Generalized Equations of State for the Calculation of Thermodynamic Properties of Hydrocarbon Mixtures

Monika Thol [C, S], Robin Beckmüller, Tobias Dietl and Roland Span
Thermodynamics, Ruhr University Bochum, Bochum, NRW, Germany
m.thol@thermo.rub.de

Eric W. Lemmon
Applied Chemicals and Materials Division, NIST, Boulder, Colorado, U.S.A.

The knowledge of thermodynamic properties is important for safe and efficient design in energy and process engineering. Accurate properties for mixtures are currently provided through fundamental equations of state in terms of the Helmholtz energy. These models are based on existing pure-fluid equations of state, which are combined in binary mixture models considering pairwise interactions of every component involved in the mixture. For multicomponent mixtures, the pairwise interactions are weighted by the composition and combined in a multifluid approach.

The parameters of the binary mixture models are adjusted to experimental data. Depending on the data situation, the mixing approach can range from quite simple to fairly complex based on simple combining rules or comprehensive departure functions, respectively. As a guideline, the more comprehensive and accurate the data, the more accurate the modeling of the mixing parameters can be. Since experiments are costly and time-consuming, investigations in the laboratory generally focus on the main components of the mixture, e.g., methane, ethane, and propane for natural gases. However, recent investigations [1] showed that trace elements such as long chain hydrocarbons (e.g., pentanes or hexanes) also have a significant impact on the accuracy of the mixture model. Therefore, these components should be modeled as accurately as possible. However, this work is hindered by the lack of accurate measurements for mixtures with long chain hydrocarbons – the required data base is not available.

To overcome this problem, a new approach is presented here, which combines the idea of applying a generalized mixture model for fluid groups with a new functional form of the departure function and modern fitting techniques. Preliminary results for methane-rich multicomponent hydrocarbon mixtures (including alkanes from methane to decane) and CO_2-rich and hydrogen-rich mixtures with hydrocarbons are presented as examples.

References

[1] *M. Thol, M. Richter, E. F. May, E. W. Lemmon, and R. Span (2019), "EOS-LNG: A Fundamental Equation of State for the Calculation of Thermodynamic Properties of Liquefied Natural Gases", J. Phys. Chem. Ref. Data 48, 033102*