

# ***Uncertainty: Concepts, definitions, standards, and application to experimental thermochemical and thermophysical property data***

**Authors:** Robert D. Chirico, Eugene Paulechka, Vladimir Diky, Ala Bazyleva

**Institution:** National Institute of Standards and Technology

## **1. Introduction: Why are Uncertainties Important?**

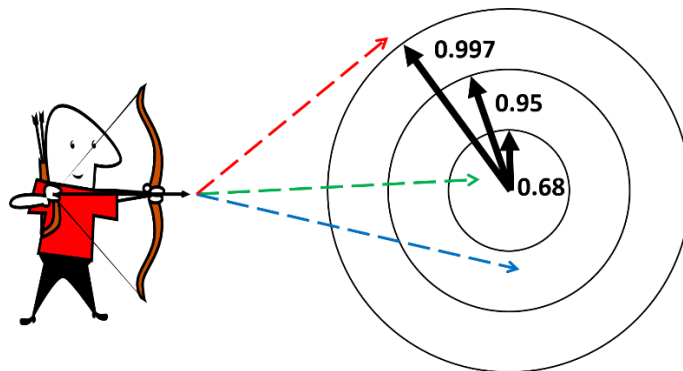
The primary purpose of this book is to present and compare various methods for correlation and prediction of thermophysical properties of gases and liquids. These comparisons are made based on the relative degree of accord with critically evaluated experimental data. In this context, *critical evaluation* means assessment of the uncertainty for the experimental values based on an array of information, including experimental descriptions provided by the authors of the study, comparisons with well established models and correlations, comparisons with other reports of the experimental values in the literature, the experience and knowledge of the particular evaluator, as well as knowledge codified in software systems for computer-aided evaluation.

Beyond the specific needs of this book, it can readily be argued that reliable uncertainties for experimental data are at the core of advancement in the practice and application of all scientific research. In the forward of the first edition of the *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results (1993)*, the Director of NIST, John W. Lyons, summarized the essential nature of uncertainties; “It is generally agreed that the usefulness of measurement results, and thus much of the information that we provide as an institution, is to a large extent determined by the quality of the statements of uncertainty that accompany them.”<sup>1</sup> Reliable uncertainties are a fundamental requirement for the advancement of science. Without reliable uncertainties, it is not possible to determine if a theory is supported or fails, if a process-design model is adequate or must be refined, or if better experimental data (*i.e.*, data with smaller

uncertainties) are required to resolve key questions, whether they arise in development of fundamental theory or in a practical application, such as equipment sizing or safety analysis. If uncertainties for experimental data are poorly known (*i.e.*, we have no characterization of the reliability), the data are of no value for any of the tasks mentioned above.

In the context of this book, reliable uncertainties for experimental data are essential in determining if the data can be used as a meaningful discriminator between various predictions and correlations. Figure 1 provides an analogy for this concept, where the center of the target represents the measured experimental value, and the rings represent regions of probability or “levels of confidence” that the *true* - but unknowable - value lies within that region. (The exact *true value* is unknowable because it is impossible to make a measurement with zero uncertainty.)

For the sake of the example, we assume that the probability distribution for the measurement result is Gaussian or “normal”.<sup>2</sup> The innermost black ring in the figure encloses a range of values for which there is a 68 percent probability (~1 standard deviation) that the true value is within that ring, while the second black ring encompasses the region of 95 percent probability (~ 2 standard deviations), and the third (outer) ring that of 99.7 percent probability (~3 standard deviations).



**Figure 1.** An analogy for comparison of data predictions and correlations with experimental property values.

The red, green, and blue arrows (Fig. 1) indicate values estimated with three alternative predictions or models. Both the blue and green arrows fall within the region of 95 percent probability, and although the green arrow is in slightly better agreement with the experimental value (*i.e.*, closer to the center of the target), there remains a significant probability (5 percent) that the *true value* lies outside of the second black ring. In contrast, the red arrow has landed outside of the third (outer) ring, where there is less than a 0.3 percent probability that the true value is in this region. Although it is not possible to state unequivocally that a particular prediction is “right” or “wrong”, it is accepted practice in the field that values in agreement within the 95 percent range of probability are considered to be in accord. In this case, the experimental value serves as an adequate discriminator between the red and green or red and blue estimates but is of only marginal value in judging the relative quality of the estimates represented by the blue and green arrows. Details of model comparisons will be addressed in a separate chapter of this book.

If all experimental data reported in the literature included reliable uncertainties with well-defined levels of confidence, the task of comparing predictions and correlations would be quite straightforward. Unfortunately, this is not the case and extensive critical evaluation of published experimental data is required to assign best estimates of the uncertainties. All experimental data used in this book for comparison of models and predictions have been critically evaluated within the Thermodynamics Research Center (TRC) of the National Institute of Standards and Technology (NIST; mixtures and pure components) and the Design Institute for Physical Property Data (DIPPR<sup>®</sup>; pure components).

The remainder of this chapter provides a historical perspective on the assessment of uncertainty and an overview of the philosophy and procedures that underlie modern methods of

uncertainty assessment, as outlined in the *Guide to the Expression of Uncertainty Measurement* (also known as the GUM).<sup>3</sup> This approach to uncertainty assessment was developed through international cooperation that included national metrology institutes from around the world, including NIST. Finally, some challenges that are specific to experimental data evaluation in the field of thermophysical and thermochemical properties are discussed.

## 2. Historical Background

The word *uncertainty* is used widely in the English language and has multiple definitions that depend on context. For example, uncertainty is a characteristic of something that is not definitely ascertainable or fixed, as in time of occurrence, number, dimensions, or quality, but can also indicate a lack of confidence or assurance (*i.e.*, an *uncertain* smile), something that is dependent on chance or unpredictable factors (*i.e.*, an *uncertain* outcome), a trait that is unreliable or undependable (*i.e.*, as in *uncertain* loyalties), *etc.*<sup>4</sup> In fact, most definitions of uncertainty have little to do with numerical values, while for the present purposes we are concerned *only* with uncertainty as it applies to numerical results of experimental studies.

For centuries scientists have used a wide variety of terms and phrases when labeling uncertainty information. These terms include *accuracy*, *absolute accuracy*, *error*, *absolute error*, *uncertainty*, *absolute uncertainty*, *maximum uncertainty*, *reproducibility*, *precision*, *known to within...*, *confidently given to...*, *measured to...*, *reliable to...*, *believed to be reproducible to...*, *personally guaranteed to be...*, the symbol +/-, and many more.<sup>5</sup> Unfortunately, none of these terms has a quantitative meaning.

To address the problem of poorly defined uncertainties, *The Guide to the Expression of Uncertainty in Measurement (the "GUM")* was developed over a period of 17 years, culminating with its initial publication in 1993.<sup>3</sup> The GUM was prepared by a working group consisting of

experts nominated by the Bureau International des Poids et Mesures (BIPM), the International Electrotechnical Commission (IEC), the International Organization for Standardization (ISO), and the International Organization of Legal Metrology (OIML). The GUM was developed through cooperation between eleven national metrology institutes.

The GUM describes a philosophy of uncertainty assessment put into mathematical language, without being overly prescriptive or formulaic. When followed, this approach yields well defined uncertainties with specified “levels of confidence” (*i.e.*, probabilities that the true value lies within the given range). Uncertainties are labeled as *standard* or *expanded*. For the *standard uncertainty*, the *level of confidence* (one standard deviation) is part of the definition. For the *expanded uncertainty*, the *level of confidence* must be given explicitly. Without the adjectives *standard* or *expanded*, the term *uncertainty* retains its more general meaning.

An overview of the GUM guidelines is given below. This overview is provided to give the reader sufficient background to understand the framework used in modern critical evaluations of experimental measurements of thermophysical properties reported in the literature. Readers are encouraged to consult the original publications for full details.<sup>1,3</sup>

### **3. Key Documents: The GUM, NIST 1297, and VIM**

As noted above, the *The Guide to the Expression of Uncertainty in Measurement (the “GUM”)* was first published in 1993. Subsequent modifications have been minor and largely for clarification and repair of typographical errors, with the most recent version released in 2008.<sup>3</sup> A closely related document is *NIST Technical Note 1297 (1994 Edition): Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*.<sup>1</sup> The NIST document is more terse than the GUM while providing, essentially, the same information. Lastly, the *International vocabulary of metrology – Basic and general concepts and associated terms (the “VIM3”)*

provides definitions for many common terms found in uncertainty analysis, as well as metrology.<sup>6</sup> The above documents are freely available online (see references), as are the VIM3 definitions with annotations.<sup>7</sup>

In the following section, the concepts and methods of the GUM are discussed within the context of application to uncertainty assessment for experimental thermophysical properties. This discussion is provided to aid the reader in understanding the general data-evaluation process used in assessing the experimental values employed to test the models describe in this book, and it is not meant as a guide for the practicing experimentalist or data evaluator. The terms and definitions provided in this section are in accord with those provided in the GUM<sup>1,3</sup> and VIM<sup>6</sup> to the extent practicable.

#### **4. Uncertainty Assessment for Thermophysical Properties: the GUM Approach**

Some basic concepts and terms need to be defined at the outset. The result of an experimental property measurement is an approximation or estimate of the value of the quantity being sought. The result of the measurement is complete only when accompanied by a quantitative statement of its uncertainty. The quantity to be determined is called the *measurand*, and it is assumed to have an exact value that is unknowable. The *value of the measurand* is also termed the *true value* of the property. Examples of measurands are the critical temperature of hexadecane, the vapor pressure of naphthalene at the temperature  $T = 400$  K, or the gas-phase composition of a two-phase mixture of (ethanol + water) at  $T = 350$  K and pressure  $P = 0.1$  MPa. We presume that these quantities have single exact (*i.e.*, “true”) values, but it is impossible to make a measurement with zero uncertainty.

Uncertainty in a measurement result generally arises from multiple sources or components. In the GUM approach, these components are grouped into two types; those which are evaluated

by statistical methods (“Type A”) and those evaluated by other means (“Type B”). Although this categorization has led to much discussion of whether a particular component is type A or type B, in practice, the distinction is not of high importance, as all uncertainty components are combined without regard to type. In the field of thermophysical properties, the uncertainty components of type A are experimental repeatabilities, while other important components, such as sample purity, calibration data, uncertainties assigned to reference data, equipment manufacturer’s specifications, *etc.*, are type B. Repeatability is defined as the closeness of the agreement between the results of successive measurements for the same measurand carried out under the same conditions of measurement and may be expressed quantitatively in terms of the dispersion characteristics of the results.<sup>3</sup> Repeatability conditions include the same measurement procedure, observer, measuring instrument, location, and repetition over a short period of time. Generally, the type B components are far more important in the assessment of uncertainties for thermophysical properties than the simple repeatability. The key point here is that categorization of uncertainty components into types is not essential in the uncertainty evaluation process. Similarly, other common ill-defined categorizations of uncertainty components, such as “random” or “systematic”, do not alter the evaluation process.

In essentially all determinations of thermophysical properties, the experimental value  $y$  for the measurand  $Y$  (*i.e.*, true value of the property whose value is sought) is not obtained directly. The measurement result  $y$  (*i.e.*, the *estimate* of  $Y$ ) is determined from  $N$  other quantities or pieces of information  $x_1, x_2, \dots, x_N$  through a functional relation  $f$ :

$$y = f(x_1, x_2, \dots, x_N) \tag{1}$$

The uncertainty in  $y$  is obtained through the law of propagation of uncertainty through combination of the uncertainties in each contributor  $x_i$ . It is important to note that the function  $f$

may include information that is difficult to quantify, such as the effect of sample purity or experience of the experimentalist. Nonetheless, these contributors must be considered. This point is amplified below.

In most practical measurements of thermophysical properties, the probability distribution characterized by a measurement result  $y$  is approximately normal (Gaussian). This implies that one standard deviation  $u(y)$  corresponds to a level of confidence of ~68 percent, or if written  $y \pm u(y)$ , there is a level of confidence of ~68 percent that  $y - u(y) \leq Y \leq y + u(y)$ . In other words, there is a ~0.68 probability that the true value lies in the range  $y \pm u(y)$ . The quantity  $u(y)$  is defined as the *standard uncertainty* in  $y$ . It is the convention in the field of thermophysical properties that values should be reported<sup>8</sup> with a 95 percent level of confidence; however, this level of confidence cannot be considered a default or assumed. For a normal distribution, a 0.95 level of confidence is  $2 \cdot u(y)$  and is termed the “expanded uncertainty in  $y$  with 95 percent (or equivalently, 0.95) level of confidence.” The level of confidence must be stated explicitly because the expanded uncertainty refers to any multiple of  $u(y)$ . For example, if this measurement result  $y$  was reported as  $y \pm 3u(y)$ , the uncertainty is still termed the *expanded uncertainty*, but with ~0.997 level of confidence.

The standard uncertainty  $u(y)$  for measurement result  $y$  (eq. 1) is estimated with the law of propagation of uncertainty as follows.

$$u(y) = \left[ \sum_{i=1}^N \left( \frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^N \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u(x_i, x_j) \right]^{0.5} \quad (2)$$

The partial derivatives  $\partial f / \partial x_i$  are termed *sensitivity coefficients*, as they reflect the sensitivity of  $y$  to uncertainty in  $x_i$ . In the second term (*i.e.*, the double summation) within the large brackets of eq. 2,  $u(x_i, x_j)$  represents the covariance between parameters  $x_i$  and  $x_j$ . In the experimental

determination of thermophysical properties this term often is not significant and eq. 2 can be simplified.

$$u(y) = \left[ \sum_{i=1}^N \left( \frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \right]^{0.5} \quad (3)$$

In the GUM,<sup>3</sup> a subscript c is added to the symbol  $u(y)$  [*i.e.*,  $u_c(y)$ ] and  $u_c(y)$  is termed the *combined* standard uncertainty to emphasize that this quantity is obtained through combination of the standard uncertainties in the parameters  $x_i$ . In the measurement of thermophysical properties, common variables, such as temperature and pressure, are themselves determined through combinations of other quantities (voltages, electrical currents, values of resistance and voltage standards, *etc.*) with contributing uncertainties, so distinction between a *combined standard uncertainty* and a *standard uncertainty* becomes ambiguous and arbitrary. We use only the term *standard uncertainty* here, with the understanding that it necessarily is obtained through combination of the uncertainties for contributors  $x_N$  to the measurement process.

The NIST Guide for the Expression of Uncertainty (Technical Note 1297)<sup>1</sup> states, “...the function  $f$  [here, eq. 1] should express not simply a physical law but a *measurement process* (our emphasis), and in particular, it should contain all quantities that can contribute a significant uncertainty to the measurement result.” In measurement of thermophysical properties (and phase equilibria), typical input parameters  $x_i$  include temperature, pressure, and phase compositions, and possibly density, as one would expect based on the constraints of the Gibbs phase rule. However, in the GUM approach, *all* potential sources of uncertainty must be considered and these include sample purity (including decomposition during the experiment), as well as, uncertainties in properties of reference materials and calibrants, laboratory conditions (humidity, temperature, atmospheric pressure, *etc.*), skill of the apparatus operator, appropriateness of

calibration materials, corrections for systematic errors, *etc.* Though some of these are difficult to put into a mathematical form, they must be included in the uncertainty assessment.

A key contributor to uncertainty that is rarely considered in published uncertainty assessments for thermophysical properties is sample purity. The effect of impurities on measurement results can vary considerably depending upon the property and the nature of the impurity. For example, if densities are measured for an ionic liquid (IL) with mass fraction purity 0.98, results are very different if the impurity is water, which is a common impurity in hygroscopic ILs, or simply an isomer of the IL. Authors rarely consider sample purity in their uncertainty analyses. In 2005, a study was made of reporting practices for experimental thermophysical properties, using the determination of critical temperature as a case study.<sup>5</sup> Of 600 articles reviewed, involving ~2000 reports of a critical temperature, only one article<sup>9</sup> considered sample purity as part of the uncertainty assessment. Amongst the 2000 experimental values, some were made on samples with purities as low as 96 percent without consideration of sample quality. In most cases, only repeatability - which is only the lower limit for the uncertainty - was considered in the uncertainty assessments. As noted earlier, repeatability is a relatively small contributor to the uncertainty in measurement of thermophysical properties.

## **5. The Uncertainty Budget**

The most informative approach to reporting an uncertainty analysis in an experimental report is through use of a tabular *uncertainty budget*. The benefits of an uncertainty budget include unambiguous listing of all considered uncertainty sources together with the associated standard uncertainties, sensitivity coefficients, and degrees of freedom. (Detailed information concerning tabular uncertainty budgets can be found on the NIST website.<sup>10</sup>) With this approach, the major contributors to the measurement uncertainty are clear, and the work of the independent reviewer

in determining if important uncertainty sources were overlooked is eased considerably. At this time, uncertainty budgets are rarely seen in the literature outside of some reports from national metrology institutes. As stated in the GUM, the functional relationship for determination of a measurement result (eq. 1) should include *all* sources of uncertainty. This ideal is hardly fully achievable, however; a high-quality uncertainty analysis is much closer to this ideal than a poor one, and explicit listing of all uncertainty sources considered and their estimated contributions within a concise tabular uncertainty budget is invaluable in judging the quality of the assessment. The value of the tabular uncertainty budget is gaining recognition in the field of thermophysical properties, and it is hoped that these will become a common feature in the literature. Although rare, examples of tabular uncertainty budgets can be found (cf. reference 11).

In the absence of an uncertainty budget or explicit consideration of key aspects by the authors of a given experimental report, the data evaluator is forced to make estimates for missing uncertainty contributions. These estimates are based on many factors, including the evaluator's knowledge base for the methods used, known chemical properties of the substance or family of substances studied, likely impurities and their effect, knowledge of calibration methods and calibrants, as well as less tangible considerations, such as the historical reliability of results from a particular research group or laboratory. In the absence of explicit and accurate information from the experimentalists, all estimates are necessarily conservative. Methods used by modern data evaluators are addressed more extensively later in this chapter.

## **6. Reference Materials and Standard Reference Materials**

In the measurement of thermophysical properties, the apparatus used is often calibrated or tested through measurements involving a substance with known properties. Such substances are known as *reference materials* or *standard reference materials*. A *reference material* is a

substance – typically, a pure compound or mixture of a specified composition – for which property values have been critically evaluated with a high degree of confidence (*i.e.*, the uncertainty is well established). It is the responsibility of the experimentalist to obtain or synthesize the sample. Examples of pure compounds with well established property values are liquid water,<sup>12,13</sup> used for calibration of viscometers, densimeters, and some vapor-pressure apparatus (particularly comparative ebulliometers); and sapphire<sup>14</sup> used to calibrate differential scanning calorimeters (DSC) for the measurement of heat capacities.

In many cases, substances are used as reference materials even though the uncertainties for the reference values are not well established. It is simply assumed that the uncertainties in the reference values are much smaller than those generated with the apparatus being tested or calibrated. Examples include benzoic acid, copper, or heptane used to test a calorimeter in determination of heat capacity or naphthalene used to test apparatus used for measurement of sublimation pressures.

In contrast to a *reference material*, a *standard reference material* is a physical material with a certified property value that can be used to test or calibrate a particular apparatus. Certification is done, typically, at a national metrology institute from whom the material can be purchased with a certificate stating the property value and its uncertainty with a well-defined level of confidence. Examples include toluene for the measurement of liquid densities over wide ranges of temperature and pressure [see NIST Standard Reference Material (SRM) 211d],<sup>15</sup> molybdenum for determination of enthalpy and heat capacities for the temperature range  $273.15 < (T/K) < 2800$  [see NIST SRM 781D2],<sup>16</sup> and benzoic acid, used for calibration of combustion calorimeters [see NIST SRM SRM 39j].<sup>17</sup>

It is essential that uncertainties in property values for calibrants be properly propagated into uncertainties of experimental results. Propagation of the uncertainty in calibrant property values in the field of combustion calorimetry (*i.e.*, the enthalpy of combustion of benzoic acid) has been well established since the mid-20<sup>th</sup> century.<sup>18</sup> In other disciplines, application of appropriate uncertainty-propagation procedures by authors is inconsistent, particularly in the measurement of viscosity and density with commercial instruments. Even for combustion calorimetry, some modern reports fail to use the well-established procedures, which has led to development of a website (maintained at NIST) designed to aid experimentalists in providing complete results for publication, while simultaneously providing updates for some of metadata used in typical data reduction.<sup>19</sup> Complete descriptions of the updated metadata are planned,<sup>20</sup> as well as reiterated and updated recommendations for the reporting requirements for combustion calorimetry.<sup>21</sup>

In general, proper propagation of uncertainties in calibrant values to uncertainties in the reported property values often falls to the data evaluator, who must be equipped with the necessary knowledge and tools to provide meaningful uncertainty estimates.

## **7. Challenges for the User of Experimental Data from the Literature**

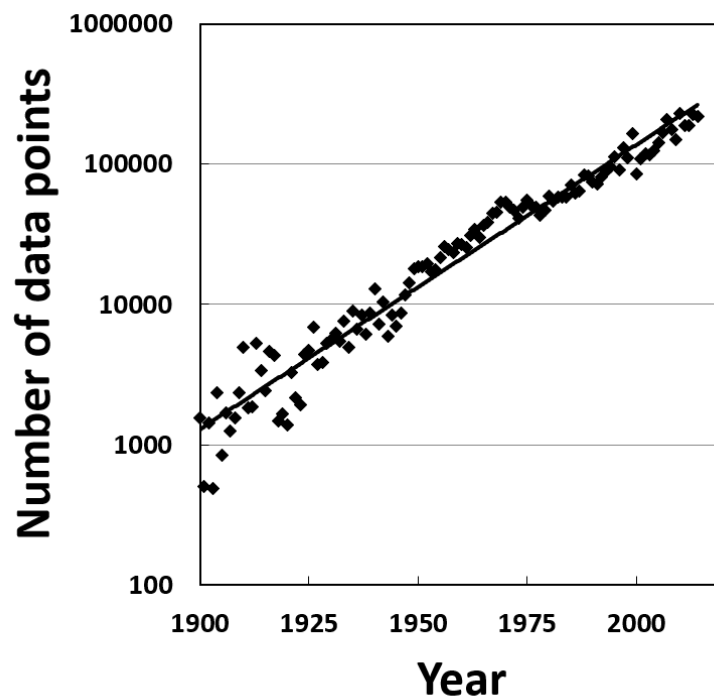
In the field of thermophysical-property and phase equilibrium measurements, the GUM was largely ignored by researchers prior to 2005, with the exception of some reports from national metrology institutes. In contrast, experimental procedures and comprehensive uncertainty assessment had been codified and used in the field of combustion calorimetry for more than 60 years,<sup>18</sup> and it is still valid today with minor modifications in language only.<sup>20</sup> This unfortunate state only started to change when key journals began to require use of the GUM language in reporting of uncertainties.<sup>22</sup> The *IUPAC Guidelines for Reporting of Phase Equilibrium Measurements (IUPAC Recommendations 2012)*<sup>8</sup> made application of the GUM procedures a

requirement in all reports of experimental results for all types of phase equilibrium, as well as for thermophysical and thermochemical measurements on pure compounds. While many key journals have made implementation of these IUPAC guidelines a requirement for their authors, enforcement has been inconsistent. Overall, these developments have promoted awareness of the GUM in the field, but its general and appropriate application remains uncommon. It is our opinion that substantial progress will be made only when the GUM philosophy and procedures are embraced fully by the research community and become part of the core curriculum for all scientists and engineers working in this field.

Although the user of thermophysical property data might consider data quality (*i.e.*, property values with well-defined uncertainties) to be of paramount importance, there are many factors that motivate scientific publication, leading to - at times - competing criteria used to judge quality by the parties involved. Stakeholders in the publication process include article authors (university professors, graduate students, postgraduate researchers, government and industrial laboratory scientists, *etc.*); journal editors, who are also commonly university professors; peer reviewers, who are like the authors by definition; journal publishers; and data users, such as process engineers, model and correlation developers, scientific policy developers, and regulatory agencies. For many of these, the act of publication itself is the primary goal, while subsequent use of the experimental data is secondary. Publication allows degrees to be awarded, tenures granted, new issues published, research grants justified, *etc.* Major *users* of property data, such as those involved in process design and optimization or theory, correlation, and prediction development, are not well represented in the publication or peer-review process. In addition, the data users rarely have the detailed knowledge of key experimental details necessary to critique and improve the uncertainty assessments provided in most publications.

Exacerbating these problems is the fact that journal publishers are known to compete on the basis of submission-to-publication time, perhaps, in part, due to ease of measurement. In contrast, assessment of data quality is a difficult and time-consuming process. In some highly competitive fields, speed of publication is a significant concern, but this is rarely the case in the field of thermophysical properties, where most authors consider the professional standing of the journal to be paramount. Nonetheless, peer reviewers are strongly encouraged to work quickly and often do not have the time or resources to assess the relevant literature, much less to analyze large tables of numerical results for anomalies and inconsistencies. As peer reviewers are drawn from the same pool as authors and editors, they typically reside on the data-producer side of the process, rather than the data-user side, so there is little motivation to do labor-intensive assessments of numerical results.

Another major challenge for the modern data evaluator is the continued acceleration in the quantity of experimental data produced worldwide. Figure 2 shows the number of experimental values (“data points”) for thermophysical properties that were abstracted by NIST TRC from literature dating from ~1800 to the present. The acceleration in data production is ~6% per year, as shown by the dashed curve. This increase implies a doubling of the rate of data publication every 12 years. The growth rate in scientific publications for all fields was analyzed in 2010 and it was concluded that (1) the overall growth rate was near 4.7% per year and (2) the growth rate did not decrease in the previous 50 years.<sup>23</sup> The rate of accumulation for thermophysical-property data readily exceeds that of science in general.



**Figure 2.** Black bars represent the number of experimental thermophysical-property values abstracted by NIST/TRC in a given year for articles published since 1900. The line was calculated based on an increase in the rate of publication of 6 percent per year.

The increase in productivity for thermophysical property measurements is supported, in part, by progress in measurement science, including development of high-precision commercial apparatus for measurement of temperature, pressure, and chemical composition, as well as fully automated data acquisition systems for key properties, such as density, viscosity, heat capacity, *etc.* Unfortunately, this increase in productivity can readily result in data of poor quality due, in part, to the fact that automated commercial equipment does not require involvement of personnel with high degrees of expertise and in-depth knowledge of the measurement principles involved. In addition, untenable uncertainty claims made by some equipment manufacturers seeking a competitive edge, when combined with a demonstrated<sup>5</sup> weak understanding within the scientific community of the meaning of uncertainty and its assessment, readily leads to grossly optimistic

uncertainty assessments. If the uncertainties are of poor quality, meaningful application of the results in model and correlation assessment is lowered substantially.

## 8. Examples of Common Problems in Articles Reporting Thermophysical Properties

In this section, we provide examples of the sort of in-depth knowledge that is necessary to critically assess published reports of measured thermophysical properties. Due to recent efforts, the completeness and reporting quality for many articles has improved, but uncertainty assessment remains a problematic area.<sup>24</sup>

### 8.1 Example 1: Uncertainty contribution from sample impurity

In this example, we consider the contribution of sample impurity to the uncertainty in a measurement of liquid density for a single component. This contribution must be considered for any density measurement irrespective of the measurement principle. If the chemical identity and volumetric behavior of the impurity in mixtures with the main component are known, the effect of the impurity can be computed with a high degree of confidence; however, such information is seldom available, and approximate methods must be used.

The uncertainty due to sample impurity can be estimated approximately based on the following assumptions.

- (1) The impurity is a single component;
- (2) the main component and impurity have densities  $\rho$  differing by a fraction  $\alpha$  at all temperatures, where  $\alpha = \{\rho(\text{impurity})/\rho(\text{main component}) - 1\}$ ; and,
- (3) the excess volume for the mixture (main component + impurity) is zero.

With these assumptions, the following expression is obtained for the relative standard uncertainty in the measured density  $u_r(\rho)$  due to the impurity contribution:

$$u_r(\rho) = |\alpha| \cdot (1 - w_s) / (1 + \alpha \cdot w_s), \quad (4)$$

where  $w_s$  is the sample purity expressed as a mass fraction. This formula can be used if the impurity and its density are known or if the density of the impurity can be reasonably estimated.

In the majority of published density studies, commercial samples are employed, the sample purity is specified by the supplier, and the identity of the impurity is not known. In this case, a further simplification is needed, and the average of the two possible scenarios (*i.e.*, a heavier or lighter impurity) can be used:

$$u_r(\rho) = |\alpha| \cdot (1 - w_s) / (1 - (\alpha \cdot w_s)^2), \quad (5)$$

and  $\alpha$  can be assumed to be 0.1 (*i.e.*, the densities of the main component and impurity differ by 10 percent, which is a conservative estimate). Application of equation (5) to a sample with 0.99 mass fraction purity yields  $u_r(\rho) = 0.001$ , which corresponds to roughly  $u(\rho) \approx 1 \text{ kg}\cdot\text{m}^{-3}$  for many substances. Reports of density measurements for single components with mass fraction purities as low as 0.95 are not uncommon in the literature.

Over the last 25 years or so, densities of pure compounds and mixtures are typically measured with commercial vibrating U-tube densimeters. These instruments require calibration with fluids of known density; typically, water and air. Uncertainty claims by equipment manufacturers are often remarkably small. For example, one commonly used instrument is accompanied by the following uncertainty information: “reproducibility” of  $0.005 \text{ kg}\cdot\text{m}^{-3}$ , and “accuracy (*under ideal conditions and for low densities/viscosities*)” of  $0.007 \text{ kg}\cdot\text{m}^{-3}$ .<sup>25</sup> The terms “reproducibility” and “accuracy” do not have well-defined numerical definitions, and the “ideal conditions” or the range of “low densities/viscosities” are not specified. If “accuracy” is assumed to mean “standard uncertainty”, these values might be appropriate if measurements are made near the calibration point (*i.e.*, on very dilute aqueous solutions prepared from degassed high-purity water), but are clearly inappropriate beyond that. Nevertheless, many researchers use

statements of the manufacturers as uncertainty estimates for all of their measured values, which leads to the common problem in the literature of uncertainties for measured densities being underestimated by several orders of magnitude.

## **8.2: Example 2: Uncertainty associated with calibrant property values**

In this example, we consider the contribution of uncertainty in calibrant values to the uncertainty in a measurement result. Specifically, we consider the measurement of viscosity with a commercial viscometer, but the concepts are also applicable to the measurement of heat capacities with a differential scanning calorimeter or densities with a vibrating tube densitometer.

Commercial viscometers are used in the large majority of viscosity studies and these always require calibration. Calibration is preferred to computations based on the precise determination of the physical characteristics of the instrument (*e.g.*, diameter and length of a capillary, density and radius of a falling ball, *etc.*), which invariably deviate from the ideal shapes assumed in the equations used to model the experiment. Water is commonly used as a calibration fluid, as its viscosity is well studied.<sup>12,26</sup> The 2009 IAPWS reference equation gives the viscosity  $\eta$  of liquid water between 253.15 K and 383.15 K at 0.1 MPa with a relative expanded uncertainty (0.95 level of confidence)  $U_r(\eta)$  equal to 1 percent.<sup>12</sup> (Values for temperatures below that of normal melting and above normal boiling are for metastable liquid water at 0.1 MPa.) Only the single value at  $T = 293.15$  K and  $P = 0.101325$  MPa has been assessed to have a smaller uncertainty ( $U_r(\eta)$  equal to 0.17 percent with 0.95 level of confidence).<sup>27</sup> Toluene has been suggested recently as a reference material for viscometry in the temperature range from 263 K to 373 K and 0.1 MPa pressure with an expanded uncertainty of 0.7% (0.95 confidence level).<sup>26</sup>

Through careful technique, it is possible to obtain a repeatability of 0.1 percent - or even lower - in viscometric measurements. Unfortunately, this repeatability, which represents only a lower limit for the standard uncertainty, is often reported by researchers as the standard uncertainty for the measured viscosities. Clearly, the uncertainty in the viscosity values for the calibration fluids far outweigh such repeatabilities in determining the uncertainty in the measurement result (see Eq. 3).

The uncertainty associated with calibrant property values must be considered for any apparatus requiring calibration with a reference material. Consequently, proper assessment of literature values can only be done with an in-depth knowledge of the physical properties of the calibrants, as well as the evaluated uncertainties in their reference property values.

**Example 3: Propagated uncertainty in the composition of a binary mixture**

Uncertainty in the composition of a binary mixture is a contributor to the uncertainty in any property measurement for that mixture, and, in the case of phase equilibrium studies, may be the primary focus of the study. This example is illustrative for composition analyses made with analytical methods or for estimation of composition uncertainty due to sample impurities.

Here, we consider a binary mixture for which relative standard uncertainties in the amounts of components 1 and 2 are  $u_r(n_1) = u(n_1)/n_1$  and  $u_r(n_2) = u(n_2)/n_2$ , respectively. Propagation of uncertainties for the mole fraction of the first component  $x_1 = n_1/(n_1 + n_2)$  gives

$$u(x_1) \approx x_1 x_2 \sqrt{u_r(n_1)^2 + u_r(n_2)^2} \quad (6)$$

If  $u_r(n_1) = u_r(n_2)$ , then eq. (1) simplifies to

$$u(x_1) \approx x_1 x_2 u_r(n) \sqrt{2} \quad (7)$$

This equation would be appropriate if, say, the amount of each component was determined with a relative standard uncertainty of 1 percent using gas-liquid chromatography. In this case, the

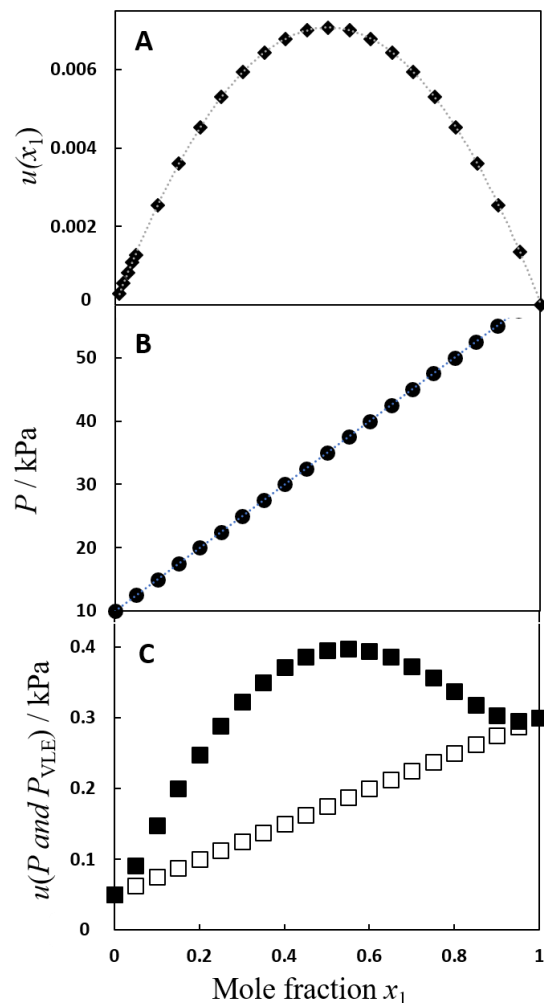
relative standard uncertainty in the composition of the mixture would reach its maximum value ( $u_r(n)\sqrt{2}/4$ ) at the equimolar composition.

Extension of Eq. 7 to a three-component system yields the following:

$$u(x_1) \approx x_1 u_r(n) \sqrt{(x_2 + x_3)^2 + x_2^2 + x_3^2} \quad (8)$$

In Eqs. (6) through (8), the component indices are interchangeable. When assessing the uncertainty of a property for any mixture, the composition uncertainty must be propagated into the uncertainty of the property value, as per Eq. 3. The magnitude of this contribution depends on the sensitivity of the property to changes in composition (*i.e.*,  $\partial f/\partial x_i$  of Eq. 2).

Figure 3 shows the results of the uncertainty calculation for measured vapor-liquid equilibrium pressures  $P_{VLE}$  as a function of composition for a hypothetical binary mixture. For the example, the standard uncertainty in composition is taken as 2 percent (or  $u_r(n_1) = 0.02$ ) and the standard uncertainty for the measured pressure is  $u_r(P) = 0.005$ . Figure 3A shows the standard uncertainty in  $x_1$ , as per equation 6. Figure 3B shows the measured VLE pressures, which are taken as linear with composition to simplify the calculations. The filled symbols in Figure 3C show the standard uncertainty  $u(P_{VLE})$  with propagation of  $u(x_1)$  and  $u(P)$  into that of the measurement result  $u(P_{VLE})$ . The unfilled symbols at the bottom of the figure show the result obtained for  $u(P_{VLE})$  that is obtained if the uncertainty in composition is ignored, resulting in estimated uncertainties that are too low by more than a factor of two near  $x = 0.5$ .



**Figure 3.** Example of propagation of uncertainty in composition for a binary mixture. Details are provided in the text.

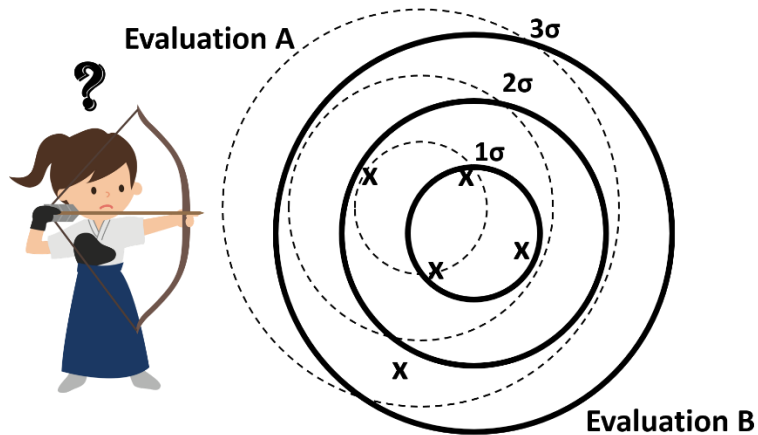
**Example 4: Uncertainty for binodal composition determined by titration**

A binodal composition (or liquid-liquid equilibrium (LLE) composition or liquid-liquid solubility) can be determined by titration of a transparent solution of known composition with another liquid or solution until turbidity is observed. The procedure can be reversed and, thus, the turbid system can be titrated to a clear solution. In many experiments, the volume of titrated solution is on the order of (10 to 50) mL. The volume of droplet depends, in part, on the composition of the solution, and for water, it is typically ~0.03 mL or somewhat larger. To

estimate the uncertainty in the endpoint, one can assume that the densities of both solutions are  $\sim 1000 \text{ kg}\cdot\text{m}^{-3}$  and the volume of the titrated solution is 30 mL. Then, in a best-case scenario that includes reliable detection of the turbidity upon addition of a single droplet, a well-calibrated burette, an accurate mass of the initial solution, and good temperature control over the entire apparatus, the standard uncertainty for the mass fraction can be estimated  $u(w) \approx 0.03 / 30 = 0.001$ . This value is an estimate of the lower limit of uncertainty for these measurements. This value also represents an approximate lower limit of solubility that can be determined by titration. Considering all contributions,  $u(w) \approx 0.005$  is realistic limit.

## **9. Modern Uncertainty Assessment Procedures (Critical Evaluation)**

**9.1. Introduction.** The phrase “critically evaluated data” is often encountered in descriptions of collections of property values. Unfortunately, the term is poorly defined, and can mean as little as averaging a few values of ill-defined origin or can imply an extensive analysis of carefully curated experimental data. Any data collection that is claimed to be “critically evaluated” without a description of how the evaluation is done is necessarily suspect. A high-quality critical evaluation involves consideration of numerous factors, some of which cannot be readily quantified, but which can be used in weighting the results of one report relative to another. The degree of the relative weighting will depend on the knowledge, experience, and established procedures of the particular evaluator or evaluating organization. Because of such factors, it is extremely unlikely that any two critical evaluations will agree exactly in value and uncertainty, but if both are done well, the evaluations should be consistent within the specified uncertainties. This concept is depicted in cartoon form in Figure 4.



**Figure 4.** An analogy to reinforce the concept that critical evaluation does not produce a unique result. The two overlapping targets represent two independent critical evaluations for the same property that are different, but consistent.

In Figure 4, the archer could represent, for example, an experimentalist wishing to use a critically evaluated property value to aid in calibrating an instrument; or - as in the case of the present book – a researcher seeking reference data to evaluate alternative models or predictions. Independent critical evaluations are represented in figure 4 by the two three-tiered targets (dashed lines represent evaluation A and solid lines represent evaluation B). Though the evaluations are based on the same experimental values (the **X**'s), the evaluating organizations used different weighting factors and arrived at slightly different, but consistent results. The experimentalist/researcher will need to further weigh the results of the critical evaluations in carrying out their work. The “weighting” of the critical evaluations could be based on the quality of the uncertainty assessments provided with each evaluation, but clearly, there is no single correct answer. This example further reinforces the concept that the exact *true value* of a given property is unknowable.

The following sections (9.2 – 9.8) describe the various factors used in critical evaluation of the property values used in this book. Although details of the methods used by the organizations

involved (NIST/TRC and DIPPR<sup>®</sup>) differ, both are based on a thorough search and collection of the primary experimental literature and evaluation through consideration of the factors below. All evaluations by DIPPR<sup>®</sup> are for pure compounds, while those at NIST/TRC are for pure and binary and ternary mixtures. Some factors discussed below are necessarily for mixtures only.

**9.2. Article content analysis.** The general quality of the content of an article reporting experimental property results can be judged against the *Guidelines for Reporting of Phase Equilibrium Measurements (IUPAC Recommendations 2012)*.<sup>8</sup> In spite of the title, these recommendations can be applied to all reports of thermophysical and thermochemical property measurements, and a simple checklist is provided that enumerates the key information that should be given (*e.g.*, complete chemical sample information, appropriate detail of apparatus and experimental procedures, “stand-alone” tables with all quantities and uncertainties well defined, data validation through consistency checks and model fitting where possible, and assessment and comparison with previously published data). Full details and descriptions are given in the IUPAC recommendations.<sup>8</sup>

A report that is closely aligned with the IUPAC guidelines of 2012<sup>8</sup> is strongly preferred to one that forces the evaluator do such things as guess the probable sample purity, assume calibrations were done appropriately, deduce the meaning of poorly defined uncertainties, or even guess key experimental conditions, such as temperature and pressure, when not given. Weightings of the experimental data based on this assessment is at the discretion of the evaluator. Each evaluating organization may have some general “rules of thumb” for this sort of general assessment, but any rigorous algorithm is not possible.

**9.3. Literature comparisons.** Evaluation of any reported values necessarily includes comparison with the existing literature, which requires extensive search, collection, and

information extraction. General chemical search systems such as Chemical Abstracts (SciFinder)<sup>28</sup> and Reaxys<sup>29</sup> are valuable search tools, but often give inadequate information to assess what has been reported, resulting in the collection of many irrelevant articles, such as those reporting correlations and estimations. Other scientific databases such as Web of Science<sup>30</sup> can also be useful, but they are hampered by a non-scientific, human language-based search syntax.

High-quality measurements of thermophysical properties were first reported as early as the 19<sup>th</sup> century, and the most efficient way to access the older data is through reference books and reviews. This is extremely labor intensive because of the absence of electronic indexes in most cases, and simply locating and obtaining key reference books is a difficult search task in itself. The often-overlapping content of reference books increases the work needed to execute a comprehensive data search.

Property evaluations for this book are based on two extensive and well-curated databases of experimental property values: (1) the DIPPR<sup>®</sup> Database<sup>31</sup> of experimental properties and (2) the NIST/TRC SOURCE Database.<sup>32</sup> The DIPPR<sup>®</sup> Database was created in support of property evaluations for specific pure compounds (49 properties for ~2500 compounds) and is available through American Institute of Chemical Engineers (AIChE).<sup>31</sup> The NIST/TRC SOURCE Database is the experimental data archive associated with the NIST ThermoData Engine, which is available through NIST (Standard Reference Database 103a<sup>33</sup> and 103b<sup>34</sup>). The NIST/TRC SOURCE Database is not focused on specific chemical systems, but has the goal of coverage for as many pure, binary, and ternary chemical systems as is practical. At present this includes property data for 24000 pures, 57000 binary mixtures, 17000 ternary mixtures, and 8000 chemical reactions.

**9.4. Consistency with endpoints.** In the evaluation of properties for mixtures, an important consideration is the comparison of mixture values with independently evaluated endpoint properties, such as pure-component values for binary mixtures and binary endpoints for multi-component mixtures. Specific examples are consistency of vapor-liquid equilibria with pure-component vapor pressures or solid-liquid equilibria with pure-component melting temperatures. If the coverage of the composition space is extensive, comparison with endpoints is a simple extrapolation task. If composition gaps are wide, the comparison will require data modeling.

In many cases, available experimental data for pure components is more extensive and of higher quality (*i.e.*, lower uncertainty) than that for mixtures. This allows an added insight into the quality of the mixture results, which would not be possible through consideration of the mixture data in isolation. Multiple examples of the use of pure-component data to identify anomalous results for mixtures have been reported in articles authored by members and associates of the NIST Thermodynamics Research Center.<sup>24,35</sup> These methods have even been used to “repair” literature reports, where components were misidentified or experimental conditions (temperature or pressure) were incorrectly specified.

As noted above with regard to article content analysis, uncertainties deduced through endpoint-consistency analysis in critical evaluation for a specific chemical system will necessarily vary between evaluator or evaluating organization. Nonetheless, endpoint-consistency analysis is an essential tool in assessment of data for multicomponent systems, and is practical only where an extensive database of experimental properties is available.

**9.5. Property prediction.** The primary purpose of property predictions in critical evaluation of experimental data is the efficient identification of gross errors. Often, predicted (or computed) property values have only rough estimates of uncertainty themselves or none at all, which greatly

reduces their value in critical analysis. Evaluation of uncertainties for prediction methods is a research area that has been largely ignored in the field of thermophysical properties, but recently advancement have begun to be made, particularly in the area of prediction of enthalpies of formation for organic compounds.<sup>36,37</sup> Nonetheless, some property predictions have been established to be as good or better than experimental determinations, such as those for virial coefficients and heat capacities of simple dilute gases, (*cf.*, references 38 and 39]), and gas-phase enthalpies of formation for many types of organic compounds.<sup>36</sup>

Property prediction methods vary considerably in the extent of their physical basis and reliance on experimental data used for parameterization. Well known group-contribution methods include those for enthalpies of formation, heat capacities, and entropies of organic compounds in the ideal-gas state by Benson,<sup>40</sup> and UNIFAC predictions, first described by Fredenslund et al.<sup>41</sup> for prediction of phase equilibria involving vapors and liquids. The effectiveness of these predictions is evidenced by the continued interest in extending and improving their experiment-based parameterizations (*cf.*, references 42-44). The prediction of critical properties for pure compounds with the method of Joback<sup>45</sup> is another well-known example of such a method, with parameters published in the previous version of this book.<sup>46</sup> All group-contribution methods are strongly dependent on the quality of the underlying experimental values.

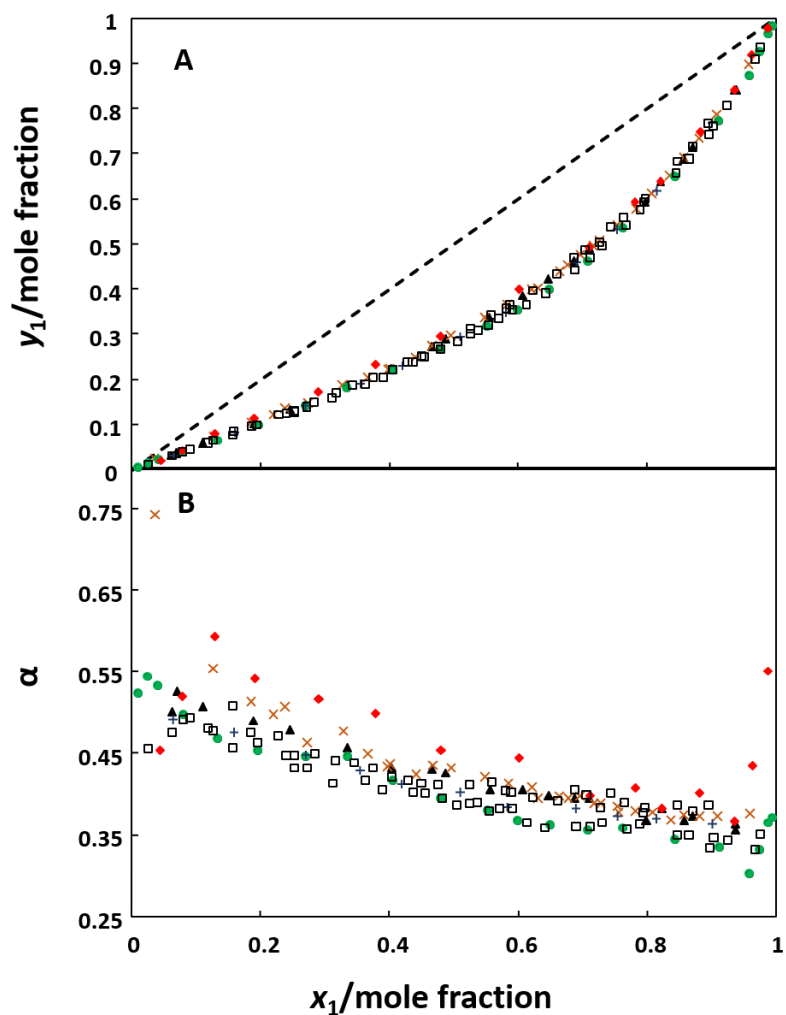
Other more recently developed prediction methods are COSMO-based models for phase equilibrium<sup>47-49</sup> and predictions for critical constants based on Quantitative Structure–Property Relationships (QSPR) methodology combined with the Support Vector Machines (SVM) regression.<sup>50</sup> Although all of these methods still require critically-evaluated property values for parameterization, the underlying quantum chemical methods allow the parameters to be founded

on a more physical basis than the earlier group methods. Of the results for these newer methods that are based, in part, on the results of computational chemistry, computed enthalpies of formation have been most extensively analyzed, and uncertainties near those for the best experimental studies have been established.<sup>37</sup>

**9.6. Single-property Regression and Visualization.** Fitting of models (*i.e.*, mathematical equations) to property data is an essential aspect in the critical evaluation process for any property, even including those that are invariant as per the Gibbs Phase Rule, such as the solid-liquid-gas triple point temperature or the critical temperature and pressure. Models are useful for many purposes, including comparison of multiple data sources, calculation of derivatives necessary for propagation of uncertainty in variables, extrapolations for end-point consistency assessment, data scatter detection (random deviations), and possibly, data bias (*i.e.*, deviations correlated with state variables). Inadequate models or erroneous data may cause bias, and determining whether the model or the data are at fault is challenging, particularly with models involving a flexible number of parameters, where overfitting is a concern. Any model must be physically valid and in accord with validity rules, whether empirical or theoretical. Such rules define numerical ranges of valid model parameters and shapes of temperature, pressure, and composition dependence.

Visual analysis requires efficient generation of alternative graphical representations, and tools that allow transformation of plots into functions of any model variable are necessary. In recent articles concerning assessment of data quality for vapor-liquid equilibria, Mathias<sup>51,52</sup> has recommended use of “K values” (the ratio of the mole fraction of a component in the vapor to that in the liquid) and relative volatility  $\alpha$ , where  $\alpha = y_1*(1-x_1)/\{x_1*(1-y_1)$ . VLE measurements often cover a broad range of compositions (from 0 to 1 mole fraction). When multiple data

sources are plotted on a single  $xy$ -diagram, it is difficult to assess the relative quality of the datasets, particularly at the composition extremes (Figure 5a). However, when the compositions are converted to relative volatility (Figure 5b), the relative data scatter becomes clear. A general solution for revealing model and data behavior near composition endpoints has been proposed in the literature.<sup>53</sup> For binary mixtures, it consists of the transformation of the composition variable  $z$  (mole or mass fraction) to  $\log\{z/(1-z)\}$  for plotting.



**Figure 5.** (A) Gas-phase composition against liquid phase composition. (B) Relative volatility  $\alpha$  (defined in the text) against liquid phase composition. The chemical system is {toluene (1) + cyclohexane(2)} and values based on the following sources are shown:  $\square$ ,<sup>54</sup>;  $\blacklozenge$ ,<sup>55</sup>;  $\bullet$ ,<sup>56</sup>;  $\times$ ,<sup>57</sup>;  $+$ ,<sup>58</sup>;  $\blacktriangle$ .<sup>59</sup>

The quality of a modeling result can be analyzed algorithmically or visually. Numerical criteria are used at NIST/TRC to determine the model sufficiency (termed “adequacy”) and model bias. The adequacy  $A$  is calculated as

$$A = (1/n) \sum (d_i/U_i)^2, \quad (9)$$

where  $n$  is the number of data points,  $d_i$  is the deviation from the model for the  $i$ -th data point, and  $U_i$  is the expanded uncertainty (0.95 level of confidence) associated with it. Bias is estimated from the absolute weighted deviations. Details have been published in reference 60. Although this chapter is concerned with critical evaluation of experimental data from the literature, it is apparent that if validated experimental data are used, the derived adequacy and bias can be used to judge the relative efficacy of alternative models. Consistency with experimental data, as well as general thermodynamic consistency must be considered in assessment of any model, and this topic follows.

## 9.7. Thermodynamic consistency

**9.7.1. Equations of state (EOS) (pure compounds).** Implementation of an EOS allows, in principle, evaluation of all thermodynamic properties of the system simultaneously. In general, an EOS establishes a relationship between the thermodynamic variables of the system, temperature  $T$ , volume  $V$ , and pressure  $P$ . For one mole of pure substance, the equation of state can generally be expressed as

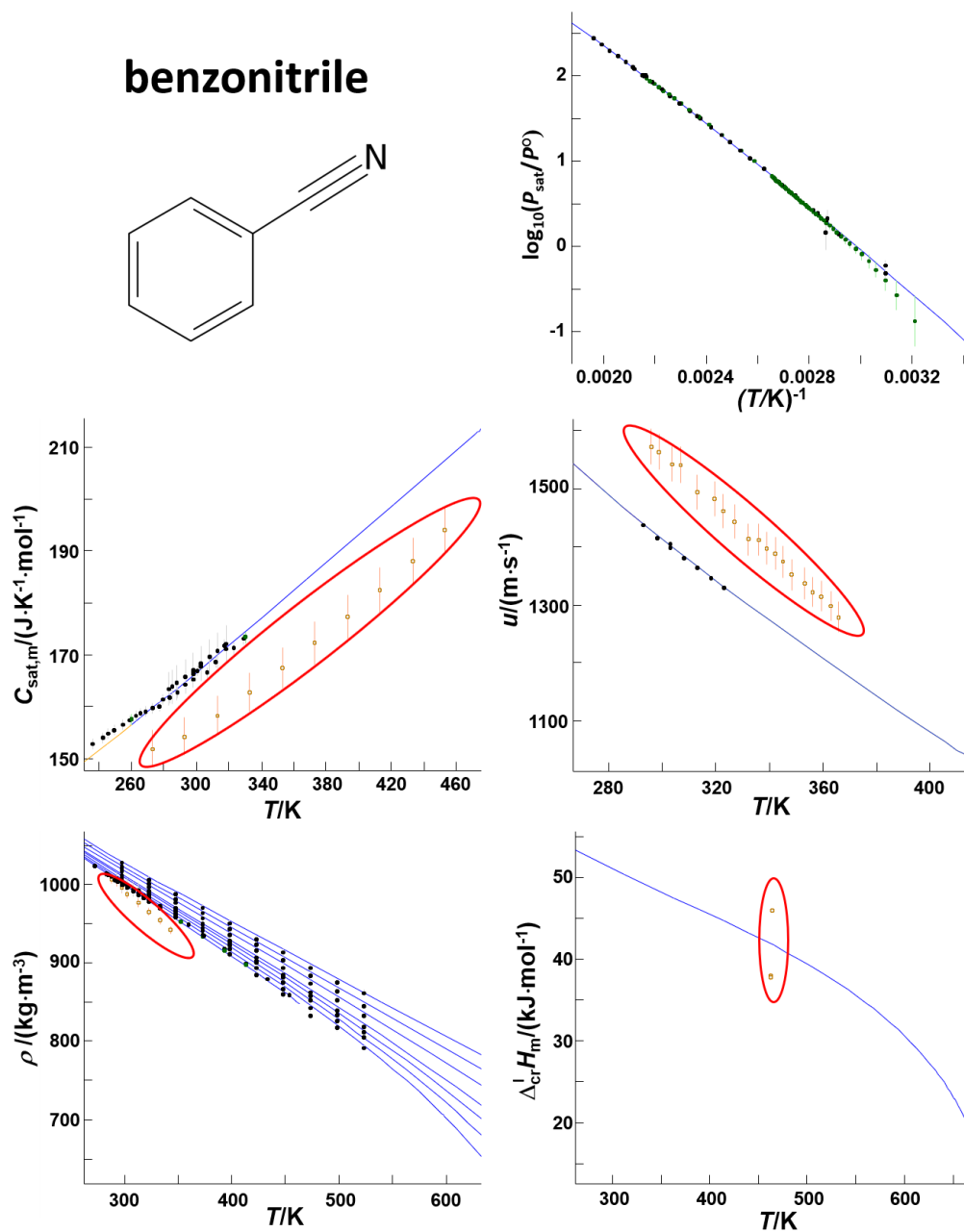
$$PV = RT + f(T, P) \quad (10)$$

where  $R$  is the gas constant. EOS range considerably in complexity from the van der Waals EOS<sup>61</sup> to the 56-parameter Span-Wagner EOS that is used for water.<sup>62</sup> Selection of an EOS for a particular compound depends strongly on the particular data scenario (*i.e.*, the variety, quality,

and extent of the available experimental data). In spite of this complexity, even a relatively simple EOS can be helpful in identifying inconsistent or anomalous data.

At NIST/TRC a range of EOS can be deployed on demand for various data scenarios. These include the Volume-Translated Peng-Robinson,<sup>63</sup> plus several subsequent variants,<sup>64-67</sup> the Modified Sanchez-Lacombe,<sup>68,69</sup> the PC-SAFT (with and without association),<sup>70</sup> and the 12-term Span Wagner formulation (polar and non-polar).<sup>71</sup> For the types of compounds considered in this book, equations of state are limited to those modeling the liquid and gas phases. The solid state must also be considered, but alternative consistency tests must be applied, as described later in this chapter (section 9.7.2).

A sample result obtained through application of the 12-term Span-Wagner EOS is shown in Figure 6, where simultaneous consideration of measured values for vapor pressure, enthalpy of vaporization, liquid density, liquid heat capacity, and speed of sound allowed identification of anomalous property values in the literature for benzonitrile. The simultaneous consideration of all properties was particularly valuable for evaluation of enthalpy of vaporization, speed of sound, and liquid heat capacity, where large inconsistency is seen between the few existing datasets. References to the experimental data plotted in Figure 6 can be found in reference 72.



**Figure 6.** Results of application of the 12-term Span-Wagner EOS to experimental values of vapor pressures  $P_{\text{sat}}$ , liquid density  $\rho$ , enthalpy of vaporization  $\Delta_{\text{cr}}^1 H_m$ , and liquid heat capacity  $C_{\text{sat},m}$ , and speed of sound  $u$  for benzonitrile. The blue lines represent values calculated with the equation of state. Anomalous values are circled in the figures.

**9.7.2. Properties represented by separate equations (pure compounds).** As noted above, equations of state for molecular compounds are typically limited to the fluid phases (gas and liquid), and consistency with solid phases cannot be addressed. However, thermodynamic

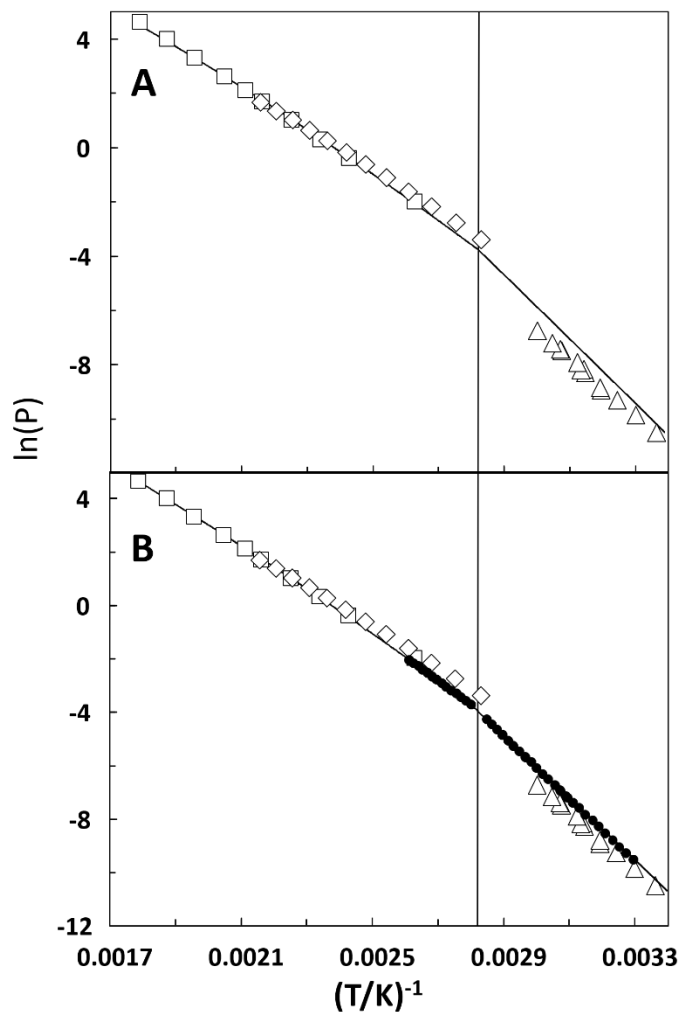
consistency between properties of gas, liquid, and solid phases can be determined through consistency requirements that are checked and enforced for models associated with different phases.

Software implementation of extensible thermodynamic constraints in the NIST/TRC critical analysis tool *ThermoData Engine* (TDE) has been described in the literature.<sup>73</sup> The principles of consistent evaluation are similar to those for EOS fitting and are based on an objective function that combines the effect of deviations from fitted data and violation of thermodynamic constraints. Thermodynamic constraints implemented in TDE involving both fluid and solid phases are consistency between (1) vapor and sublimation pressure at the triple point, (2) enthalpy of fusion, vaporization, and sublimation at the triple point, (3) sublimation pressure and the gas-solid heat capacity difference, and (4) sublimation pressure and enthalpy of sublimation. Particular constraints on models for individual properties are also implemented. Examples are the Waring constraint,<sup>74</sup> which helps ensure a valid shape for the vapor pressure curve, and the compressibility-factor  $Z$  constraint, which ensures for a subcritical gas that  $Z$  is less than one and increases with temperature with a negative second derivative with respect to temperature along isobars (see reference 73 for details).

When different properties are represented by independent equations, inconsistencies can become apparent. In the absence of information that would allow rejection of some data, the uncertainty in the assessed property values is necessarily as large as the difference between the available data and property values derived through consistency enforcement. An example of such an assessment follows.

Figure 7A shows a plot of vapor and sublimation pressures for 3-methoxy-4-hydroxybenzaldehyde (commonly known as vanillin). The crystal-liquid-gas triple point

temperature  $T_{\text{tp}}$  and enthalpy of fusion  $\Delta_{\text{cr}}^1 H_{\text{m}}$  near ambient pressure have been reported many times in the literature, and the assessed values have the expanded uncertainty  $U(T_{\text{m}}) \approx 1$  K and relative expanded uncertainty  $U_{\text{r}}(\Delta_{\text{cr}}^1 H_{\text{m}}) \approx 0.1$ , respectively, with 0.95 level of confidence. The normal melting temperature and  $T_{\text{tp}}$  may be taken as equivalent due to measurement uncertainties. In Figure 7A, it is apparent that extrapolations of the vapor pressures for the liquid and solid do not meet at  $T_{\text{tp}}$ . The blue lines represent the critically evaluated vapor pressures  $p$  with relative expanded uncertainty  $U_{\text{r}}(\Delta_{\text{cr}}^1 H_{\text{m}}) \approx 0.2$  for both phases within 30 K of  $T_{\text{m}}$ . The large uncertainties in the assessed vapor and sublimation pressures reflect the poor thermodynamic consistency between the experimental values. This result is in spite of the small scatter (*i.e.*, good repeatability) for the individual datasets.



**Figure 7.** Vapor and sublimation pressures for vanillin. The vertical line indicates the triple-point temperature, and the blue curves represent the critically evaluated property values. The symbols  $\square$ ,  $\Delta$ ,  $\diamond$ , and  $\bullet$ , represent experimental values reported in references 75-78, respectively.

Recently, new vapor and sublimation pressures were reported for vanillin that support the above analysis.<sup>78</sup> As seen in Figure 7b, the new vapor and sublimation pressures are in excellent accord at  $T = T_m$ . In addition, the change in slope of the plot at  $T = T_m$  is consistent with the evaluated enthalpy of fusion, adding further confidence in the new measurement results. Relative expanded uncertainties (0.95 level of confidence) for the vapor and sublimation pressures near  $T$

$= T_m$  are now reduced confidently to  $U_r(p) \approx 4$  percent for both phases, as a result of the thermodynamic consistency analysis.

### 9.7.3. Consistency tests for phase equilibrium studies on binary mixtures.

Development and application of consistency tests for all types of phase equilibrium measurements continues to be an active area of research. The purpose of this section is not to exhaustively describe the variety of consistency tests used in the literature, but rather to provide an overview of how some common tests are used collectively in the assessment of phase equilibrium data at NIST/TRC.

For the assessment of VLE binary data, an algorithm is used that combines four widely used tests of consistency based on the requirements of the Gibbs-Duhem equation in combination with a check of consistency between the property values at the composition extremes of the VLE binary data and the corresponding pure-component vapor pressures.<sup>35</sup>

A VLE data set must satisfy the constraint established by the Gibbs-Duhem equation,

$$\sum x_i d\bar{M}_i - \left(\frac{dM}{dP}\right)_{x,T} dP - \left(\frac{dM}{dT}\right)_{x,P} dT = 0 \quad (11)$$

where  $M$  is a molar thermodynamic property;  $\bar{M}_i$  is a partial molar property; and  $T$ ,  $P$ , and  $x$  are temperature, pressure, and liquid composition, respectively. The summation here and in the following equations is over the  $i$  components in the chemical system. If the property  $M$  is the excess Gibbs energy  $G^E$  divided by  $RT$ , where  $R$  is the gas constant, then,

$$M \equiv \frac{G^E}{RT} = \sum x_i \ln \gamma_i \quad (12)$$

and,

$$\sum x_i d \ln \gamma_i - \frac{V^E}{RT} dP + \frac{H^E}{RT^2} dT = 0 \quad (13)$$

where  $\gamma$  is an activity coefficient;  $V^E$  is the excess volume; and  $H^E$  is the excess enthalpy.

Equations 11 to 13 are the foundation for the VLE consistency tests used in the algorithm.

Specific consistency tests used in the algorithm are the *Herington Test*<sup>79</sup> that provides an indication of the compliance with the Gibbs-Duhem equation over the entire composition range, the *Van Ness Test*<sup>80</sup> that shows how well an activity coefficient model can reproduce the experimental data, the *Point Test*<sup>81,82</sup> that is used to assess the differential properties of  $G^E$ , and the *Infinite Dilution Test*<sup>81,82</sup> provides a test of the limiting behavior of  $G^E/(x_1x_2RT)$  and the activity coefficients  $\gamma_1$  and  $\gamma_2$ . The effectiveness of each test depends upon the particular data scenario (*i.e.*, the range in  $T$ ,  $P$ , and  $x$ , and the data density to allow meaningful extrapolations and calculation of derivatives). Test results are combined with a measure of the consistency with pure-component vapor pressures to yield an overall numerical quality factor for the dataset. The quality factors are useful in weighting individual datasets when multiple sets are available for a given chemical system. Full details and many examples are provided in reference 35. A high-pressure equation of state (EOS) test was subsequently added to expand the range of application.<sup>83</sup>

In the case of LLE data, the Gibbs-Duhem equation can also be applied; however, the experimental data needed to test for consistency are commonly lacking.<sup>84</sup> The large majority of experimental LLE data are obtained near atmospheric pressure, and are reported as LLE temperatures  $T$  as a function of composition. Such data are fitted with an empirical equation with an adjustable number of parameters. This approach is useful in identifying anomalous datasets, but only when numerous consistent measurements are available. Prediction of LLE data with group-contribution models (*i.e.*, UNIFAC) or other methods based on computed molecular

parameters (*e.g.*, COSMO) do have the well-defined uncertainties needed to be useful in the critical evaluation process.

The primary consistency test for solid-liquid equilibria (SLE) is based on the equation

$$\ln\left(\frac{1}{\gamma_1 x_1}\right) = \frac{\Delta_{\text{cr}}^1 H_m}{RT_m} \left(\frac{T_m}{T} - 1\right) - \frac{\Delta C_p}{R} \left(\frac{T_m}{T} - 1\right) + \frac{\Delta C_p}{R} \ln\left(\frac{T_m}{T}\right) \quad (14)$$

where  $x_1$  and  $\gamma_1$  are the mole fraction and activity coefficient of component 1 in the liquid phase,  $T_m$  and  $\Delta_{\text{cr}}^1 H_m$  are the temperature and molar enthalpy of melting of component 1,  $\Delta C_p$  is the heat capacity of the liquid minus that of the solid at the melting temperature,  $R$  is the gas constant, and  $T$  is the SLE temperature. Two criteria are assessed in the limit of  $x_2 \rightarrow 0$ ; (1) the limiting intercept must be in accord with the normal melting temperature of component 1, and (2), the limiting slope must be in accord with the enthalpy of fusion of component 1. Examples are provided in reference 84.

Due to the limited variety and amount of experimental VLE, LLE, and SLE data available for ternary mixtures, consistency checks are largely limited to comparisons with results for the component binary systems at the ternary composition extremes.<sup>84</sup> This is analogous to assessing the consistency of properties of binary systems with those of their pure constituents. Such assessments are only possible with extensive and well curated collections of experimental data, such as those that underlie the critically evaluated experimental data used in this book.

Analysis of thermodynamic consistency, particularly for vapor-liquid equilibrium experiments, continues to be an active area of research. Some recent examples include work by Olson,<sup>85</sup> Wisniak et al.,<sup>86</sup> and Carrero-Mantilla et al.<sup>87</sup>

**9.8. Trends in a series of compounds (pure components).** A less rigorous but still powerful check can be based on variation of property values in families of compounds with systematic

structural differences, such as incremental variation with addition of  $-CH_2-$  or functional groups. Less common structural differences can also be harnessed, and constructing sets of related substances can be automated.<sup>88</sup> Variation of property values in such sets should be generally smooth, excluding the smallest molecules in the set, odd-even effects, and some property-specific effects, such as formation of plastic crystals and micellization. This approach is most effective in identifying anomalous data that can skew a critical assessment toward unphysical results.

## **10. Summary**

Evaluation of prediction and correlation methods can only be based on comparisons with critically evaluated property data founded on experimental measurements. To be of use in these comparisons the critically evaluated data must have well-defined uncertainties with a reliable level of confidence. An international standard (the GUM) has been established that outlines the philosophy and procedures to be used in assessment of uncertainties in measurement. Although this standard has been in place for more than 25 years, it is only rarely well applied in studies of thermophysical properties and phase equilibria published in the scientific literature. In this chapter, we have summarized the GUM approach and described some of the challenges encountered when trying to apply the GUM procedures to uncertainty assessment for published experimental data. Some specific examples are given of common errors and omissions in uncertainty assessments encountered in the modern literature. Finally, an overview is given of tools and procedures for the assessment of uncertainties assigned to reference data used for evaluation of the prediction and correlation methods in preparation of this book.

## **11. Disclaimer**

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