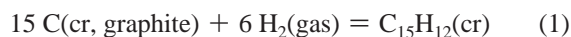


Figure 3. Structure of the **Property** [complex] element in the *PureOrMixtureData* block. The arrows indicate the locations of extensions to the schema for special crystal phase specifications; **sPhaseDescription** [string].

enthalpy of formation of 4-methylphenanthrene¹⁵ based on the reaction



is represented, and the carbon crystal lattice type *graphite* is stored in the element **sPhaseDescription** [string]. Similarly, when representing the enthalpy of formation for sulfur-containing compounds,¹⁶ the standard state of sulfur at the temperature $T = 298.15 \text{ K}$ is often chosen to be *rhombic*, which is represented analogously.

Accommodation of Multiple Solvents for Reaction Data. It is common for thermodynamic studies that address speciation to involve measurements with electrochemical cells. A comprehensive description of electrochemical cells is outside the scope of ThermoML at this time. Nevertheless, the option to represent multiple solvents for electrochemical cells provides the means to unambiguously associate the property of interest with a particular experiment reported in a data source (journal article). The element **Solvent** [complex] was included in the ThermoML IUPAC standard,⁶ and has been extended in this version to any number of solvents. The location of this modification within the *ReactionData* block is shown in Figure

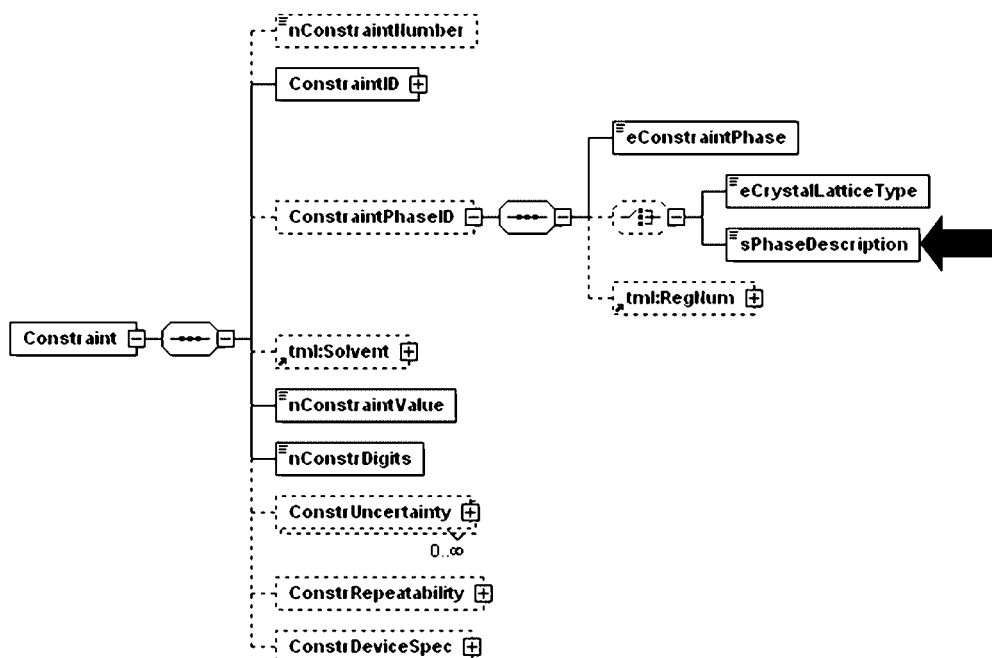


Figure 4. Structure of the **Constraint** [complex] element in the *PureOrMixtureData* block. The arrow indicates the location of the extension to the schema for special crystal phase specifications; *sPhaseDescription* [string].

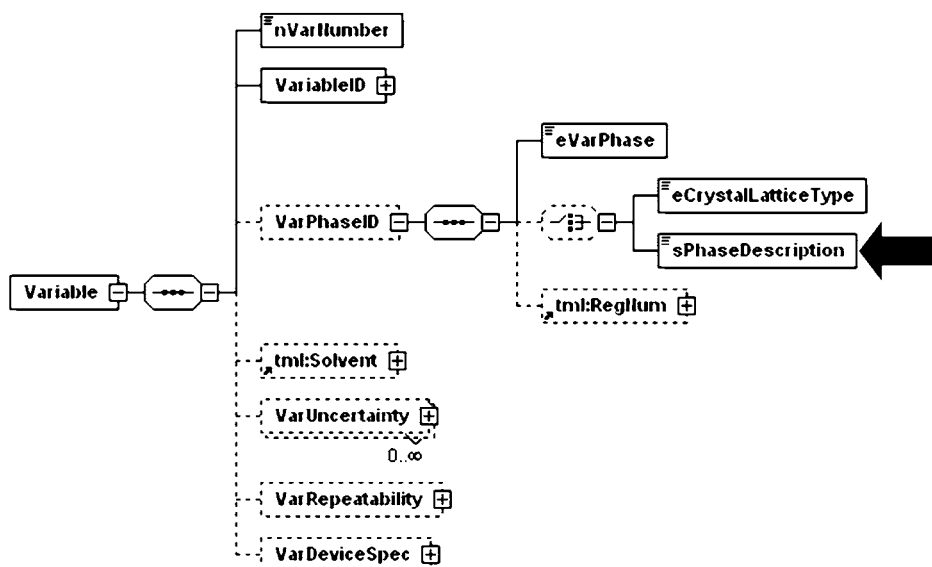


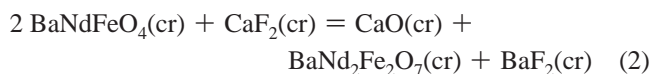
Figure 5. Structure of the **Variable** [complex] element in the *PureOrMixtureData* block. The arrow indicates the location of the extension to the schema for special crystal phase specifications; *sPhaseDescription* [string].

6, where the notation 0..∞ below the Solvent [complex] element indicates that any number of solvents can be specified. Each solvent is associated with a separate liquid phase, such as *solution 1*, *solution 2*, etc.

Electron Number of an Electrochemical Reaction. Specification of a reaction for an electrochemical cell includes the *electron number*, which is the number of electrons transferred in the balanced electrochemical reaction and is a positive integer.¹⁷ The element **nElectronNumber** [numerical, integer] has been accommodated in the *ReactionData* block (Figure 6).

Application of the element **nElectronNumber** [numerical, integer] is demonstrated in *Use Case 2*. This use case is based on an electrochemical study by Rakshit et al.¹⁸ designed to

determine the Gibbs energy of formation of BaNdFeO₄(cr) for which the electron number is 2 for the cell reaction:



Specification of Standard State for Individual Reaction Participants. The optional element **eStandardState** [enumeration] was included in the ThermoML IUPAC standard⁶ but only within the subelement **Property** [complex] of the *ReactionData* block (Figure 9) and, thereby, was associated with all participants of the given reaction. The element **eStandardState** [enumeration] is now included for all reaction participants

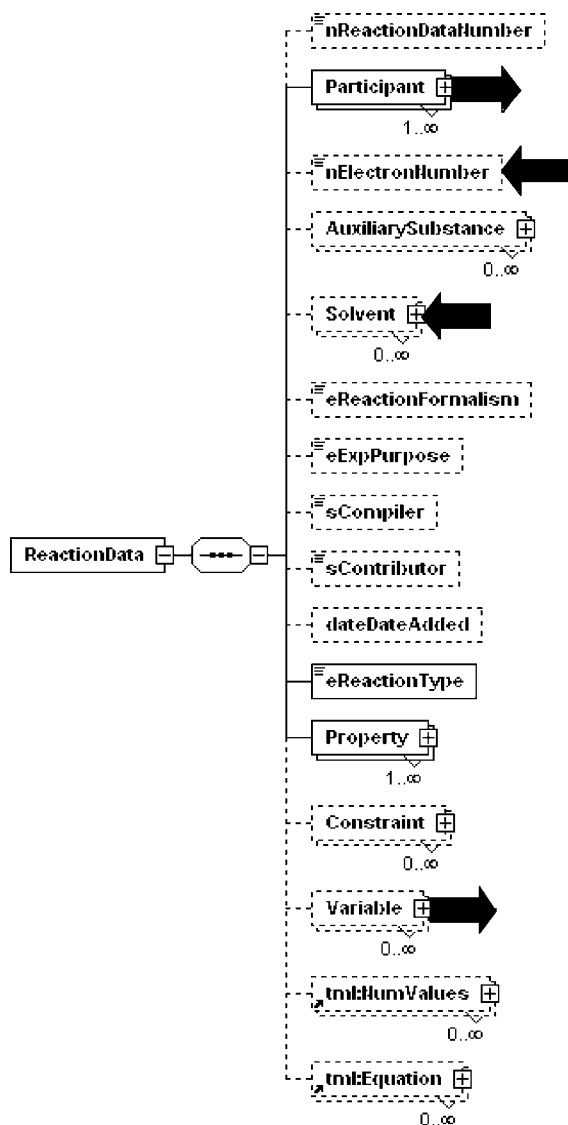


Figure 6. Structure of the *ReactionData* block. The arrows indicate the location of extensions to the schema for this block.

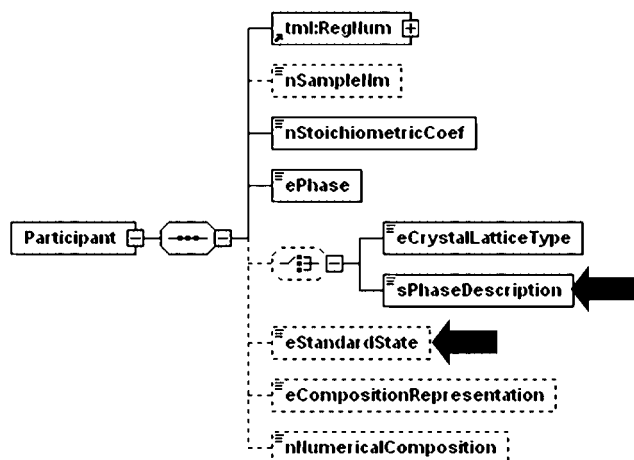


Figure 7. Structure of the *Participant* [complex] element in the *ReactionData* block. The arrows indicate the locations of extensions to the schema for special crystal phase specifications and individual standard states for reaction participants.

(Figure 7) with the dashed arrow in Figure 9 indicating that the element was part of the ThermoML standard prior to the present extensions. The enumeration list for *eStandardState* [enumera-

tion] remains unchanged: (pure compound, pure liquid solute, standard molality [1 mol kg⁻¹] solute, standard concentration [1 mol dm⁻³] solute, infinite dilution).

The use of *eStandardState* [enumeration] is demonstrated in *Use Case 3* for uniform application to all participants of a reaction (within *Property* [complex] of the *ReactionData* block; Figure 9) and for individual assignment to each participant through representation as a subelement of *Participant* [complex] (Figure 7). The use case is based on a study of the dissociation constants of some amines and alkanolamines by Hamborg and Versteeg.¹⁹ Reaction 1 of the article (for piperazine) is represented using *eStandardState* [enumeration] for the reaction, whereas reaction 2 (also, for piperazine) is represented with *eStandardState* [enumeration] for each participant.

Extension of Variable Specification for Reaction Data. The optional element *VarPhaseID* [complex] was included in the ThermoML IUPAC standard,⁶ but only within the *PureOrMixtureData* block. The element *VarPhaseID* [complex] is now included in the *ReactionData* block (Figure 8), where its substructure has been expanded.

Extensions to Enumeration Lists for Speciation and Complex Equilibria

Properties in ThermoML⁶ are categorized into eleven groups within the *PureAndMixtureProperty* block and two groups within the *ReactionProperty* block, as shown in Figure 10. The *PropertyGroup* [complex] element includes the individual property groups as subelements for the *PureAndMixtureProperty* block and *ReactionProperty* block. Names for specific properties are enumerated within the element *ePropName* [enumeration], which is a subelement of each property group (Figure 10). Common experimental methods are enumerated for each property within the element *eMethodName* [enumeration]. The element *sMethodName* [string] allows storage of methods that are not enumerated. The complete list of property groups, properties, and experimental methods within the ThermoML IUPAC standard are summarized in Table 1 of the reference.⁶ Extensions for properties related to biomaterials were published in reference.⁴ Extensions described here for speciation and complex equilibria involve the additions of some new properties and experimental methods, but no new property groups were added in the process.

Reaction Property: Potential Difference of an Electrochemical Cell, *V*. Electrochemical cells are commonly used to study speciation, and the addition of this property allows direct representation of reported potential difference. These potential differences must be associated with reactions or transport processes and are included in the *ReactionStateChangeProp* group, as shown in Table 1. Representation of measured potential differences is included in *Use Case 2* (Supporting Information), which was described in the previous section.

The inadequate reporting of experimental measurements and results continues to pollute the literature. The omission of essential information negates the future use of the otherwise valuable data. A prominent example of this artifact can be found in the literature reporting equilibrium constants, representing a significant component of the information pertaining to speciation and complex equilibria. Three categories of information are essential for complete description of equilibrium constants: (1) the reaction and the conditions under which the reaction was studied (temperature *T*, pressure *p*, the solvent(s), ionic strength *I*, etc.); (2) the definition or basis of calculation of the equilibrium constant for the reaction, including the units used; and (3) the value of the equilibrium constant. Unfortunately,

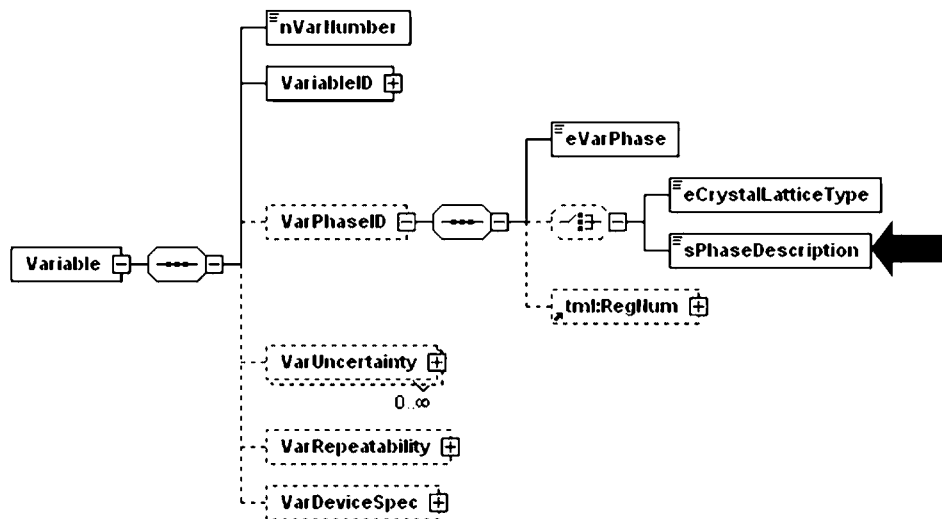


Figure 8. Structure of the **Variable** [complex] element in the *ReactionData* block. The arrow indicates the location of the extension to the schema for special crystal phase specifications; `sPhaseDescription` [string].

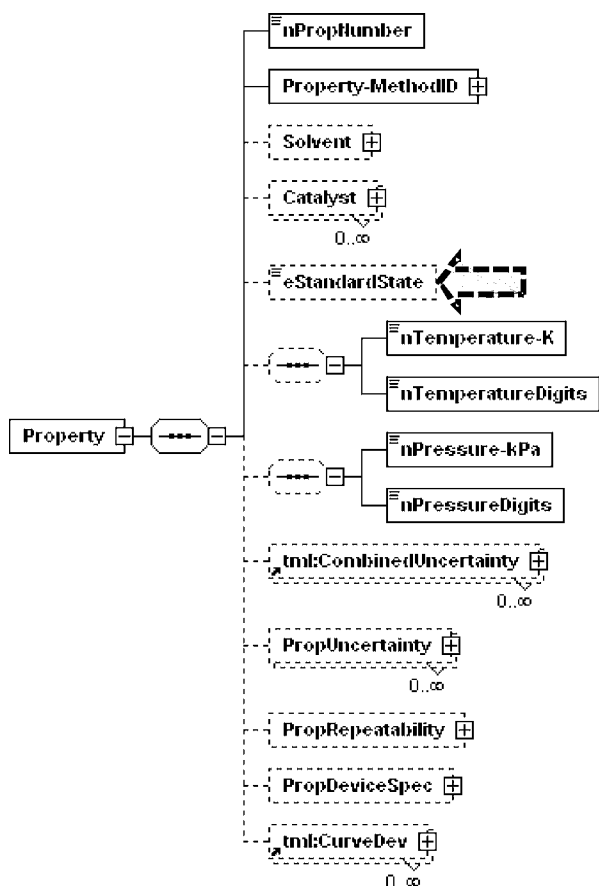


Figure 9. Structure of the **Property** [complex] element in the *ReactionData* block. The arrow indicates the location of the `eStandardState` [enumeration] element in the ThermoML IUPAC standard.⁶

the reporting of these basic and also essential items has been inadequate in too many studies reported in the literature. The nature of XML precludes enforcement of reporting requirements within ThermoML, but the unambiguous representation of all information allows application of simple and automated external checks for completeness.

Mixture Property: Mean Ionic Activity and Mean Ionic Activity Coefficient. The mean ionic activity and mean ionic activity coefficient,¹⁷ have been added to the *ActivityFugaci-*

tyOsmoticProp group (Table 1). These properties were determined by Ciavatta et al.²⁰ for NaCl in (NaCl + water) through electrochemical measurements. Representation of these properties is demonstrated in *Use Case 4* in the Supporting Information.

Mixture Property: Transport Number. The transport number (formerly the *transference* number)¹⁷ has been added to the *TransportProp* group (Table 1) of the *PureOrMixtureData* block. Transport numbers were determined for the component ions of LaCl₃ in aqueous solution by Longworth and MacInnes.²¹ The representation of a transport number in ThermoML for the La³⁺(aq) ion is provided in the Supporting Information.

Logarithmic Representation of Equilibrium Constants. Equilibrium constants can range over many orders of magnitude, and consequently, are often reported in the literature as the logarithm of the property. Numerical representation of these quantities can lead to awkward formulations with numerous zeroes, resulting in an increased likelihood of transcription errors. As equilibrium constants are at the core of speciation data, both natural logarithm and decadic logarithm representations have been added to ThermoML. The ThermoML IUPAC standard⁶ had five representations of equilibrium constants, and these included the thermodynamic equilibrium constant and four representations in terms of various composition measures. Each of these can now be represented as the natural or decadic logarithm, and are listed in Table 1. This extension is demonstrated within *Use Case 3* with the dissociation constants reported by Hamborg and Versteeg¹⁹ (Table 10 of ref 19).

Methods for Properties of Reactions. The extensive reviews published by the *OECD Nuclear Energy Agency* include short descriptors for experimental methods used to determine properties associated with speciation and complex equilibria. These methods are listed in Table 2.1 (page 10) of the first book in the series concerning the thermodynamics of uranium.^{11a} Some of these methods had been incorporated within ThermoML, but many were not. New methods added to `eMethodName` [enumeration] for all reactions are: anion exchange, cation exchange, colorimetry, conductivity measurement, coulometry, cryoscopy, distribution between two phases, cell potential with glass electrode, ion selective electrode, rate of reaction, molar volume determination, polarography, potentiometry, proton relaxation, cell potential with quinhydrone electrode, cell potential with redox electrode, spectrophotometry, solubility measurement,

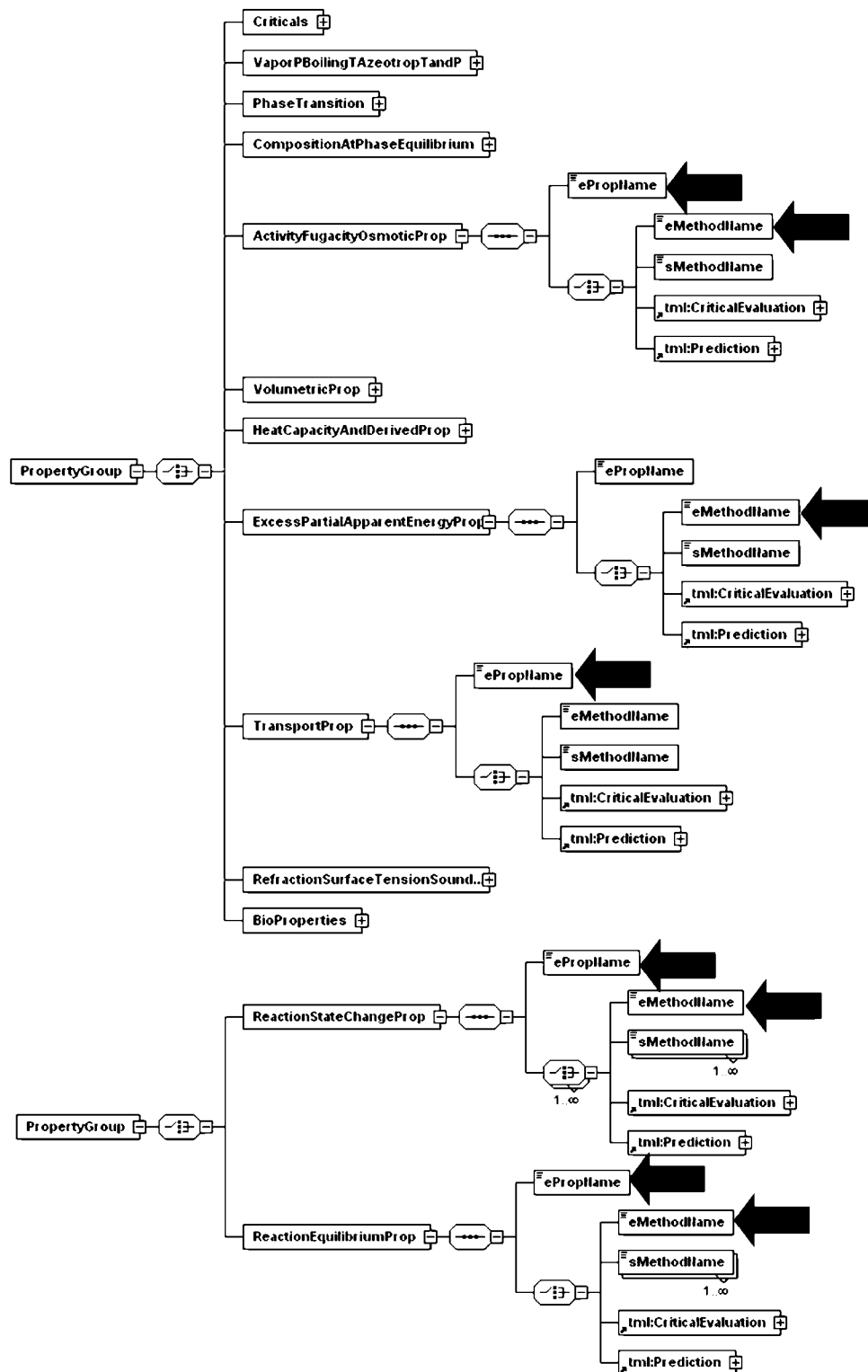


Figure 10. Structure of the **PropertyGroup** [complex] element in the *PureOrMixtureData* block (upper figure) and the *ReactionData* block (lower figure). The arrows indicate the locations of new properties and methods in the schema.

transient conductivity, thermal lensing spectrophotometry, solvent extraction, and voltammetry.

Methods for Properties of Pure Compounds and Mixtures. Extensions have also been made in the enumerated methods for properties for the **ActivityFugacityOsmoticProp** [complex] and **ExcessPartialApparentEnergyProp** [complex] elements within the *PureOrMixtureData* block. The new method *Potential difference of an electrochemical cell* is added to the list for

eMethodName [enumeration] within both of these complex elements. The locations of these extensions are indicated in Figure 10.

Enthalpy of Ion Formation

Values for the enthalpy of ion formation in the gas phase are most commonly calculated with measured ionization and appearance energies.^{22,23} Sources for these values include the

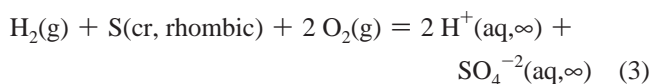
Table 1. Property Groups that are Modified with the Present Extensions to ThermoML^a

| property group | property | unit |
|--|--|--|
| ActivityFugacityOsmoticProp | <i>Mean ionic activity</i> | dimensionless |
| | <i>Mean ionic activity coefficient</i> | dimensionless |
| | Activity | dimensionless |
| | Activity coefficient | dimensionless |
| | Osmotic pressure | kPa |
| | Osmotic coefficient | dimensionless |
| TransportProp | <i>Transport Number</i> | dimensionless |
| | Viscosity | Pa·s |
| | Kinematic viscosity | m·s ⁻¹ |
| | Fluidity | Pa ⁻¹ ·s ⁻¹ |
| | Thermal conductivity | W·m ⁻¹ ·K ⁻¹ |
| | Electrical conductivity | S·m ⁻¹ |
| | Molar conductivity | S·m ² ·mol ⁻¹ |
| | Thermal diffusivity | m ² ·s ⁻¹ |
| | Self-diffusion coefficient | m ² ·s ⁻¹ |
| | Binary diffusion coefficient | m ² ·s ⁻¹ |
| | Tracer diffusion coefficient | m ² ·s ⁻¹ |
| | ReactionStateChangeProp | <i>Potential difference of an electrochemical cell</i> |
| Molar enthalpy of reaction | | kJ·mol ⁻¹ |
| Specific internal energy of reaction at constant volume | | J·g ⁻¹ |
| Molar internal energy of reaction at constant volume | | kJ·mol ⁻¹ |
| Molar Gibbs energy of reaction | | kJ·mol ⁻¹ |
| Molar entropy of reaction | | J·K ⁻¹ ·mol ⁻¹ |
| ReactionEquilibriumProp | Thermodynamic equilibrium constant | dimensionless |
| | <i>Natural logarithm of the thermodynamic equilibrium constant</i> | dimensionless |
| | <i>Decadic logarithm of the thermodynamic equilibrium constant</i> | dimensionless |
| | Equilibrium constant in terms of molality | (mol·kg ⁻¹) ⁿ |
| | <i>Natural logarithm of the equilibrium constant in terms of molality</i> | dimensionless |
| | <i>Decadic logarithm of the equilibrium constant in terms of molality</i> | dimensionless |
| | Equilibrium constant in terms of amount concentration (molarity) | (mol·dm ⁻³) ⁿ |
| | <i>Natural logarithm of the equilibrium constant in terms of amount concentration (molarity)</i> | dimensionless |
| | <i>Decadic logarithm of the equilibrium constant in terms of amount concentration (molarity)</i> | dimensionless |
| | Equilibrium constant in terms of partial <i>p</i> , | (kPa) ⁿ |
| | <i>Natural logarithm of the equilibrium constant in terms of partial <i>p</i></i> | dimensionless |
| | <i>Decadic logarithm of the equilibrium constant in terms of partial <i>p</i></i> | dimensionless |
| | Equilibrium constant in terms of mole fraction | dimensionless |
| | <i>Natural logarithm of the equilibrium constant in terms of mole fraction</i> | dimensionless |
| <i>Decadic logarithm of the equilibrium constant in terms of mole fraction</i> | dimensionless | |

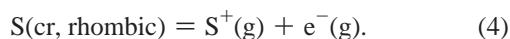
^a Properties in italicized type are additions to the schema.

compilations by Wagman (the *NBS Tables*),²² Chase et al. (the “JANAF Tables”),²⁴ and Rosenstock et al.²³ In ThermoML, the electron is represented in reactions as an ion with the name “electron”, chemical formula “e”, and charge “-1”. For a reaction involving an electron, these quantities are assigned to the following elements in the *Compound* block; **sCommonName** [string], **sFormulaMolec** [string], and **nCharge** [numerical, integer].

Representations of the enthalpy of ion formation in ThermoML are demonstrated with values from the *NBS Tables*,²² and are included as *Use Case 6* in the Supporting Information. Formation properties of ions at infinite dilution are represented as properties of complete reactions involving H₂ and aqueous H⁺ at infinite dilution for which the reaction is



The following reaction for formation of an ion in the gas phase is also included in *Use Case 6*:



Future Extensions

Extensions described in the present paper in combination with those described previously for biomaterials⁴ will constitute new recommendations for the extension of the ThermoML IUPAC standard.⁶

Acknowledgment

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Supporting Information Available:

Six use cases. The use-case numbers and the properties or elements that they demonstrate are listed here. *Use Case 1* demonstrates the element **sPhaseDescription** [string]. The example involves the enthalpy of formation for a hydrocarbon.¹⁵ *Use Case 2* demonstrates the element **nElectronNumber** [numerical, integer]. This use case includes an example of the reaction property *Potential difference of an electrochemical cell*, *V*. The use case is based on an electrochemical study designed to determine the Gibbs energy of formation of an inorganic compound.¹⁸ *Use Case 3* demonstrates the element **eStandardState** [enumeration] for all participants of a reaction at once and for each participant individually. This use case includes an example of the logarithmic representation of an equilibrium constant in ThermoML. The use case is based on a study of the dissociation constants of some amines and alkanola-

mines.¹⁹ Use Case 4 provides examples of representation in ThermoML of the mixture properties *mean ionic activity* and *mean ionic activity coefficient*. The use case is based on a study of the (NaCl + water) system.²⁰ Use Case 5 provides an example of representation of transport numbers for an ion in solution. The particular chemical system used in the example is aqueous LaCl₃.²¹ Use Case 6 provides an example of representation for the enthalpy of ion formation at infinite dilution and for a gaseous ion. The use case demonstrates representation of values from the *NBS Tables*.²² The complete text of the ThermoML schema (in text format) with the extensions described here, plus those for biomaterials.⁴ This material is available free of charge via the Internet at <http://pubs.acs.org>.

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