

## **Accuracies of Energies and Entropies Derived from “Isochoric” Measurements: Implications for the Design of a Simple Automated Apparatus**

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Enthalpies and entropies are of importance to the design of fluid process equipment such as compressors and heat exchangers. It is especially difficult to measure enthalpies of vaporization for mixtures using conventional calorimetric techniques. An alternative approach is to derive the energies and entropies from *PVT* measurements. This approach is valid, although seldom used, for connecting properties across the two-phase vapor-liquid region. In this work, we assess the potential for obtaining energy data from *PVT* measurements with accuracy comparable or superior to that of calorimetric measurements. We have made such measurements in the past with our existing isochoric apparatus, but this design does not allow for convenient automation of the measurements, and the rate of data acquisition is too slow.

In this work, we assess the feasibility of a very simple design which is easily automated, but exploits the capabilities of existing pressure transducers. Because most transducers are far more precise when held at fixed temperature, the new design operates with a small portion (the pressure transducer) of the total sample volume held at a fixed temperature while the main cell changes temperature along the “isochore”. Proper design of the cell reduces the error introduced by holding a small volume at constant temperature to approximately the same magnitude as that introduced by temperature and pressure distortions of the cell volume. Because no sample container is truly isochoric over a significant range of temperature and pressure, adjustments must be made to correct for non-isochoric effects. We have developed a strategy that allows us, when using the new design together with a second apparatus, capable of isothermal density measurements, to achieve derived energies and entropies which are competitive in accuracy with calorimetric measurements, but with a procedure and design that is easily automated.