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# Uncertainty of thermodynamic properties available via online data banks: Vapor pressure as case study

Lecuna, M.<sup>1</sup> and Sassi, G.<sup>2</sup>

**Key words:** uncertainty evaluation, montecarlo simulation, vapor pressure data

Online databanks are a convenient source of information whenever thermodynamic properties are required for calculations, in both scientific and engineering environment. The data listed in these repositories is usually reported along with a range of validity and their sources. The values of the thermodynamic properties can usually be retrieved from databases and handbooks, in the form of tables, curves or correlations with regression parameters. Most of the times, no information is given on the uncertainty of the reported estimates, let alone regression parameters in the case of correlations [Dong (2005)]. Evaluating the sources of uncertainty in any model is fundamental to verify the significance of the results for a specific application. Knowing the uncertainty, makes the difference between trusted values and random values. Depending on the model where the property is required and its application (the use of results), the contribution to the total uncertainty of thermodynamic properties and constants can surpass the contributions of other experimental input quantities. In this work, the methods described in the “Guide for the expression of uncertainty in measurement” [JCGM (2008)] are used to evaluate the uncertainty of a thermodynamic property of a pure substance, calculated based on the constants and references reported in two important online data banks (NIST and Dortmund Databank) [NIST (2017)] [Dortmund (2016)]. The vapor pressure is considered as case study and several definitions with their relevant sources of uncertainty are presented.

The aim of the work is to highlight the limitations of properties data commonly used in engineering estimations, as well as the importance of accounting for their uncertainty. Following established metrological guidelines, a full procedure have been developed, with particular considerations aimed to account for the ‘quality’ of the realization of the definition of the measurand as a source of uncertainty of the property.

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<sup>1</sup> Maricarmen Lecuna

Politecnico di Torino, Corso Duca degli Abruzzi 24, e-mail:  
maricarmen.lecuna@polito.it

<sup>2</sup> Guido Sassi

Politecnico di Torino, Corso Duca degli Abruzzi 24, e-mail:  
guido.sassi@polito.it

## 1. Data and Methodology

Antoine Equation model was considered as measurand equation based on the availability of data in many databases and databanks. Monte Carlo algorithm was implemented to estimate the uncertainty of the regression parameters and the coefficient of determination was introduced into the uncertainty analysis to account for the suitability of the model. Finally, a comparison was performed, between the results of vapor pressure estimated with databanks correlations and the results obtained with regressions over different sets of raw experimental data (retrieved from the databanks references). The Antoine equation parameters of five substances, namely acetone, acetonitrile, ethanol, butanol and methanol, were listed from NIST and Dortmund databanks and the references associated to them were identified. A total of ten data sets were identified, with articles dating back to 1926.

Both the linearized and non-linearized equations were used to estimate the parameters of regression: A, B and C constants. Montecarlo simulations have been performed to estimate the probability distributions of each regression parameter. After obtaining the uncertainty of each parameter, an uncertainty budget of the vapor pressure can be built. Besides the regression parameters, the temperature is the only influence quantity. An additional influence quantity was introduced in the budget to account for the suitability of the model to the experimental data, i.e., the realization of the definition of the measurand as source of uncertainty. The suitability of the model was estimated as function of the coefficient of determination of the models obtained in Montecarlo simulations.

The sensitivity to the dataset was analysed performing the same procedure with different sets of data. The obtained results were similar to those reported by the databanks in terms of precision, however differences in the uncertainty were observable based on the number and distribution of the available experimental points. The form of the equation (linearized or non linear) was observed to play an important role in the increase of the uncertainty of the property.

With this work we evidence the importance of relying on experimental data and raise awareness of the impact that introducing correlation constants could have on results, if a proper quantification of uncertainty is omitted. The use of a case study illustrates how datasets could be improved just by applying formal metrological procedures to already available raw data.

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