New Approaches for the Development of Helmholtz-Energy Based Multi-Parameter Property Models for Fluid Mixtures with Limited Data

Jessica Buchenfeld[1, S, C], Eric W. Lemmon[2], Roland Span[1] and Monika Thol[1]

[1]*Chair of Thermodynamics, Ruhr University Bochum, Bochum, Germany*
[2]*Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO, U.S.A.*
Jessica.Buchenfeld@thermo.ruhr-uni-bochum.de

In the field of energy and process engineering, thermodynamic properties are essential for the design and optimization of processes and technical facilities. In this context, mixtures play an important role. Accurate properties for binary and multicomponent mixtures are currently provided through fundamental multiparameter equations of state in terms of the Helmholtz energy. In mixture models, the pure-fluid parts are combined at corresponding states via the composition, where there are four reducing parameters that can be adjusted to experimental data. In order to achieve higher accuracies, the model can be extended by an arbitrarily complex departure function, which is empirical. This increases the flexibility of the equation so that, for example, fluids that are physically very different from each other and can no longer be described with the corresponding states approach can also be modeled.

The reducing parameters as well as the coefficients and exponents of the departure function are adjusted to experimental data. The departure function with an arbitrarily high number of adjustable parameters poses a numerical challenge and requires a large amount of experimental data with conventional adjustment strategies. This is already a problem when modeling pure fluids, as laboratory experiments are time-consuming and cost-intensive. In the case of mixtures, the composition is an additional variable, which makes it even more difficult to measure the entire fluid surface. Therefore, boundary conditions are used to control the physical behavior of the equations of state to ensure correct extrapolation behavior despite high numerical flexibility. For pure substances, this has proven to be very successful over the last 20 years, so that empirical Helmholtz energy equations of state can now be developed for comparably poorly measured fluids. Similar research for fitting mixture equations has not been fully investigated. In this work, possible boundary conditions for the development of mixture models are presented.