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Establishing benchmarks for the Second Industrial Fluids Simulation Challenge☆

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Abstract

This manuscript outlines the procedures used to establish benchmark property data for the Second Industrial Fluids Simulation Challenge. The process involved acquisition of some new data, evaluation of the literature data, and generation of recommended values with careful uncertainty estimates.

Keywords: Vapor pressure; Heat of vaporization; Acetone; Butyramide; Heats of mixing; Enthalpies of mixing; Henry's constant; Solubility

1. Introduction

In order to judge the entries in the Second Fluid Properties Simulation Challenge [1], a benchmarking committee was established that was comprised of several of the authors of this paper (Friend, Frurip, and Olson). As in the first contest [2], the mandate of the committee was to determine best values for the physical property questions posed in the Challenge based on a thorough evaluation of the available literature and on new experimental measurements, as necessary. A key part of the activity was to determine robust uncertainty estimates for the benchmarks, as these also played a role in the evaluation of challenge entries.

In this paper, we outline the procedures used to establish the 40 benchmark property values required for the three problems of the second event. Complete descriptions of the benchmark procedures for all of the posed problems are found in this report. The results of new experimental measurements are included as part of the discussion. Additional contributors to the project are listed in the acknowledgements of this paper. The interested reader is encouraged to consult a more detailed discussion of the various strategies used to obtain physical property data, and some reflections on the role of experiment in the continuing evolution of the property infrastructure. These issues were discussed in a paper published as part of the first Simulation Challenge [3].

2. Recommendations for Problem 1–1: acetone vapor pressure and heat of vaporization

2.1. Problem conditions and recommended values

Vapor pressure		
Problem conditions	330 K	375 K
Recommended values	(104.04 ± 0.3) kPa	(390.3 ± 1.0) kPa
Problem conditions	425 K	460 K
Recommended values	(1184 ± 6) kPa	(2225 ± 1) kPa
Heat of vaporization		
Problem conditions	330 K	375 K
Recommended values	(29.07 ± 0.15) kJ/mol	(25.92 ± 0.13) kJ/mol
Problem conditions	425 K	460 K
Recommended values	(21.4 ± 0.4) kJ/mol	(17.1 ± 0.4) kJ/mol

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2.2. Primary source of recommendation

The values indicated above were calculated from the equation of state of Lemmon and Span [4].

2.3. Justification for recommendation

The equation of state in Ref. [4] contains the current recommended formulation for the thermodynamic properties of acetone, based on an extensive evaluation of property data available in the literature. The formulation, in the form of a reduced Helmholtz energy correlation, was based on temperatures on the ITS-90 scale. The work of Lemmon and Span [4] considered PVT data, second virial coefficients, isobaric heat capacities, sound speeds, enthalpies, heats of vaporization, and saturation properties (including vapor pressures). Their work summarized the complete data set, and the full set of references is not provided here.

For the current benchmarking exercise, calculations based on the formulation of Ref. [4] were compared with experimental data, emphasizing the vapor pressure, enthalpy, heat of vaporization, and heat capacity data in the region of current interest. All available experimental data, including those incorporated in the NIST TRC Source database [5] and the AIChE DIPPR database [6], were considered.

2.4. Determination of uncertainty

The uncertainties of the formulation of Lemmon and Span were discussed in Ref. [4], and are based largely on comparisons with the experimental database. The total uncertainty given here includes that derived from experimental uncertainties, focusing on potential impurities in the sample. Because the main impurity in acetone samples is water, we have examined experimental information on acetone/water mixtures; this information indicates that a water impurity of up to 1% has little effect on vapor pressures, within the uncertainty range considered here. In particular, the estimated uncertainties in the formulation for acetone are 0.1% in the saturated liquid density between 280 and 310 K, 0.5% in density in the liquid phase below 380 K, and 1% in density elsewhere. The uncertainties in vapor pressure were estimated as 0.25% between 290 and 390 K, 0.5% from 270 to 290 K and 0.5% above 390 K. The uncertainties in heat capacities and speeds of sound, which are representative of derivative properties, have been estimated as 1%.

Multiple data sets, including heat capacities, sound speeds and single phase enthalpies, help to establish the uncertainties in the Helmholtz energy equation of state and the recommended values with uncertainties presented here. All thermodynamic properties can be calculated directly from the Helmholtz energy equation by taking various derivatives. Thus, the inclusion of such properties as the speed of sound and heat capacities in the determination and assessment of the equation of state impacts the uncertainty estimates.

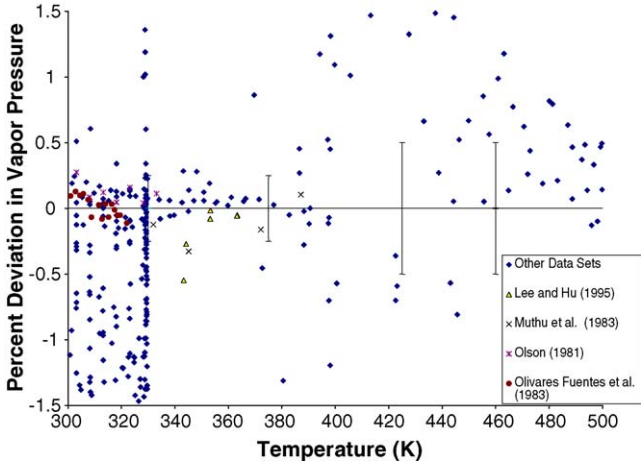

Fig. 1. Comparisons of vapor pressures calculated with the equation of state of Lemmon and Span [4] to experimental data [7–10]; points denoted "Other Data Sets" are cited in Ref. [4]. The benchmark points and their uncertainties are also shown.

Fig. 1 shows the deviation between the vapor pressure experimental data and vapor pressures calculated from the Helmholtz energy equation of state; this plot includes data from multiple sources, but excludes data outside the given temperature range and those with deviations of more than ±1.5%. Fig. 2 shows the region between 325 and 335 K in closer detail. Between 280 and 330 K, many of the experimental vapor pressure points are represented by the equation of state to within 0.2% as shown in Fig. 1. The more recent data of Lee and Hu [7], Muthu et al. [8], Olivares Fuentes et al. [9] and Olson [10] indicate that the uncertainty in the equation is about 0.25% between 290 and 390 K. The scatter in the data above 400 K increases up to 2%, although at 50 K below the critical temperature, several data sets show

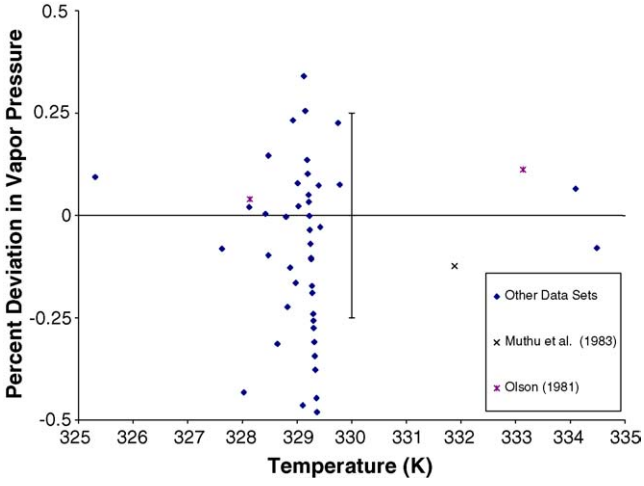

Fig. 2. Comparisons of vapor pressures calculated with the equation of state of Lemmon and Span [4] to experimental data in the range 325–335 K [8,10]; points denoted "Other Data Sets" are cited in Ref. [4]. The benchmark point at 330 K and its uncertainty are also shown.