Thermodynamic Reference Data

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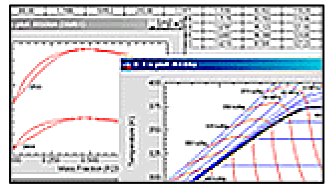
Databases are the primary technology transfer vehicle by which we deliver our collective expertise in fluid properties to our customers. Much of our theoretical, modeling, and experimental efforts are directed toward improving and extending the databases to meet customer needs.

NIST expands the REFPROP (Reference Properties) database to include over 20 new fluids of industrial importance including hydrogen sulfide, carbon monoxide, nitrous oxide, toluene, xenon, and R227ea.



New "short-form" equations of state (EOS) for twenty new fluids describe all of the thermodynamic properties using a fixed functional form based on the Helmholtz energy. The short fixed form allows us to calculate properties for fluids with limited data sets but with higher accuracies (typically 0.1 % to 0.5 % in density, 1 % to 3 % in liquid heat capacities and sound speeds) than previously attained for these fluids. REFPROP has also been improved by the addition of equations for the dielectric constant of both pure fluids and mixtures.

The REFPROP database has been the *de facto* standard in the refrigeration industry for many years. NIST was a key player in the new ISO standard for refrigerant properties, which adopts the same formulations as those used in REFPROP.

These new short-form equations of state are based on state-of-the-art EOS for reference fluids. We have advanced the state-of-the-art for EOS with new formulations for R125 and propane containing new terms and using new fitting techniques designed to make the equations more fundamentally sound. (Traditional high-accuracy EOS were highly empirical and did not have the proper behavior beyond the range of the data, while theoretically based EOS had proper qualitative behavior but were not of high accuracy.) The new functional form eliminates certain nonphysical behavior in the two-phase region. The addition of nonlinear fitting constraints has yielded an equation that achieves proper phase stability, *i.e.*, only one solution exists for phase equilibrium at a given state. We have developed new fitting techniques to ensure proper extrapolation of the EOS at low temperatures, in the vapor phase at low densities, and at very high temperatures and pressures.

Development and validation of these high-accuracy equations of state require extensive, high-accuracy experimental data, and our recent measurements include the heat capacity (C_V) and density (p-ρ-T) of propane. Between C_V and p-ρ-T, our measurements cover the entire fluid range from the triple point to 500 K, including low-density gas states and compressed liquid states up to 36 MPa. The p-ρ-T data include extensive measurements near the gas-liquid critical point. These data, combined with new terms in the EOS, allow us to determine (using only single-phase data) the critical point at least as accurately as the available literature values.

CSTL researchers will port the computational engine of REFPROP to the Thermo-Data Engine (TDE), a new NIST database providing on-demand correlation of experimental data. This will give TDE the advantage of the inherent thermodynamic consistency of representing properties with equations-of -state versus the present approach of representing different properties with discrete correlations. Models for aqueous (water-based) systems and hydrocarbon mixtures containing hydrogen and helium will also be developed.