Determination of Thermodynamic Properties of Liquids from Comprehensive Speed-of-Sound Data Sets by Thermodynamic Integration

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Based on comprehensive and accurate speed-of-sound data sets measured in the laboratory of the authors, accurate values of the density, isobaric heat capacity, and further properties for several fluids, such as n-butane, isobutane, n-pentane, and toluene, were determined by the method of thermodynamic integration [M.J. Dávila, J.P.M. Trusler, J. Chem. Thermodynamics, 41,35, 2009]. The initial values for the density and isobaric heat capacity required for the numerical integration of the partial differential equations were derived from the speed-of-sound data and very accurate density data sets at low pressures. For each fluid, a correlation of the speed-of-sound data as a function of temperature and pressure was developed with the linear structural optimization technique of Wagner [Fortschr.-Ber. VDI-Z., Reihe 3, Nr. 39, 1974]. Comparisons with literature data, equations of state, and accurate density data, which were measured with a vibrating-tube instrument in the laboratory of the authors, demonstrate that very accurate values for the density and isobaric heat capacity can be determined by the method of thermodynamic integration at little cost and with uncertainties comparable to those of the best experimental techniques. The high accuracy is achieved by a fine manual adjustment of the initial conditions so that the derivatives of the density and isobaric heat capacity exhibit physically reasonable behavior. This powerful method reduces the effort for density measurements in the liquid region and improves the data basis for the development of wide-ranging Helmholtz energy formulations.