Empirical Multiparameter Equations of State – State of the Art and Steps to Come

Roland Span [C, S]
Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Bochum, Germany

Eric W. Lemmon
Thermophysical Properties Division, National Institute of Standards and Technology, Boulder, Colorado, U.S.A.

Empirical multiparameter equations of state are the most accurate source of calculations available to date for the description of the thermodynamic properties of fluids. Commonly formulated as fundamental equations of state in terms of the reduced Helmholtz energy since the 1980s, they allow for a consistent calculation of all kinds of thermodynamic properties. In the 1990s, empirical multiparameter equations of state were able to describe properties of well measured fluids within the accuracy of the most accurate experimental data available – a generation of reference equations of state became available, which are used in a multitude of scientific and technical applications today. Key to this broad application was the development of user friendly software tools. Towards the end of the 1990s it became obvious that the number of fluids for which data sets were available that were sufficiently broad and accurate for the development of reference equations of state was rather limited. Ongoing experimental efforts extended this basis to further technically important fluids, and in parallel new methodical approaches were developed to address the large number of technically important fluids for which data sets were more restricted. Thus the number of fluids for which accurate multiparameter equations of state were available could be increased quite significantly. Current work aims at the extension of this approach to strongly associating fluids. Around 1995, approaches describing well measured binary and multi component mixtures with an accuracy comparable to the accuracy achieved for pure fluids became available. These models are now commonly used for many refrigerant mixtures, for ammonia-water systems, for mixtures of air components and for natural gases. The development described above has always been an interaction between experimental work, detailed analysis of available data sets, and the development of new methodologies. Nonlinear direct fitting to a broad variety of data types, optimization of the functional form, inclusion of terms addressing special needs, investigation of the extrapolation behavior, and finally the development of suitable mixture models have been key steps. This talk will review relations between these methodologies and what has been achieved over the last several decades. Based on the description of this status quo, we will address the question of what the likely future developments in the field of multiparameter equations of state will be. This includes the further development of fitting and optimization strategies, the description of strongly associating fluids, inclusion of data resulting from molecular simulation, and challenges resulting from the accurate description of technically highly relevant mixtures.