New VLE and Calorimetric Data for Binary Mixtures of Light Hydrocarbons, and Stringent Tests of Equations of State at Low Temperatures and High Pressures

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New *PTxy* data are reported for binary mixtures of methane + ethane, methane + propane, methane + 2-methylpropane, and methane + butane over a temperature range from (203 to 273) K at pressures up to 9 MPa. Isobaric heat capacity data are reported for liquid mixtures of methane + propane and methane + butane at pressures between (4.7 and 6) MPa and temperatures between (108 and 178) K. The VLE measurements help identify the literature data sets which are erroneous or have relatively large uncertainties but are still frequently included in the development of new equations of state. The new data are compared with both the GERG-2008 and Peng Robinson EOS as implemented in commercial process simulation software. While the multi-parameter EOS generally describes the VLE data more accurately than the cubic EOS as the critical region is approached, there are important cases such as CH_4 + C_4H_{10} at 244 K where the simpler EOS is significantly more accurate. When compared with the mixture heat capacity measurements, the GERG EOS predictions were generally within (2 to 5) % of the data, whereas the Peng-Robinson EOS predictions deviated by around 10 %. However, when extrapolated to 118 K and butane mole fractions of 0.4, the deviations in the mixture heat capacities predicted by two EOS increased to 110 % and 21 % for the GERG and cubic EOS, respectively. These comparisons also suggest a method of identifying measurement conditions where new experimental data would be most valuable.