

An Improved Helmholtz Energy Model for Properties of Air and Related Systems

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The work presented in this communication is derived from the Helmholtz energy model previously presented by Estela-Uribe [1] for the prediction of thermodynamic properties of air. The objective was to improve on the overall performance of the new model as compared with respect to results obtained with the reference equation of state and mixture model for air by Lemmon et al. [2]. On the other hand, this application to air and related systems is a test case for the model to be extended further to much more complex systems, such as natural gas. The new model retains most of the structure of the model of [1], i.e. the mixture residual Helmholtz energy is given as the sum of a leading term plus a correction term. The leading term is an extended corresponding states (ECS) model with temperature- and density-dependent shape factors relative to nitrogen and conventional one-fluid mixing rules with constant binary interaction parameters. The reference-fluid properties are calculated with the Span et al. [3] reference equation of state for nitrogen. The correction term is a local composition (LC) mixing rule of a binary interaction temperature- and density-dependent function. The LC model is based upon the generalised van der Waals partition function and a coordination number model for square-well fluids. Unlike the model of [1], in which the correction function was linear in density, in this work that function is quadratic in density, which upon differentiation in the zero-density limit leads to mixture second virial coefficients that are consistently quadratic in composition. Although this is a small correction in numerical terms, it is nonetheless an important technical advantage of the new model. The results obtained, in terms of percentage average absolute deviations (AAD), were: for air, AAD of 0.090 for densities, 0.58 for isochoric heat capacities, 0.15 for speeds of sound, 0.28 for bubble-point saturation pressures, 0.30 for dew-point saturation pressures, 3.98 for bubble-point saturation densities, 1.36 for dew-point saturation densities and 1.87 cm³/mol for second virial coefficients. For binary systems: for (N₂ + O₂), 0.0057 for orthobaric densities and 0.63 for saturation pressures; for (N₂ + Ar), 0.14 for densities and 0.34 for saturation pressures and for (O₂ + Ar), 0.039 for orthobaric densities and 0.31 for saturation pressures. For oxygen, 0.067 for densities, 0.044 for saturation pressures, 0.14 for saturated-liquid densities and 0.11 for saturated-vapour densities. For argon, 0.055 for densities, 0.34 for saturation pressures, 0.032 for saturated-liquid densities, 0.45 for saturated-vapour densities, 0.15 for isochoric heat capacities, 0.14 for isobaric heat capacities and 0.011 for speeds of sound. These results compare very favourably with those obtained with the model of [1] and are entirely comparable to those obtained with the two models of [2]. Given these good results, the model will be further extended to natural gas systems.

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[3] R. Span, E.W. Lemmon, R.T. Jacobsen, W. Wagner, *Int. J. Thermophys.*, 19 (1998) 1121-1132.