Development of a Reference Equation of State for Natural Gases and Other Multicomponent Mixtures Covering the Gas and Liquid Region Including the Vapor-Liquid Phase Equilibrium

O. Kunz [S] and W. Wagner [C]
Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, Bochum, Germany

M. Jaeschke
Ruhrgas AG, Dorsten, Germany

We are working on a reference equation of state for the thermodynamic properties of natural gases and other multicomponent mixtures covering the gas and liquid region including the vapor-liquid phase equilibrium. The project was initialized a few years ago as part of a research project which was carried out in cooperation with companies of the European natural gas industry. The present status of the development is a new reference equation of state for natural gases. This fundamental equation currently covers 18 natural gas components, namely methane, nitrogen, carbon dioxide, ethane, propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, n-heptane, n-octane, water, hydrogen, carbon monoxide, oxygen, argon and helium. The formulation is explicit in the reduced Helmholtz energy, with its independent variables: density, temperature, and composition. Similarly to existing mixture models, we calculate the Helmholtz energy as the sum of the ideal gas contribution, a contribution from the pure fluid equations combined at the reduced temperature and the reduced density of the mixture, and a departure function. The reducing functions used for temperature and density depend on the mole fraction. The new equation of state allows the properties of typical natural gases to be calculated with the highest possible accuracy. The uncertainty in density and in speed of sound at typical pipeline conditions is less than ±0.1%. The same is true for the uncertainty in density of various types of natural gases in the temperature range from 270 K to 350 K at pressures up to 30 MPa. In order to be predictive for a wide range of compositions, which means to be predictive for a variety of different natural gases, the new equation of state was developed using only data of binary mixtures. Comparisons with experimental multicomponent mixture data show that the new reference equation not only allows a very accurate description of the thermodynamic properties of typical and other common natural gases, but for the first time also enables the accurate description of rich natural gases (RNG), liquefied natural gases (LNG), compressed natural gases (CNG) and liquefied petroleum gases (LPG). Furthermore, the new equation of state is able to describe both natural gases containing a high fraction of hydrogen (hythanes) and binary mixtures of natural gas components with hydrogen very accurately. Besides the accurate handling of special gases, we also consider describing accurately the thermodynamic properties of air including its vapor-liquid phase boundary.