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

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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 souce 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.

References

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