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An improved Helmholtz energy model for air and the related systems

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ABSTRACT

In this work a Helmholtz energy model is applied to the prediction of thermodynamic properties of air, the related binary mixtures and the intervening pure components. The Helmholtz energy of the mixture is represented as two contributions: one from a proven accurate extended corresponding states model and the other is a correction term. The corresponding states model relies on pure-component shape factors relative to nitrogen and extension to mixtures with the van der Waals one-fluid mixture model with ordinary combining rules. The correction term is temperature-, density- and composition-dependent with the use of a theoretically consistent local composition model with a coordination number model derived from lattice gas theory. For air the obtained average absolute deviations in densities were 0.090 per cent, 0.15 per cent in speeds of sound, 0.28 per cent in bubble-point pressures and 0.30 per cent for dew-point pressures. For the three associated binary mixtures, the absolute average deviations in densities were within 0.14 per cent and 0.63 per cent for bubble-point pressures. For oxygen and argon, the absolute average deviations were within 0.07 per cent in densities, 0.45 per cent in VLE properties and 0.012 per cent in speeds of sound.

1. Introduction

The purpose of this work is to present a model for the prediction of thermodynamic properties of air and the related binary and pure-component systems that is an improved development of a model published previously [1].

As it is widely known, Helmholtz energy models are useful and very accurate tools for the prediction of thermodynamic properties of both pure fluids and mixtures due, in part, to the formal relationship between the residual Helmholtz energy and the thermodynamic surface and derived properties. This is proven by the success of the multiparameter fundamental or reference equations of state (EoS) in predicting almost all the thermodynamic properties with accuracy within the experimental uncertainty over a very wide range of physical conditions with outstanding examples being the reference EoS's for methane [2], nitrogen [3] and carbon dioxide [4]. For the application to mixtures two avenues may be followed: one is the treatment of the mixture as a pseudo-pure component for which an EoS is developed such as the recent fundamental EoS for air by Lemmon et al. [5], whereas the other approach is the mixture models that express the mixture Helmholtz energy as the contribution of ideal-mixture and excess terms, examples of which are those published by Lemmon et al. [6,7] and the model dedicated for air that was also published in [5].

An alternative avenue to produce very accurate approximations to the residual Helmholtz energy is the generalised corresponding states models (ECS), examples of which have been presented by the author et al. for pure fluids [8] and for natural gas systems [9]. Building upon that experience and following the general approach of the Helmholtz energy mixture models, the author and colleagues [1,10] proposed that a very accurate mixture model can be construed from an ECS model, which gives the basic contribution to the residual Helmholtz energy, complemented with a correction term that accounts for a supplemental contribution due to the differences in intermolecular forces between unlike species.

The structure of the model presented in this work is very similar to that of [1], i.e. the mixture Helmholtz residual energy is given as the contribution of an ECS term plus a correction term which is a temperature- and density-dependent mixing rule in terms of local compositions, which are, in turn, calculated from a coordination number model for square-well fluids. Unlike the model of [1], in which the correction term depended on temperature and density and the density functionality was linear, in this work the correction term depends on the mixture reduced temperature and density and the density functionality is quadratic. The rationale for this device is twofold: the correction term is more flexible as the reducing functions for temperature and density are dependent on composition by means of a mixture model and the use of a quadratic density function allows for the whole model to render second virial coefficients

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that are formally quadratic in composition. Although these features yield small improvements in absolute numerical terms, which are nonetheless significant given the very high accuracy of this kind of models, they are important technical and formal advantages of this model. As a result, the new model performs very satisfactorily with respect to the model of [1] and, more importantly, it improves on the results of that model to make them more comparable to the results of the two reference models of [5] over ranges as wide as $60 \leq T/\mathrm{K} \leq 1500$ and $p/\mathrm{MPa} \leq 228$ for volumetric, caloric and vapour–liquid equilibrium (VLE) properties of air and the related systems (binary mixtures and pure components).

As the performance of model proposed herein will be extensively compared to that of the two models published in [5], it is convenient to review how those two models were constructed. The reference EoS is a state-of-the-art multiparameter model for the Helmholtz energy with 3 adjustable coefficients for the ideal-gas contribution and 19 adjustable coefficients for the residual part. The reducing parameters are the temperature and density at the maxcondentherm and the reference EoS was fitted to densities, isochoric heat capacities, speeds of sound and second virial coefficients data sets of air. In the Helmholtz energy mixture model the ideal-mixture part incorporates residual Helmholtz energy contributions for the pure components involved, which are given by reference equations of state, and the excess contribution involves five adjustable parameters. The reducing parameters are given by mixing rules with another six adjustable parameters and the mixture model was fitted to densities and saturation pressures of the $(N_2 + O_2)$, $(N_2 + Ar)$ and $(O_2 + Ar)$ systems.

2. Theory

Given that the scope of this work is to extend the application of a model reported previously [1], the theoretical background is given summarily.

2.1. Extended corresponding states theory

The corresponding states condition for a mixture is defined [11] as

$$Z_x(T, \rho) = Z_0\left(\frac{T}{f_x}, h_x\rho\right), \tag{1}$$

$$\Phi_x^{\mathrm{res}}(T, \rho) = \Phi_0^{\mathrm{res}}\left(\frac{T}{f_x}, h_x\rho\right). \tag{2}$$

Thus, the mixture properties are equated to those of a single hypothetical fluid. In Eqs. (1) and (2), Z is the compression factor, Φ^{res} is the dimensionless residual Helmholtz energy, the superscript 'x' indicates mixture properties, the subscript '0' denotes the reference fluid and the mixture scaling parameters f_x and h_x are given by one-fluid mixing rules:

$$h_x = \sum_i \sum_j x_i x_j h_{ij} \tag{3}$$

and

$$f_x h_x = \sum_i \sum_j x_i x_j f_{ij} h_{ij}. \tag{4}$$

The unlike scaling parameters f_{ij} and h_{ij} are given by the conventional combining rules

$$f_{ij} = \xi_{ij}(f_{ii} f_{jj})^{1/2} \tag{5}$$

and

$$h_{ij} = \eta_{ij}\left[\frac{1}{8}(h_{ii}^{1/3} + h_{jj}^{1/3})^3\right], \tag{6}$$

where ξ_{ij} and η_{ij} are binary interaction parameters and f_{ii} and h_{ii} are given by

$$f_{ii} = \left(\frac{T^c}{T_0^c}\right)\theta_{ii}(T_r, \rho_r) \tag{7}$$

and

$$h_{ii} = \left(\frac{\rho_0^c}{\rho^c}\right)\varphi_{ii}(T_r, \rho_r), \tag{8}$$

in which θ_{ii} and φ_{ii} are temperature- and density-dependent pure-component shape factors and the subscript 'r' indicates reduced properties.

2.2. Local composition theory

The number of molecules N_{ji} of species j surrounding any molecule of species i is readily given by the radial distribution function provided that a suitable model intermolecular potential is used to calculate the pair correlation function $g_{ji}(r)$ between species i and j. The square-well (SW) intemolecular potential model is quite suitable for this purpose because it is easier to use than other model intermolecular potentials while it retains the basic qualitative features of the "true" intermolecular potential and it allows for the same cut-off distance L_{ji} to be used for all the components in a mixture. The definition of the SW potential is given by

$$u_{ij}(r) = \begin{cases} \infty, & r \leq \sigma_{ij} \\ -\varepsilon_{ji}, & \sigma_{ij} < r < \lambda\sigma_{ij} \\ 0, & r \geq \lambda\sigma_{ij} \end{cases} \tag{9}$$

where $\lambda\sigma_{ij}$ is the width of the potential well which serves as the obvious cut-off distance because beyond that $u_{ij}(r) = 0$, σ is the molecular diameter and $-\varepsilon$ is the potential well depth. If it is assumed that λ is the same for all the mixture components, N_{ji} given by the radial distribution function up to the first coordination shell is given by

$$N_{ji}(L_{ji}) = 4\pi\rho_{n,j}\int_0^{\lambda\sigma_{ji}} g_{ji}(r)r^2\,dr. \tag{10}$$

Local composition (LC) models are usually defined in terms of the ratio between the local mole fraction of molecules j around molecules i to the local mole fraction of molecules i surrounding molecules i. The local composition of molecules of species j surrounding any molecule of species i is defined as

$$x_{ji} = \frac{N_{ji}}{\sum_k N_{ki}}. \tag{11}$$

Here, the total number of molecules surrounding any central molecule of species i, or total coordination number of species i, is $N_{ci} = \sum_k N_{ki}$.

LC models must comply with conditions regarding the low-density behaviour and the invariance of the combinatory counting of species. In the low-density limit it is known [12] that $\lim_{\rho \to 0} g_{ji}(r) = \exp(-u_{ji}(r)/k_B T)$, so that from Eq. (9) and carrying out the integration of Eq. (10), the result is

$$\lim_{\rho_n \to 0} N_{ji} = \frac{4\pi}{3}x_j\rho_n\sigma_{ji}^3(\lambda^3 - 1)\exp\left(\frac{\varepsilon_{ji}}{k_B T}\right). \tag{12}$$

Here, $\rho_{n,j} = x_j\rho_n$, where x_j is the bulk mole fraction of component j and ρ_n is the number density of the mixture. Therefore, the LC model can be expressed as

$$\lim_{\rho_n \to 0}\frac{x_{ji}}{x_{ii}} = \lim_{\rho_n \to 0}\frac{N_{ji}}{N_{ii}} = \frac{x_j}{x_i}\frac{\sigma_{ji}^3}{\sigma_{ii}^3}\exp\left[\frac{(\varepsilon_{ji} - \varepsilon_{ii})}{k_B T}\right]. \tag{13}$$

It is clear, then, that in the low-density limit the mixture would not be random, i.e. $x_{ji}/x_{ii} \neq x_j/x_i$. This is due to the finite value of the