

## Determination of Heat Capacities at Constant Volume from Isochoric and Isothermal Data

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It is well known that thermodynamics allows calculation of calorimetric properties for fluids from equations of state using experimental pressure/density/temperature data. However, the technique has found little use because these data lacked enough accuracy to approach calorimetric measurements. However, with the introduction of highly accurate magnetic suspension densimeters, it has become interesting to check the technique once again. The approach of this work is to use an analysis of experimental first and second derivatives of pressure with respect to temperature at constant density along with residual properties to determine energies, entropies and heat capacities. Those derivatives can come from fitting isochoric data or from using numerical differentiation. The uncertainty of the heat capacities is a function of the uncertainty of the fit used to characterize the isochoric data and the impact of using numerical and analytical derivatives to solve for real properties. This work applies the methodology to experimental isochoric and isothermal data of a ternary mixture with mole fractions of 0.95014 methane, 0.03969 ethane and 0.01017 propane. The matrix of the data contains 10 isochores and 5 isotherms covering a range of temperature from 140 to 500 K at pressures up to 200 MPa. In addition, the paper proposes a new strategic way to develop experimental design and data acquisition techniques to allow building a complete thermodynamic characterization of fluids using a highly accurate magnetic suspension densimeter (MSD).