Caloric Properties from Empirical Fundamental Equations of State

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For well measured, technically and scientifically relevant fluids and fluid mixtures empirical multiparameter formulations in form of fundamental equations of state have been established as reference for thermodynamic properties. Well known examples for reference equations of state are those for carbon dioxide[1], nitrogen[2], and water[3] – equations of state for fluids with excellent data sets, which are frequently applied not only in technical applications but also for calibration purposes. A number of fluids that are only relevant for technical applications are described with very high accuracy today, too; in particular this is true for some refrigerants[4]. Among the mixture models, the development of accurate property models based on multiparameter fundamental equations of state has focused on natural gas[5] and CO_2-rich[6] mixtures. Some of these models were formally accepted as international standards[7,8], others have been established as de facto standards by the scientific community and by internationally used software products[9].

The drawback of empirical multiparameter equations of state is that they can only achieve high accuracy for fluids, for which accurate experimental data are available. Studies on suitable mathematical structures for fundamental equations of state, the use of algorithms optimizing their mathematical structure, and finally the use of constraints in nonlinear fitting[4] have significantly improved the numerical stability of multiparameter equations of state[10]. They extrapolate well and yield reasonably accurate results in (limited) regions without data as well. However, multiparameter equations of state still depend on the availability of accurate experimental data in broad ranges of states, and estimates for the uncertainty of property values calculated from such equations can only be established by comparison to experimental data.

A crucial advantage of fundamental equations of state is that values for all thermodynamic properties are calculated from derivatives or from a combination of derivatives of a single surface spanning over temperature and density, respectively over temperature, density and composition for mixtures. Different properties calculated from a fundamental equation of state are not necessarily accurate, but they are always consistent to each other. As a consequence, fundamental equations of state can be based on data for those properties that can be measured with highest accuracy.

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Today, multiparameter fundamental equations of state are mostly based on density and speed of sound data at homogeneous states. Highly accurate equipment for density[11,12] and speed of sound[13,14] measurements has been developed to provide the required data for pure fluids and mixtures. Beside this, accurate information on vapour-liquid equilibria is mandatory to precisely describe the location of the phase boundary. Extensive data sets have been provided for pure reference fluids and a number of mixtures.

Experience shows that fundamental equations of state based on highly accurate density and speed of sound data describe caloric properties like heat capacities more accurately than the available experimental data. For diluted gas states this statement and its limits can easily be proven. However, for higher density and correspondingly large residual effects these relations become more complex. To date it is not possible to base traceable uncertainty statements for caloric properties on deviations observed for densities or speeds of sound. Mathematical approaches can be derived, but to verify or to falsify their applicability, comprehensive sets of highly accurate data for heat capacities or enthalpy differences would be required at least for some reference fluids.

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