Physical-Constant Based p-V-T Equations-of-State

Leslie Woodcock [C, S]
Physics, University of Algarve, Faro, Algarve, Portugal
lvwoodcock@ualg.pt

Since van der Waals renowned two-term equation for Andrews experimental CO2 p-V isotherms, incorporating his "continuity of gas and liquid" hypothesis, cubic equations for thermodynamic fluid property data banks require ever-increasing numbers of terms and fitted parameters as the experimental measurements have increased in intensity and accuracy [1]. Functional forms that accommodate the hypothesis of "continuity of gas and liquid" along critical and supercritical isotherms may become inadequate in the vicinity of the critical temperature (T_c) and pressure (p_c), and the supercritical density mid-range between gas- and liquid-like states. A mesophase, within percolation loci that bound gas and liquid states by discontinuities in 3rd derivatives of Gibbs energy, has been identified [2]. State functionals of the mesophase density are linear combinations. Both gas- and liquid-state pressures can be represented by 3- or 4-term virial expansions. Gas states require only known virial coefficients, and physical constants belonging to the fluid, i.e. Boyle temperature (T_B), T_c, p_c and coexisting densities of gas (ρcG) and liquid (ρcL) at T_c. A notable finding is that for isotherms below T_B, the contribution of 4th-virial term is near-zero within experimental uncertainty. Use can be made of a symmetry between gas and liquid in the state-function rigidity $(dp/d\rho)T$ [2] to specify lower-order liquid-state coefficients. Selected isotherms were previously reported for exemplary fluids, CO2, argon, water and SF6, with focus on the critical region [3]. Here, we report equations-of-state for argon, over the whole equilibrium fluid range, and compare with the Tegeler-Span-Wagner equation for experimental data via the NIST fluid thermophysical property database [4].

References:

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