# Mixture Models for Refrigerants R-1234yf/134a, R-1234yf/1234ze(E), and R-134a/1234ze(E) and Interim Models for R-125/1234yf, R-1234ze(E)/227ea, and R-1234yf/152a

lan H. Bell<sup>a)</sup> Applied Chemicals and Materials Division, National Institute of Standards and Technology, Boulder, CO 80305

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In this work new thermodynamic models for refrigerant mixtures are provided for the binary pairs R-1234yf/134a, R-1234yf/1234ze(E), and R-134a/1234ze(E) based on new reference measurements of speed of sound, density, and bubble-point pressures. Fitting the very accurate liquid-phase speed of sound and density data reproduces the bubble point pressures to within close to their uncertainty, yielding deviations in density less than 0.1%, and speed of sound deviations less than 1% (and less than 0.1% for R-1234yf/134a). Models are also presented for the binary pairs R-125/1234yf, R-1234ze(E)/227ea, and R-1234yf/152a based solely on bubble-point measurements.

Keywords: mixture models; thermodynamics; refrigerants; equation of state

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## I. INTRODUCTION

The fourth generation of refrigerants comprises largely mixtures containing halogenated olefins<sup>24</sup>, for instance to find non-flammable blends to replace the workhorse refrigerant R-134a<sup>25</sup>. In order to reliably assess novel mixtures, new mixture models in the form of equations of state (EOS) are needed for each of the binary pairs included in the candidate mixtures. Of the 6 binary mixtures we selected for study, current models are all based upon estimation schemes or unpublished models in REFPROP 10.0<sup>26,27</sup>. New reference experimental measurements are needed to improve the mixture models. As is outlined below, these measurements were obtained as part of the larger project, forming the foundation for the mixture models. This work begins the process of filling in the holes where important mixture models need to be updated or developed<sup>26</sup>.

The components considered in this work are all relatively similar and some information about them is presented in Table I. Two (R-1234yf and R-1234ze(E)) are stereoisomers, and the three main components of the comprehensive measurements have a hydrocarbon backbone with the replacement of four hydrogens by fluorines (as indicated by the 4 as the right-most numerical digit). Therefore we might expect (as we see here), that mixtures of these compounds would behave in a relatively simple way, with nearly ideal mixing behaviors. This makes refrigerant mixtures such as these ideal candidates for the development of highly accurate mixture models.

TABLE I. Metadata on the pure components, sorted by normal boiling point temperature. Numerical values are taken from the respective EOS and are rounded for presentation; the unrounded value from the EOS should be used. M: molar mass.

| name                      | hash $^{\dagger}$ | $T_{\rm NBP}$ / K | $T_{\rm crit}$ / K | p <sub>crit</sub> / MPa | $M / \text{kg mol}^{-1}$ |
|---------------------------|-------------------|-------------------|--------------------|-------------------------|--------------------------|
| R-125 <sup>28</sup>       | 25c5a3a0          | 225.060           | 339.173            | 3.61770                 | 0.120021                 |
| R-1234yf <sup>29</sup>    | 40377b40          | 243.692           | 367.850            | 3.38440                 | 0.114042                 |
| R-134a <sup>30</sup>      | ff1c0560          | 247.076           | 374.210            | 4.05928                 | 0.102032                 |
| R-152a <sup>31</sup>      | 63f364b0          | 249.127           | 386.411            | 4.51675                 | 0.066051                 |
| R-1234ze(E) <sup>32</sup> | 9905ef70          | 254.177           | 382.513            | 3.63490                 | 0.114042                 |
| R-227ea <sup>33</sup>     | 40091ee0          | 256.810           | 374.900            | 2.92500                 | 0.170029                 |

†: The hash used in REFPROP to define the mixture models is generated from the SHA256 hash of the standard InChI key from hashlib.sha256(StdInChIkey).hexdigest()[2:9] + "0" with the hashlib module from the Python standard library

## II. DATA

#### A. New measurement data

As part of the larger scope of work within this project, measurements of speed of sound (liquid phase), density (gas and liquid phase), and vapor-liquid equilibria (VLE) were carried out for the binary mixtures R-1234yf/134a, R-1234yf/1234ze(E), and R-134a/1234ze(E). These speed of sound and bubble-point results are presented in a set of papers in the literature<sup>2,7</sup>. The datasets are presented in Table II and shown graphically in Fig. 1. Most of our measurements extend up to 10 or 20 MPa, with the exception of the speed of sound data for R-134a/1234ze(E), which extend up to 50 MPa. The interim report from the project includes the full set of measured data<sup>6</sup>, though additional analysis and screening of the data was carried out following report preparation. For an additional three mixtures (R-125/1234yf, R-1234ze(E)/227ea, and R-1234yf/152a), measurements of bubble points were carried out<sup>7</sup>. These datasets form the core of data used in this study because their experimental uncertainties are small and carefully assessed. Other data from the literature are compared with the models developed in this work.



FIG. 1. Location of the new experimental data points in the p-T plane for each of the three primary blends and for each property. The solid and dashed curves are the vapor pressure curves for the first and second fluids (in order) forming the binary pair.

TABLE II. Set of comprehensive measurements carried out in the greater NIST study. The mole fractions  $z_1$  are the discrete compositions prepared (SOS: speed of sound, PVT:  $\underline{p}-v-T$ , VLE: bubble-point measurement, N: number of data points,  $U(\chi)$ : mean value of combined expanded (k = 2) uncertainty in measured quantity (density in the case of PVT, speed of sound for SOS, and bubble-point pressure for VLE))

| pair (1/2)         | kind | <i>T /</i> K | $z_1$ / mole frac. | Ν   | $\overline{U(\pmb{\chi})}$ / % |
|--------------------|------|--------------|--------------------|-----|--------------------------------|
| R-1234yf/1234ze(E) | VLE  | 270 - 360    | 0.324, 0.638       | 48  | 0.219                          |
| R-1234yf/134a      | VLE  | 270 - 360    | 0.3199, 0.6467     | 39  | 0.169                          |
| R-134a/1234ze(E)   | VLE  | 270 - 360    | 0.3341, 0.6631     | 24  | 0.17                           |
| R-1234yf/1234ze(E) | PVT  | 230 - 400    | 0.33584, 0.6666    | 225 | 0.0357                         |
| R-1234yf/134a      | PVT  | 230 - 400    | 0.33634, 0.66759   | 226 | 0.0375                         |
| R-134a/1234ze(E)   | PVT  | 230 - 400    | 0.3325, 0.66356    | 175 | 0.042                          |
| R-1234yf/1234ze(E) | SOS  | 230 - 345    | 0.33584, 0.6666    | 131 | 0.0801                         |
| R-1234yf/134a      | SOS  | 230 - 345    | 0.33634, 0.66759   | 118 | 0.0793                         |
| R-134a/1234ze(E)   | SOS  | 230 - 345    | 0.32916, 0.67102   | 304 | 0.0624                         |

# B. Existing literature data

The collection of experimental data was initially based upon the survey of Bell *et al.*<sup>26</sup>, followed by the addition of one dataset from Tomasetti<sup>1</sup>. All the datasets are included in the SOURCE database, accessible through NIST TDE<sup>34</sup>, and are listed in the tables in Section V B. Aside from the sources listed, there is additionally one speed of sound dataset<sup>35</sup>, two references reporting critical loci<sup>16,17</sup>, and one reporting specific heats<sup>9</sup>.

# C. Error metrics

In this work the relative deviation in an arbitrary quantity  $\chi$  is defined by

$$\Delta_{\%}(\boldsymbol{\chi}) = 100 \times \left(\frac{\boldsymbol{\chi}_{\text{TW}}}{\boldsymbol{\chi}_{\text{exp}}} - 1\right)$$
(1)

where the subscript TW indicates the value obtained from the model developed in this work, and the subscript exp indicates the experimental value. The average absolute relative deviation (AAD) in a quantity  $\chi$  is defined by

$$AAD_{\chi} = mean(abs(\vec{\Delta}_{\%}(\chi)))$$
(2)

where  $\vec{\Delta}_{\mathscr{H}}(\chi)$  is the vector of deviations, and AAD is therefore on a percentage basis.

#### III. MODELING

#### A. Multi-fluid model

The most accurate thermodynamic mixture models available today in the reference software libraries (NIST REFPROP<sup>27</sup>, CoolProp<sup>36</sup>, TREND<sup>37</sup>) are based upon the Helmholtz energy. Derivatives of the Helmholtz energy can be used to obtain all other thermodynamic properties. The Helmholtz energy (divided by the molar gas constant *R* and the temperature;  $\alpha = a/(RT)$ ) is given as the sum of residual and ideal gas contributions:

$$\alpha = \alpha^{\rm r} + \alpha^{\rm (ig)} \tag{3}$$

The ideal gas portion does not enter into the fitting, and is therefore not further discussed here. The molar gas constant R, which is now an exactly defined value according to CODATA<sup>38</sup>, is instead implemented as the mole-fractionweighted average of the molar gas constants used in developing the EOS for the pure fluids.

The mixture model for the residual portion is given by

$$\boldsymbol{\alpha}^{\mathrm{r}}(\tau, \boldsymbol{\delta}, \mathbf{z}) = \boldsymbol{\alpha}^{\mathrm{r}}_{\mathrm{CS}} + \boldsymbol{\alpha}^{\mathrm{r}}_{\mathrm{dep}} \tag{4}$$

where  $\alpha_{CS}^{r}$  is the corresponding states contribution given by

$$\alpha_{\rm CS}^{\rm r} = \sum_{i=1}^{N} z_j \alpha_{0,i}^{\rm r}(\tau, \delta) \tag{5}$$

where z is the vector of mole fractions. The pure fluid contributions  $\alpha_{0,i}^{r}$  are given at the mixture reduced states  $\tau$  and  $\delta$ . The reduced density  $\delta = \rho / \rho_{red}(\mathbf{z})$  and reciprocal reduced temperature  $\tau = T_{red}(\mathbf{z})/T$  are defined based on the reducing functions given in a common form by

$$Y_{\text{red}}(\mathbf{z}) = \sum_{i=1}^{N} z_i^2 Y_{\text{crit},i} + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} 2z_i z_j \frac{z_i + z_j}{\beta_{Y,ij}^2 z_i + z_j} Y_{ij}$$
(6)

where *Y* is the parameter of interest, either molar volume  $v = 1/\rho$  or temperature *T*. The necessary parameters are given by

$$T_{ij} = \beta_{T,ij} \gamma_{T,ij} (T_{\text{crit},i} T_{\text{crit},j})^{0.5}$$
(7)

$$v_{ij} = \frac{1}{8} \beta_{\nu,ij} \gamma_{\nu,ij} \left( v_{\text{crit},i}^{1/3} + v_{\text{crit},j}^{1/3} \right)^3$$
(8)

The departure contribution in Eq. (4) is given by

$$\alpha_{\rm dep}^{\rm r} = \sum_{i=1}^{N} \sum_{j=i+1}^{N} z_i z_j F_{ij} \alpha_{ij}^{\rm r}(\tau, \delta) \tag{9}$$

where  $F_{ij}$  is the scaling factor, normally equal to 1.0 if a departure term has been fit, and zero if not.

The departure function  $\alpha_{ij}^{r}(\tau, \delta)$  for the binary pair *ij* is in principle an arbitrary mathematical function that takes the value of zero at zero density, yields a good representation of the experimental data for the mixture, and has reasonable extrapolation behavior.

As is summarized in Ref. 39, the standard thermodynamic properties may be expressed in terms of derivatives of the Helmholtz energy with a concise derivative representation given by

$$\Lambda_{ij}^* = \tau^i \delta^j \left( \frac{\partial (\alpha^*)^{i+j}}{\partial \tau^i \partial \delta^j} \right) \tag{10}$$

where \* is one of ig (ideal gas), r (residual), or tot (total). Thermodynamic properties can be given by combinations of derivatives of the Helmholtz energy. For instance pressure is given by residual contributions only:

$$p = -\left(\frac{\partial a}{\partial v}\right)_T = \rho RT (1 + \Lambda_{01}^{\rm r}) \tag{11}$$

and the speed of sound w is obtained from

$$\frac{Mw^2}{RT} = 1 + 2\Lambda_{01}^{\rm r} + \Lambda_{02}^{\rm r} - \frac{(1 + \Lambda_{01}^{\rm r} - \Lambda_{11}^{\rm r})^2}{\Lambda_{20}^{(\rm ig)} + \Lambda_{20}^{\rm r}}$$
(12)

which contains mostly residual properties, except for  $\Lambda_{20}^{(ig)}$  which comes from the ideal gas. The quantity *R* is the molar gas constant, *M* is the molar mass, and all quantities on the right-hand-side are non-dimensional.

#### B. Implementation

In the course of this project and in the development of routines for tracing critical curves<sup>40</sup>, it became clear that a novel and more flexible approach was needed to obtain the thermodynamic derivatives of a mathematical model. The design constraints are that the obtained values should be fast to evaluate, but also allow for rapid prototyping of new modeling approaches. Thus the teqp library was birthed<sup>39</sup>; teqp uses automatic differentiation to obtain the derivatives needed to calculate thermodynamic properties without any hand-written derivatives, dramatically speeding up the development process. Even though automatic differentiation is used, the obtained values are in many cases still faster to evaluate than the hand-written derivatives in REFPROP while suffering only a negligible loss in numerical precision. As of publication, teqp does not include any iterative routines, rather the focus is on forwards derivatives of the residual Helmholtz energy with respect to temperature, density, and compositions, which meets the needs of this optimization campaign.

# IV. MODEL OPTIMIZATION

The fitting approach for the binary mixtures with comprehensive measurements considered only speed of sound and densimetry data (no phase equilibria data). Speed of sound and densimetry data are well-suited to optimization because they do not require a full phase equilibrium calculation, the phase equilibrium calculation being an unreliable (and slow) mixture calculation in general. The overall cost function  $C_{\$}$  was defined based upon differences between model predictions and the experimental data, and is given by

$$C_{\$} = \sum_{i} r_{\rho,i} + W \sum_{i} r_{w,i}$$
(13)

where the weighting factor W = 0.25 is used to balance deviations between the two kinds of data, and the residua  $r_{\rho,i}$  and  $r_{w,i}$  are relative deviations.

# A. Density

For density data, it would be ideal to use the residuum

$$r_{\rho,i} = \frac{\rho_{\exp} - \rho_{\text{model}}(T, p, \mathbf{x})}{\rho_{\exp}}$$
(14)

but a downside of this approach is that the calculation  $\rho_{\text{model}}(T, p, \mathbf{x})$  requires computationally costly iteration (which also can fail if the initial guess is not accurate enough). Instead we would like a non-iterative proxy that is a good stand-in for the iterative calculation. Starting from an isothermal series expansion of molar density around the experimental density yields

$$\rho = \rho_{\exp} + \Delta p \left( \frac{\partial \rho}{\partial p(T_{\exp}, \rho_{\exp})} \right)_{T, \text{fit}} + \dots$$
(15)

Truncation of higher-order terms yields the difference in density of

$$\Delta \rho = \rho - \rho_{\text{exp}} = \Delta p \left( \frac{\partial \rho}{\partial p(T_{\text{exp}}, \rho_{\text{exp}})} \right)_{T, \text{fit}}, \quad (16)$$

and the proxy residue for  $p-\rho-T$  data is therefore

$$r_{\rho,i} = \frac{p(T,\rho) - p_{\exp}}{\rho_{\exp}} \left(\frac{\partial \rho}{\partial p(T_{\exp},\rho_{\exp})}\right)_{T,\text{fit}} \approx \frac{\Delta \rho}{\rho_{\exp}}, \quad (17)$$

in which  $p(T,\rho)$  and the isothermal derivative of p with respect to  $\rho$  are evaluated simultaneously (and directly) from the equation of state. This cost function contribution has a similar behavior to Eq. (14) though it is non-iterative and thus very fast to evaluate (on the order of a few µs/evaluation in C++).

Data points along the curve where  $(\partial p/\partial \rho)_T$  approaches zero (it is zero at the critical point for a pure species) result in large contributions to the cost function, but most of the data points are relatively far from this locus.

#### B. Speed of Sound

The multi-fluid Helmholtz-explicit model has as independent variables temperature T, density  $\rho$ , and the vector of mole fractions z. Unfortunately, speed of sound is usually measured quasi-isochorically with temperature, pressure, and composition as independent variables, so internal iteration is required to solve for the mixture density given the temperature, pressure, and composition (what was attempted to be avoided in the density deviation term). In the case of speed of sound data, the initial guess density was that obtained from the model in REFPROP 10.0<sup>27</sup>. The deviations between the guess density and the final density were very small, small enough to serve as a reliable-enough starting value in any case.

Once the density has been obtained from one step of iteration, the speed of sound w is obtained from Eq. (12). In teqp,  $\Lambda_{01}^r$  and  $\Lambda_{02}^r$  are obtained from a single call, and  $\Lambda_{11}^r$  and  $\Lambda_{20}^r$ are obtained from two further calls. The ideal gas contribution  $\Lambda_{20}^{(ig)}$  is not implemented in teqp as of publication, and so this quantity was taken from the implementation in the HEOS backend of CoolProp<sup>36</sup>. The quantity  $\Lambda_{20}^{(ig)}$  does not depend on the departure function or the interaction parameters.

The speed of sound residue is therefore defined by

$$r_{w,i} = 100 \times \left(\frac{w_{\text{model}}}{w_{\text{exp}}} - 1\right) \tag{18}$$

# C. Optimization

As has been successfully applied by the author previously<sup>41</sup>, stochastic (random) global optimization provides a reliable approach that is robust to failures and computationally efficient enough for practical application.

While experiments with new model formulations were carried out (for instance the invariant reducing functions from the GERG-2004 model<sup>42</sup> were added to teqp), the end goal was always to develop thermodynamic models compatible with REFPROP 10.0<sup>27</sup>. The full set of departure functions available in REFPROP 10 is relatively narrow, with terms of the following kinds available:

•  $n_k \tau^{t_k} \delta^{d_k}$ 

• 
$$n_k \tau^{t_k} \delta^{d_k} \exp(-\delta^{l_k})$$
 (See Ref. 43)

- $n_k \tau^{t_k} \delta^{d_k} \exp(-\eta_k (\delta \varepsilon_k)^2 \beta_k (\delta \gamma_k))$  (See Eq. 7.8 from Ref. 42)
- $n_k \tau^{t_k} \delta^{d_k} \exp(-\eta_k (\delta \varepsilon_k)^2 \beta_k (\tau \gamma_k)^2)$  (Gaussian terms like those used for pure fluids)

The parameters  $l_k$  and  $d_k$  must be integers in order to yield finite contributions to the second (and higher) virial coefficients. Thus optimization of the departure function is a mixedinteger optimization problem in which the values of some parameters are integers and others are floating point values. The conventional approach for this problem is to "fit" the  $d_k$  values by manual optimization while allowing the optimizer to fit the floating point values. A similar approach was taken here. The values of  $d_k$  were set to  $d_k = k + 1$  for k starting at 0, and the same for  $l_k$ :  $l_k = k + 1$ .

The cost function defined above is minimized with global optimization. The variables  $\beta_{T,ij}$ ,  $\gamma_{T,ij}$ ,  $\beta_{v,ij}$ , and  $\gamma_{v,ij}$  were all bounded to be in [0.75, 1.25],  $n_k$  was bounded to be in [-3, 3], and  $t_k$  was bounded to be in [0, 4]. The CEGO library<sup>44</sup> was specifically designed for this particular problem, but the widely available differential evolution algorithm implemented in scipy<sup>45</sup> proved to be adequate for the optimization task, and was used for the optimization.

The departure term used was very simple:

$$\alpha_{ij}^{\mathrm{r}} = \sum_{k} n_k \tau^{t_k} \delta^{d_k} \exp(-\mathrm{sgn}(l_k) \delta^{l_k})$$
(19)

where the sgn function is the sign of the value, zero for an argument of zero, and 1 for positive arguments.

In a single evaluation of the cost function, first a Python data structure is constructed that converts an array of doubleprecision numbers (the variables in the optimization) to the necessary values of  $\beta_{T,ij}$ ,  $\gamma_{T,ij}$ , **n**, **d**, and so on in Eq. (19) and Eq. (6). This Python data structure is dumped to a string in the JSON format, which is then unpacked in the mutant construction routines of teqp. One important implementation note is that the mutant models only hold *references* to the pure fluid EOS because construction of the pure fluid EOS is the most costly part of the mixture model construction. Thus users should be careful to ensure that the pure fluid models do not fall out of scope and get prematurely de-allocated as this will result in a dangling reference to the pure fluid EOS. Construction of the mutant usually takes on the order of tens of microseconds.

# V. COMPREHENSIVE RESULTS

The first set of model results are those for the binary pairs R-1234yf/134a, R-1234yf/1234ze(E), and R-134a/1234ze(E). For each of these binary pairs, sufficient data were available to fit a reducing function in the form of Eq. (6) and a small departure function in the form of Eq. (19). In order to avoid model over-fitting, a graduated optimization approach was taken for each mixture model. The departure function defined above was given an increasing number of terms, and the statistics of fit were monitored in order to determine how many terms would be required. In all cases the variables  $\beta_{T,ij}$ ,  $\gamma_{T,ij}$ ,  $\beta_{v,ij}$ ,

and  $\gamma_{v,ij}$  were fitted. This process was done in a deterministic fashion. For each of the three binary pairs with the full complement of data, 0 to  $N_{dep}$  terms were added to the departure function for the pair. For each term count in the departure term, the optimization was repeated 5 times to hopefully find the global minimum of the cost function (although that cannot be *guaranteed* in general).

The optimized cost function as a function of the number of terms in the departure function is shown in Fig. 2 for each of the binary pairs. The cost function values for  $N_{dep} = 0$  are obtained by optimizing only  $\beta_{T,ij}$ ,  $\gamma_{T,ij}$ ,  $\beta_{v,ij}$ , and  $\gamma_{v,ij}$ . It is difficult to make out at the scale of the figure without zooming in, but all 5 replicates of the optimization result are shown, highlighting that the method quite reliably finds close to the same minimum of the cost function. There is a relatively large step decrease when adding a single term to the departure function. This result demonstrates that adjusting the four interaction parameters alone is not sufficient to obtain a good representation of the data; the departure function is needed. The reduction in cost function slows down after more than two terms are included, so the (somewhat arbitrary) decision was made to use two terms in the departure function.



FIG. 2. Cost function  $C_{\$}$  versus the number of terms in the departure function  $N_{dep}$ 

The obtained values of the interaction parameters are shown in Table III, and the departure functions are given in Table IV, Table V, and Table VI. The optimization result with two terms in the departure function appears to be a good compromise of flexibility and model fidelity.

TABLE IV. Departure function for R-1234yf/134a.

| k | п         | t        | d | l |
|---|-----------|----------|---|---|
| 0 | 0.051900  | 2.477314 | 1 | 1 |
| 1 | -0.011472 | 0.070541 | 2 | 2 |

TABLE V. Departure function for R-1234yf/1234ze(E).

| k | n         | t        | d | l |
|---|-----------|----------|---|---|
| 0 | 0.072640  | 0.012643 | 1 | 1 |
| 1 | -0.024746 | 3.992829 | 2 | 2 |

TABLE III. Interaction parameters obtained from fitting speed of sound and density data. Departure functions were fit for each binary pair. Components in each binary pair are sorted by normal boiling point temperatures, and the order matters.

| pair (1/2)         | $\beta_{T,ij}$ | $\gamma_{T,ij}$ | $eta_{v,ij}$ | $\gamma_{v,ij}$ | $F_{ij}$ |
|--------------------|----------------|-----------------|--------------|-----------------|----------|
| R-1234yf/1234ze(E) | 0.998886       | 0.993309        | 0.999302     | 0.998590        | 1.0      |
| R-1234yf/134a      | 1.000026       | 0.987057        | 1.000272     | 1.003747        | 1.0      |
| R-134a/1234ze(E)   | 0.998593       | 0.992009        | 0.998995     | 0.998621        | 1.0      |

TABLE VI. Departure function for R-134a/1234ze(E).

| k | п         | t        | d | l |
|---|-----------|----------|---|---|
| 0 | 0.068889  | 3.184446 | 1 | 1 |
| 1 | -0.004831 | 2.034344 | 2 | 2 |

#### A. NIST results

First we consider deviations in the speed of sound data in Fig. 3. For the mixture R-1234yf/134a, the speed of sound deviations are mostly significantly below 0.1%. To be sure, some of the quality of fit can be attributed to the symmetry of the mixture interactions, as partially evidenced by the near perfect overlaying of their vapor pressure curves. For the two binary pairs containing R-1234ze(E) the deviations are significantly larger, and appear to in general increase as the amount of R-1234ze(E) increases. Model deviations are only meaningful when compared with the measurement uncertainty, and in this case we have experimental uncertainties that have been carefully assessed. Figure 4 shows the model deviations compared with the combined relative uncertainties of the experimental measurements at each state point. The model deviations for R-1234yf/134a are mostly within two times the combined expanded relative uncertainties, even in the critical region, which is excellent agreement, especially considering that there is still uncertainty in the pure fluid equation of state's representation of the speed of sound. As before, the speed of sound deviations for the binary mixtures containing R-1234ze(E) are much larger than the experimental uncertainty in the binary mixture measurements.

In order to understand the deviations for R-134a/1234ze(E)and R-1234vf/1234ze(E), the speed of sound data were collected for pure R-1234ze(E). In total three datasets were used to fit the pure fluid EOS of Thol and Lemmon<sup>5</sup>: Lago, Giuliano Albo, and Brignolo<sup>4</sup> (liquid phase), Perkins and McLinden<sup>46</sup> (vapor phase), and Kano et al.<sup>47</sup> (vapor phase). A recent liquid-phase dataset is available from our group<sup>3</sup>. Figure 5 shows the deviations for the liquid-phase data. For the data obtained in McLinden and Perkins<sup>3</sup>, the path length obtained from direct measurement of the spacer length at atmospheric pressure and 293 K agreed with that obtained from speed of sound measurements with propane to within 0.03% at the same conditions, giving confidence in the obtained values. These two datasets show that while the EoS fits the single liquid-phase dataset available at the time (except for the highest temperature of 360 K), the new data from our group contradict the data from Lago, Giuliano Albo, and Brignolo<sup>4</sup>.

Indeed the same problem is seen with the measurements from Lago, Giuliano Albo, and Brignolo<sup>4</sup> for R-1234yf; their R-1234yf measurements deviate by more than 2.5% from the new EoS for R-1234yf<sup>29</sup>, calling into question their liquid-phase speed of sound data for pure R-1234ze(E) which appear to deviate systematically.



FIG. 5. Relative deviations between experimental liquid-phase speed of sound data for pure R-1234ze(E) (unpublished data from McLinden and Perkins<sup>3</sup> and data from Lago, Giuliano Albo, and Brignolo<sup>4</sup>) and the EOS<sup>5</sup>



FIG. 3. Relative deviations in speed of sound from the comprehensive measurements in Rowane and Perkins<sup>2</sup>. The average combined expanded uncertainty is shown by dashed curves and listed in the figure title.



FIG. 4. Relative deviations in speed of sound divided by combined expanded relative uncertainty at the respective state point from the comprehensive measurements in Rowane and Perkins<sup>2</sup>. The  $\pm 2$  band is shown by dashed curves.

Figure 6 shows the deviations in density for the three mixtures. Away from the critical region (see Section V B 3) the deviations are nearly all less than 0.1%, with AAD all significantly less than 0.1%. The pure fluid densities are in general not better reproduced than 0.1% by the pure fluid EOS, so this is about the best that can be achieved without overfitting. Just like for speed of sound, deviations relative to the uncertainty are considered, and shown in Fig. 7. Most of the density data are represented within 5 times the experimental uncertainty, except for in the critical region. The density deviations appear to have less sensitivity to defects in the pure-fluid EoS for R-1234ze(E) than for speed of sound.

Finally Fig. 8 shows the bubble-point deviations. Almost all of the data are represented within 1%, except for two data points for R-134a/1234ze(E) for the composition more rich in R-1234ze(E). The deviations divided by the respective combined expanded uncertainties at each individual state point are shown in Fig. 9. The deviations in pressure are mostly within two times the combined expanded uncertainties, again except for the mixture R-134a/1234ze(E). These deviations are remarkable because the bubble-point pressures were not included in the optimization procedure, only the speed of sound and density data were included.

Overall, the set of new measurements appear to be very consistent, as evidenced by the fact that fitting the speed of sound and densimetry data allows the vapor-liquid-equilibrium data to be represented to within close to their experimental uncertainties. From a certain standpoint this is not terribly surprising, as a brief thought experiment will indicate. Let us suppose that we can measure the pressure of a pure fluid along a subcritical isotherm as a function of density, including the unstable portion of the isotherm between the spinodals. This pressure curve is all that is needed to obtain the vapor pressure after applying the Maxwell conditions for phase equilibrium. Therefore for a pure fluid, perfect knowledge of the density along an isotherm would yield the correct vapor pressure by default. The extension of this argument to mixtures is somewhat more challenging because the energetic portion of the phase equilibrium is no longer defined by the lever rule (alternatively, equality of the Gibbs energy), rather it is necessary to equate chemical potentials of each component in each phase.



FIG. 6. Relative deviations in density from the comprehensive measurements<sup>6</sup>. The average combined expanded uncertainty band is shown by dashed lines and listed in the subfigure title.



FIG. 7. Relative deviations in density divided by combined expanded relative uncertainty at the respective state point from the comprehensive measurements<sup>6</sup>. The  $\pm 2$  band is shown by dashed curves.



FIG. 8. Deviations in bubble-point pressure from the comprehensive measurements in Outcalt and Rowane<sup>7</sup>. The average combined expanded uncertainty band is shown by dashed lines and listed in the subfigure title.



FIG. 9. Relative deviations in bubble-point pressure divided by combined expanded relative uncertainty at the respective state point from the comprehensive measurements in Outcalt and Rowane<sup>7</sup>. The  $\pm 1$  band is shown by dashed lines, when visible.

## B. Other Literature Data

Aside from the data from our group (see above), there are a few other datasets in the literature for the properties we measured. Some significant discrepancies can be identified. In each case, our VLE data (not included in the fitting) agrees with one of the datasets, but not the other one. The datasets are listed in Table VII and Table VIII, and the statistics of the fit are also included in the table.

# 1. VLE

For the mixture R-1234yf/134a, the VLE dataset from Shimoura, Matsuo, and Sotani<sup>35</sup> has been dropped because the deviations are greater than 30%. These large deviations suggest a systematic error in the measurements, and also call into question the speed of sound data from the same reference, perhaps explaining the significant deviations from the measurements of Rowane and Perkins<sup>2</sup>. Otherwise, the VLE dataset from Chen, Qi, and Wu<sup>12</sup> shows large deviations, some greater than 10% compared with the model from this work, while that of Kamiaka, Dang, and Hihara<sup>10</sup> agrees well with the model developed in this work, with deviations mostly significantly less than 1%, and an AAD of 0.2%.

For R-1234yf/1234ze(E), the measurements from Ye *et al.*<sup>11</sup> are in good agreement with the model; deviations are all almost less than 1% and the AAD is 0.34%. The data from Al Ghafri *et al.*<sup>9</sup> do not agree with either Ye *et al.*<sup>11</sup> or our new model.

For R-134a/1234ze(E), the measurements from Kou *et al.*<sup>8</sup> are consistent with the new model (AAD of 0.84%), while those of Al Ghafri *et al.*<sup>9</sup> again deviate systematically.

the composition coverage. pair (1/2) author  $N z_1$  / mole frac. T / K $AAD_{p_{\sigma}} / \%$ Kamiaka, Dang, and Hihara<sup>10</sup> 67 R-1234yf/134a 0.00 - 1.00 273 - 333 0.17 Chen, Qi, and Wu<sup>12</sup> 268 - 323 R-1234yf/134a 41 0.48 - 0.58 4.10 Al Ghafri et al.9 R-1234yf/1234ze(E) 3 0.66 - 0.73 274 - 342 3.58 Ye et al.<sup>11</sup> 284 - 333 R-1234yf/1234ze(E) 77 0.00 - 1.00 0.34 Al Ghafri et al.9 R-134a/1234ze(E) 3 0.49 - 0.57 274 - 341 1.79 Kou et al.<sup>8</sup> 40 R-134a/1234ze(E) 0.00 - 1.00 293 - 323 0.89

TABLE VII. Existing literature sources for VLE for the three primary binary pairs included in this work. The AAD includes the saturated vapor and liquid points; the mole fractions z combine mole fractions of the first component in the liquid and vapor phases to indicate concisely

TABLE VIII. Existing literature sources for PVT for the three primary binary pairs included in this work. The AAD includes only points for which the iterative calculations in REFPROP 10.0 were successful

| pair (1/2)         | author                                | Ν   | $z_1$ / mole frac. | <i>T /</i> K | AAD <sub>ρ</sub> / % | N <sub>fail</sub> |
|--------------------|---------------------------------------|-----|--------------------|--------------|----------------------|-------------------|
| R-1234yf/134a      | Yotsumoto et al. <sup>15</sup>        | 575 | 0.00 - 0.82        | 263 - 323    | 0.02                 | 0                 |
| R-1234yf/134a      | Akasaka <i>et al</i> . <sup>16</sup>  | 22  | 0.32 - 0.72        | 350 - 371    | 1.66                 | 6                 |
| R-1234yf/134a      | Chen et al. <sup>18</sup>             | 94  | 0.04 - 0.86        | 299 - 403    | 0.39                 | 0                 |
| R-1234yf/1234ze(E) | Higashi <sup>17</sup>                 | 14  | 0.50 - 0.50        | 355 - 374    | 2.53                 | 5                 |
| R-1234yf/1234ze(E) | Higashi <sup>13</sup>                 | 52  | 0.50 - 0.50        | 340 - 430    | 1.56                 | 5                 |
| R-1234yf/1234ze(E) | Al Ghafri <i>et al</i> . <sup>9</sup> | 37  | 0.50 - 0.50        | 252 - 404    | 0.18                 | 0                 |
| R-134a/1234ze(E)   | Zhang <i>et al</i> . <sup>14</sup>    | 101 | 0.36 - 0.57        | 270 - 300    | 0.24                 | 0                 |
| R-134a/1234ze(E)   | Al Ghafri <i>et al</i> . <sup>9</sup> | 59  | 0.50 - 0.50        | 252 - 403    | 0.11                 | 0                 |



FIG. 10. Location of data (left panel) and relative deviations in dew- and bubble-point pressure (right panels) for literature data (Kou  $(2019)^8$ , Al Ghafri  $(2019)^9$ , Kamiaka  $(2013)^{10}$ , Ye  $(2021)^{11}$ , Chen  $(2016)^{12}$ ) for vapor-liquid equilibria. The subscript TW indicates the model in this work. Open markers are dew points and filled markers are bubble points. Each marker type corresponds to a given dataset.

#### 2. PVT

The comparisons against existing experimental data are more challenging for density because of the near-critical region. These calculations are complicated by the fact that a solution may not exist thermodynamically, or that the initial guesses may not be adequate to converge to the correct solution.

As is discussed in Bell *et al.*<sup>26</sup>, mixture models may cause problems for the iterative calculations in the critical region. Figure 11 provides a demonstration. The isopleth of the phase envelope of the new mixture model (the solid curve) falls just below the points in the critical region (worst deviations on the order of 0.3 K in the temperature direction). Saturation temperatures above the maximum of the curve are not accessible by the mixture model. The model from this work but with the departure term disabled (with  $F_{ij} = 0$ ), the dashed curve, is in better agreement with the data in the critical region, but provides a worse representation of the other high accuracy data.



FIG. 11. Isopleth for equimolar composition of the binary mixture R-1234yf/1234ze(E). Solid curve is the new model, the dashed curve is with  $F_{ij} = 0$ . Points are the saturated vapor and liquid points from Higashi<sup>13</sup>. Isopleth was obtained via CoolProp's phase envelope low-level method, calling REFPROP. Failures of a saturation calculation are indicated by  $\times$  markers.

Taking into consideration the challenges of assessing density data, deviation plots for the existing data are shown in Fig. 12.

For R-1234yf/134a, the datasets of Yotsumoto *et al.*<sup>15</sup> and Chen *et al.*<sup>18</sup> are in good agreement with the new model, although systematic composition-dependent errors can be seen for Chen *et al.*<sup>18</sup>. Although the deviations for Akasaka *et al.*<sup>16</sup> are generally larger, this error metric exaggerates the errors<sup>26</sup> as a consequence of the flatness of the saturation curve near the critical point (see Fig. 11).

For R-1234yf/1234ze(E), all the measurements are at the

same bulk composition. The deviations of Al Ghafri *et al.*<sup>9</sup> are small, while Higashi<sup>13</sup> scatters more, though the same discussion about the exaggeration of the error metric applies.

For R-134a/1234ze(E), the two other datasets<sup>9,14</sup> are in good agreement with the data. The datasets cover a relatively limited range of composition.



FIG. 12. Relative deviations in density for existing data (Higashi  $(2016)^{13}$ , Zhang  $(2017)^{14}$ , Yotsumoto  $(2010)^{15}$ , Akasaka  $(2015)^{16}$ , Higashi  $(2015)^{17}$ , Al Ghafri  $(2019)^9$ , Chen  $(2015)^{18}$ ) as a function of temperature and composition for the three primary mixtures. The subscript TW indicates the model in this work. Thin vertical lines indicate temperatures or compositions corresponding to a failure of an iterative calculation in REFPROP that is not plotted.

# 3. Critical region

Although mixture critical locus data were not included in the model development, there are a few experimental data points available in the literature<sup>13,16</sup>. In Fig. 13 these critical loci data are shown, along with curves calculated from the new mixture model in this work. The curves were traced with the teqp<sup>39</sup> library. No VLE data were included in the model development for either binary pair, so it is comforting to see that the temperature and pressure of the critical loci are well represented with the new mixture models according to the admittedly very limited data in the literature.



FIG. 13. Critical loci for R-1234yf/134a (with starred data points from Akasaka *et al.*<sup>16</sup>), for R-1234yf/1234ze(E) (with starred data point from Higashi<sup>13</sup>), and for R-134a/1234ze(E). The filled black circles indicate the pure-fluid values.

An interesting point about the critical locus for R-1234yf/134a is that it has a temperature minimum at 367.69 K, which is approximately 0.1 K below the critical point of R-1234yf. This means that for temperatures between the temperature minimum of the critical curve and the critical temperature of R-1234yf there are two critical points and the *p*-*x* curve is in two unconnected portions originating from the pure fluids. This behavior is not uncommon<sup>48</sup>; the mixture carbon dioxide + ethane also shows this behavior<sup>49</sup>.

# C. Extrapolation

A new means of assessing the extrapolation behavior of equations of state is that of the effective hardness of interaction<sup>50</sup>, which we denote as  $n_{\text{eff}}$ . In the dilute-gas limit, this quantity is defined by second virial coefficients  $B_2$  and their temperature derivatives

$$\lim_{\rho \to 0} n_{\text{eff}} = -3 \frac{T \frac{dB_2}{dT} + B_2}{T^2 \frac{d^2 B_2}{dT^2} + 2T \frac{dB_2}{dT}}$$
(20)

and is plotted for two models in Fig. 14 in the dilute-gas limit as a function of temperature and composition. While the EOS for R-134a has the wrong infinite temperature limit (which 21

should approach 3/2 for all potentials that are finitely valued at all separations; derivation in appendix of Ref. 51), the mixture models appear to smoothly transition between the two pure fluids. This is as expected, but comforting to see nonetheless. The EOS for R-1234ze(E) and R-1234yf demonstrate a small bump in the vicinity of 200 K which is suspect because neither the Stockmayer fluid (a common model potential for molecules with dipole-dipole interactions) nor molecular models for water<sup>52</sup> (a molecule with strong gas phase association) show the bumps<sup>50</sup>. Otherwise, the shapes of the  $n_{\rm eff}$  curves are qualitatively similar to those of the small rigid molecules for which *ab initio* data are available<sup>50</sup>.



FIG. 14. Values of the effective hardness of interaction as a function of temperature and linearly spaced molar compositions in the dilute gas limit.

#### VI. VLE-ONLY BINARY PAIRS

The second set of model results are for the binary pairs for which we included in the optimization only bubble-point pressure measurements from our group. In this case, an alternative model fitting procedure was employed. The method described in detail in Ref. 41 was used, which uses an evolutionary optimization approach in concert with iterative bubble-point pressure calculations from REFPROP 10.0<sup>27</sup>. The interaction parameters  $\beta_{T,ij}$  and  $\gamma_{T,ij}$  were optimized, the values of  $\beta_{v,ij}$  and  $\gamma_{v,ij}$  were set to 1.0, and no departure function was used. The obtained parameters are in Table IX, and the deviations are shown in Fig. 15. The AAD for the bubble-point pressures from our measurements are all less than 0.2%. For the binary pair R-125/R-1234yf, the model is able to fully capture the bubble-point data by fitting  $\beta_{T,ij}$  and  $\gamma_{T,ij}$ , showing no systematic errors and an AAD less than 0.1% (which is much smaller than the experimental uncertainty). For the other two binary pairs, fitting only  $\beta_{T,ii}$  and  $\gamma_{T,ii}$  does not appear to be sufficient to remove the systematic temperature deviation, although the AAD are all still below 0.2%.

TABLE IX. Interaction parameters obtained from fitting bubblepoint data only. Note: no departure function. Components in each binary pair are sorted by normal boiling point temperatures and the order matters.

| pair (1/2)        | $\beta_{T,ij}$ | $\gamma_{T,ij}$ | $\beta_{v,ij}$ | γ <sub>v,ij</sub> | $F_{ij}$ |
|-------------------|----------------|-----------------|----------------|-------------------|----------|
| R-125/1234yf      | 0.999637       | 0.999356        | 1.0            | 1.0               | 0.0      |
| R-1234yf/152a     | 1.002918       | 0.983928        | 1.0            | 1.0               | 0.0      |
| R-1234ze(E)/227ea | 1.000895       | 0.993523        | 1.0            | 1.0               | 0.0      |

The other datasets from the literature are listed in Table X and their deviations are plotted in Fig. 15. For R-125/1234yf and R-1234yf/152a, the existing data do not completely agree with our measured data, demonstrating scatter in pressure up to 2%.

The existing density datasets for these three binary mixtures are those of Dang *et al.*<sup>23</sup>, Al Ghafri *et al.*<sup>9</sup>. and Tomassetti<sup>1</sup>. The data from Dang *et al.*<sup>23</sup> deviate up to 1% in density. Al Ghafri *et al.*<sup>9</sup> claim a combined expanded uncertainty of 0.2 % in the liquid phase and 2 % in the gas phase; their density data are reproduced within this band. Tomassetti<sup>1</sup> includes some two-phase points, resulting in nonsensical density deviation values. The two-phase points were dropped, and the phase was specified to be gas.

TABLE X. Literature sources for the binary pairs with VLE-only measurements included in this work. For PVT points, the AAD is a deviation in density, for VLE points, it is the deviation in bubble-point pressure. The two-phase data from Tomassetti<sup>1</sup> have been dropped in the calculation of AAD.

| pair (1/2)    | kind | author                                  | Ν   | <i>T /</i> K | AAD / % |
|---------------|------|---|-----|--------------|---------|
| R-125/1234yf  | VLE  | Kamiaka, Dang, and Hihara <sup>21</sup> | 28  | 273 - 333    | 0.55    |
| R-125/1234yf  | VLE  | Kamiaka, Dang, and Hihara <sup>10</sup> | 84  | 273 - 333    | 0.28    |
| R-125/1234yf  | VLE  | Yang <i>et al.</i> <sup>22</sup>        | 35  | 283 - 323    | 0.16    |
| R-125/1234yf  | PVT  | Dang <i>et al.</i> <sup>23</sup>        | 27  | 284 - 318    | 0.47    |
| R-125/1234yf  | PVT  | Al Ghafri <i>et al.</i> 9               | 40  | 252 - 383    | 0.26    |
| R-1234yf/152a | VLE  | Hu <i>et al</i> . <sup>19</sup>         | 60  | 283 - 323    | 0.70    |
| R-1234yf/152a | VLE  | Yang <i>et al.</i> <sup>20</sup>        | 25  | 283 - 323    | 0.60    |
| R-1234yf/152a | PVT  | Tomassetti <sup>1</sup>                 | 136 | 268 - 373    | 0.16    |



FIG. 15. Deviations for VLE-only models compared with literature data (Tomassetti  $(2021)^1$ , Hu  $(2014)^{19}$ , Yang  $(2018)^{20}$ , Al Ghafri  $(2019)^9$ , Kamiaka  $(2010)^{21}$ , Yang  $(2020)^{22}$ , Dang  $(2015)^{23}$ , Kamiaka  $(2013)^{10}$ ) as open markers. Solid markers are the fitted VLE data from Outcalt and Rowane<sup>7</sup>, with the AAD as indicated in the figure title. The two-phase data from Tomassetti<sup>1</sup> have been dropped.

#### VII. VALIDATION AND VERIFICATION

The models presented in this work were implemented in REFPROP and CoolProp. The necessary files are provided in the supplementary material. Calculated values are provided in Table XI, and it was confirmed that the upcoming version of REFPROP and CoolProp version 6.4.2 yielded the same results to 13 digits. The new equation of state for R-1234yf of Lemmon and Akasaka<sup>29</sup> is also provided in REFPROP and CoolProp formats. An updated fluid file for REFPROP for R-152a is also provided, with the coefficients rounded to agree with the original publication<sup>31</sup> in order to yield the precise values in the table.

# VIII. CONCLUSIONS

Most importantly this study demonstrates that high accuracy liquid-phase speed of sound and density data are largely sufficient to fit highly accurate thermodynamic models for mixtures of chemically similar HFO- and HFC-containing binary mixtures. With the fitting of four interaction parameters and small departure functions, the experimental data can be reproduced to nearly their experimental uncertainty. In addition, the availability of highly-accurate reference mixture measurements allows the quality of the datasets in the literature to be assessed, identifying a number of discrepancies in the mixture data, and recommending which datasets should be considered. The highly accurate mixture data show that the equation of state for R-1234ze(E) needs to be refit in order to better reproduce the new liquid-phase speed of sound data.

In a parallel project further measurements are underway on some of the binary mixtures for which only VLE measurements were available in this work. These measurements will allow refinement of the interim models up to the level of the other mixture models obtained in this work.

## IX. SUPPLEMENTARY MATERIAL

In order to ensure reproducibility of the results, the supplementary material includes 1) the Python code used to generate the check values as well as the fluid files needed for the new EOS for R-1234yf 2) models in the formats needed for REFPROP and CoolProp/teqp 3) the fitting code and the experimental data used in the fitting process

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# X. AUTHOR DECLARATIONS

#### A. Conflict of Interest

The author has no conflicts to disclose

# B. Data Availability

The supplementary material, described above, includes the data used in this study. Additional information may be obtained from the author.

- <sup>1</sup>S. Tomassetti, "pvTz properties of 2,3,3,3-tetrafluoroprop-1-ene + 1,1difluoroethane binary system measured in the two-phase and superheated vapor regions," Fluid Phase Equilib. **546**, 113173 (2021).
- <sup>2</sup>A. J. Rowane and R. A. Perkins, "Speed of Sound Measurements of Binary Mixtures of 1,1,1,2-Tetrafluoroethane, 2,3,3,3-Tetrafluoropropene, and 1,3,3,3-Tetrafluoropropene Refrigerants," J. Chem. Eng. Data (2022 (submitted)).
- <sup>3</sup>M. O. McLinden and R. A. Perkins, "A dual-path pulse echo instrument for speed of sound of liquids and dense gases and measurements on p-xylene and four halogenated-olefin refrigerants [R1234yf, R1234ze(E), R1233zd(E), and R1336mzz(Z)]," J. Chem. Thermodyn. (2022 (manuscript in preparation)).
- <sup>4</sup>S. Lago, P. A. Giuliano Albo, and S. Brignolo, "Speed of Sound Results in 2,3,3,3-Tetrafluoropropene (R-1234yf) and trans-1,3,3,3-Tetrafluoropropene (R-1234ze(E)) in the Temperature Range of (260 to 360) K," J. Chem. Eng. Data **56**, 161–163 (2010).
- <sup>5</sup>M. Thol and E. W. Lemmon, "Equation of State for the Thermodynamic Properties of trans-1,3,3,3-Tetrafluoropropene [R-1234ze(E)]," Int. J. Thermophys **37**, 1–16 (2016).
- <sup>6</sup>P. A. Domanski, M. O. McLinden, V. I. Babushok, I. H. Bell, T. J. Fortin, M. J. Hegetschweiler, M. A. Kedzierski, D. K. Kim, L. Lin, G. T. Linteris, S. L. Outcalt, R. A. Perkins, A. Rowane, and H. Skye, "Low-GWP Alternative Refrigerant Blends for HFC-134a: Interim Report (NISTIR 8395; doi: 10.6028/nist.ir.8395)," Tech. Rep. (National Institute of Standards and Technology, 2021).
- <sup>7</sup>S. L. Outcalt and A. J. Rowane, "Bubble point measurements of mixtures of HFO and HFC refrigerants," J. Chem. Eng. Data (2021), 10.1021/acs.jced.1c00654.
- <sup>8</sup>L. Kou, Z. Yang, X. Tang, W. Zhang, and J. Lu, "Experimental measurements and correlation of isothermal vapor-liquid equilibria for HFC-32 + HFO-1234ze (E) and HFC-134a + HFO-1234ze (E) binary systems," J. Chem. Thermodyn. **139**, 105798 (2019).
- <sup>9</sup>S. Z. Al Ghafri, D. Rowland, M. Akhfash, A. Arami-Niya, M. Khamphasith, X. Xiao, T. Tsuji, Y. Tanaka, Y. Seiki, E. F. May, and T. J. Hughes, "Thermodynamic properties of hydrofluoroolefin (R1234yf and R1234ze(E)) refrigerant mixtures: Density, vapour-liquid equilibrium, and heat capacity data and modelling," Int. J. Refrig. **98**, 249–260 (2019).
- <sup>10</sup>T. Kamiaka, C. Dang, and E. Hihara, "Vapor-liquid equilibrium measurements for binary mixtures of R1234yf with R32, R125, and R134a," Int. J. Refrig. **36**, 965–971 (2013).
- <sup>11</sup>G. Ye, Y. Fang, Z. Guo, H. Ni, Y. Zhuang, X. Han, and G. Chen, "Experimental Investigation of Vapor Liquid Equilibrium for 2,3,3,3-Tetrafluoropropene (HFO-1234yf)+trans-1,3,3,3-Tetrafluoropropene (HFO-1234ze(E)) at Temperatures from 284 to 334 K," J. Chem. Eng. Data **66**, 1741–1753 (2021).
- <sup>12</sup>R. Chen, Y. Qi, and D. Wu, "Experimental Study of PVTx Properties of Mixture Refrigerant R1234yf/R134a," Zhileng Xuebao 37, 18–25 (2016).
- <sup>13</sup>Y. Higashi, "Measurements of thermodynamic properties for the 50 mass% R1234yf + 50 mass% R1234ze(E) blend," Sci. Technol. Built Environ. 22, 1185–1190 (2016).
- <sup>14</sup>H. Zhang, X. Dong, Q. Zhong, H. Li, M. Gong, J. Shen, and J. Wu, "Investigation of pρTx properties for R1234ze(E) + R134a mixtures in the gas phase," Int. J. Refrig. **73**, 144–153 (2017).
- <sup>15</sup>Y. Yotsumoto, R. Sugitani, S. Matsuo, and T. Sotani, "Density Measurements of Binary Mixtures for (HFO-1234yf + HFC-134a) System," in *The* 2019 (1999) 1999 (19999) 1999 (1999)

TABLE XI. Check values obtained with CoolProp<sup>†</sup> for the model obtained from nominal values of  $\rho/\rho_{red} = 0.8$  and  $T_{red}/T = 0.8$ . The first set of lines are check values for the pure fluids followed by one check value per binary pair. Names match the fluid file in REFPROP, are case-sensitive, and are compatible with CoolProp and teqp.

| names (1/2)         | $z_1$ / mole frac. | <i>T /</i> K | ho / mol/m <sup>3</sup> | $T_{\rm red}$ / K | $ ho_{\rm red}$ / mol/m <sup>3</sup> | $\alpha^{r}$      |
|---------------------|--------------------|--------------|-------------------------|-------------------|--------------------------------------|-------------------|
| R125                | 1.0                | 424          | 3823                    | 339.173000000000  | 4779.00000000000000                  | -0.45506005234449 |
| NEWR1234YF          | 1.0                | 460          | 3344                    | 367.850000000000  | 4180.0000000000000                   | -0.46835369904081 |
| R134A               | 1.0                | 468          | 3983                    | 374.180000000000  | 4978.8301710000014                   | -0.46682448414593 |
| R152A               | 1.0                | 483          | 4457                    | 386.411000000000  | 5571.44999999999998                  | -0.50742149570151 |
| R1234ZEE            | 1.0                | 478          | 3432                    | 382.513000000000  | 4290.0000000000000                   | -0.46340978447230 |
| R227EA              | 1.0                | 469          | 2796                    | 374.9000000000000 | 3495.0000000000000                   | -0.44238576197982 |
| NEWR1234YF+R1234ZEE | 0.4                | 469          | 3399                    | 375.3687082354176 | 4248.5958020013495                   | -0.46059464176252 |
| NEWR1234YF+R134A    | 0.4                | 462          | 3698                    | 369.3375352073332 | 4622.4357404722005                   | -0.46550859128831 |
| R134A+R1234ZEE      | 0.4                | 472          | 3639                    | 377.6667671452867 | 4548.6798721226469                   | -0.46245130334193 |
| R125+NEWR1234YF     | 0.4                | 445          | 3523                    | 356.1180639764045 | 4403.7418393016087                   | -0.46390805108207 |
| NEWR1234YF+R152A    | 0.4                | 470          | 3947                    | 376.1263345627942 | 4933.3992974468383                   | -0.49252417812231 |
| R1234ZEE+R227EA     | 0.4                | 471          | 3025                    | 376.7909385171813 | 3781.0104857183564                   | -0.45129881659440 |

†: CoolProp version 6.4.2dev, revision be204ce8d5b877246c2954a9948c3d72302ff587 (SHA1 hash)

- 31st Japan Symposium on Thermophysical Properties (Fukuoka: Japan, 2010).
- <sup>16</sup>R. Akasaka, Y. Higashi, Y. Yamada, and T. Shibanuma, "Thermodynamic properties of 1,1,1,2-tetrafluoroethane (R-134a) + 2,3,3,3tetrafluoropropene (R-1234yf) mixtures: Measurements of the critical parameters and a mixture model based on the multi-fluid approximation," Int. J. Refrig. **58**, 146–153 (2015).
- <sup>17</sup>Y. Higashi, "Thermophysical Property Measurements for R1234yf + R1234ze(E) Mixture," in *International Congress of Refrigeration* (Yokohama: Japan, 2015).
- <sup>18</sup>Q. Chen, H. Qi, S. Zhang, R. Hong, and G. Chen, "An experimental study of PVTx properties in the gas phase for binary mixtures of HFO-1234yf and HFC-134a," Fluid Phase Equilib. **385**, 25–28 (2015).
- <sup>19</sup>P. Hu, L.-X. Chen, W.-B. Zhu, L. Jia, and Z. Chen, "Isothermal VLE measurements for the binary mixture of 2,3,3,3-tetrafluoroprop-1-ene (HFO-1234yf) + 1,1-difluoroethane (HFC-152a)," Fluid Phase Equilib. **373**, 80–83 (2014).
- <sup>20</sup>T. Yang, X. Hu, X. Meng, and J. Wu, "Vapor-Liquid Equilibria for the Binary and Ternary Systems of Difluoromethane (R32), 1,1-Difluoroethane (R152a), and 2,3,3,3-Tetrafluoroprop-1-ene (R1234yf)," J. Chem. Eng. Data **63**, 771–780 (2018).
- <sup>21</sup>T. Kamiaka, C. Dang, and E. Hihara, "Vapor-Liquid Equilibrium Measurements of HFC-32+HFO-1234yf and HFC-125+HFO-1234yf Refrigerant Mixture," in JSRAE Annual Conference (Kanazawa, 2010).
- <sup>22</sup>T. Yang, X. Hu, X. Meng, and J. Wu, "Vapour-liquid equilibria for the binary systems of pentafluoroethane ((R125) + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf)) and (trans-1,3,3,3-tetrafluoropropene R1234ze(E))," J. Chem. Thermodyn. **150**, 106222 (2020).
- <sup>23</sup>Y. Dang, T. Kamiaka, C. Dang, and E. Hihara, "Liquid viscosity of low-GWP refrigerant mixtures (R32 + R1234yf) and (R125 + R1234yf)," J. Chem. Thermodyn. **89**, 183–188 (2015).
- <sup>24</sup>M. O. McLinden and M. L. Huber, "(R)Evolution of refrigerants," J. Chem. Eng. Data. 65, 4176–4193 (2020).
- <sup>25</sup>I. H. Bell, P. A. Domanski, M. O. McLinden, and G. T. Linteris, "The hunt for nonflammable refrigerant blends to replace R-134a," Int. J. Refrig. **104**, 484–495 (2019).
- <sup>26</sup>I. H. Bell, D. Riccardi, A. Bazyleva, and M. O. McLinden, "Survey of data and models for refrigerant mixtures containing halogenated olefins," J. Chem. Eng. Data. **66**, 2335–2354 (2021).
- <sup>27</sup>E. W. Lemmon, I. H. Bell, M. L. Huber, and M. O. McLinden, "NIST Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 10.0, National Institute of Standards and Technology," http://www.nist.gov/srd/nist23.cfm (2018).
- <sup>28</sup>E. W. Lemmon and R. T. Jacobsen, "A New Functional Form and New Fitting Techniques for Equations of State with Application to Pentafluoroethane (HFC-125)," J. Phys. Chem. Ref. Data **34**, 69–108 (2005).

- <sup>29</sup>E. W. Lemmon and R. Akasaka, "An International Standard Formulation for 2,3,3,3-Tetrafluoroprop-1-ene (R1234yf) Covering Temperatures from the Triple-point Temperature to 410 K and Pressures up to 100 MPa," Int. J. Thermophys. (2022 (submitted)).
- <sup>30</sup>R. Tillner-Roth and H. D. Baehr, "An International Standard Formulation for the Thermodynamic Properties of 1,1,1,2-Tetrafluoroethane (HFC-134a) for Temperatures from 170 K to 455 K and Pressures up to 70 MPa," J. Phys. Chem. Ref. Data 23, 657–729 (1994).
- <sup>31</sup>S. L. Outcalt and M. O. McLinden, "A Modified Benedict–Webb–Rubin Equation of State for the Thermodynamic Properties of R152a (1,1difluoroethane)," J. Phys. Chem. Ref. Data 25, 605–636 (1996).
- <sup>32</sup>M. Thol and E. W. Lemmon, "Equation of State for the Thermodynamic Properties of trans-1,3,3,3-Tetrafluoropropene [R-1234ze(E)]," Int. J. Thermophys. **37** (2016), 10.1007/s10765-016-2040-6.
- <sup>33</sup>E. W. Lemmon and R. Span, "Thermodynamic Properties of R-227ea, R-365mfc, R-115, and R-1311," J. Chem. Eng. Data **60**, 3745–3758 (2015).
- <sup>34</sup>V. Diky, R. D. Chirico, M. Frenkel, A. Bazyleva, J. W. Magee, E. Paulechka, A. Kazakov, E. W. Lemmon, C. D. Muzny, A. Y. Smolyanitsky, S. Townsend, and K. Kroenlein, "NIST Standard Reference Database 103b: ThermoData Engine (Version 10.1)," (2017).
- <sup>35</sup>H. Shimoura, S. Matsuo, and T. Sotani, "Speed of sound measurements in dense liquid of low GWP refrigerant mixture including HFO-1234yf," in *The 32nd Japan Symposium on Thermophysical Properties* (Yokohama: Japan, 2011).
- <sup>36</sup>I. H. Bell, J. Wronski, S. Quoilin, and V. Lemort, "Pure and Pseudo-pure Fluid Thermophysical Property Evaluation and the Open-Source Thermophysical Property Library CoolProp," Ind. Eng. Chem. Res. **53**, 2498–2508 (2014), http://pubs.acs.org/doi/pdf/10.1021/ie4033999.
- <sup>37</sup>R. Span, R. Beckmüller, S. Hielscher, A. Jäger, E. Mickoleit, T. Neumann, S. Pohl, B. Semrau, and M. Thol, "TREND. Thermodynamic Reference and Engineering Data 5.0," (2020).
- <sup>38</sup>P. J. Mohr, D. B. Newell, B. N. Taylor, and E. Tiesinga, "Data and analysis for the CODATA 2017 special fundamental constants adjustment," Metrologia 55, 125–146 (2018).
- <sup>39</sup>I. H. Bell, U. K. Deiters, and A. M. M. Leal, "Implementing an Equation of State Without Derivatives: teqp," Ind. Eng. Chem. Eng. (2022 (submitted)).
- <sup>40</sup>U. K. Deiters and I. H. Bell, "Calculation of critical curves of fluid mixtures through solution of differential equations," Ind. Eng. Chem. Res. **59**, 19062–19076 (2020).
- <sup>41</sup>I. H. Bell and E. W. Lemmon, "Automatic fitting of binary interaction parameters for multi-fluid Helmholtz-energy-explicit mixture models," J. Chem. Eng. Data **61** (2016), 10.1021/acs.jced.6b00257.
- <sup>42</sup>O. Kunz, R. Klimeck, W. Wagner, and M. Jaeschke, *The GERG-2004 Wide-Range Equation of State for Natural Gases and Other Mixtures* (VDI Verlag GmbH, 2007).
- <sup>43</sup>E. W. Lemmon and R. T. Jacobsen, "Equations of State for Mixtures of R-32, R-125, R-134a, R-143a, and R-152a," J. Phys. Chem. Ref. Data 33,

593-620 (2004).

- <sup>44</sup>I. H. Bell, "CEGO: C++11 evolutionary global optimization," J. Open Source Soft. 4, 1147 (2019).
- <sup>45</sup>P. Virtanen, R. Gommers, T. E. Oliphant, M. Haberland, T. Reddy, D. Cournapeau, E. Burovski, P. Peterson, W. Weckesser, J. Bright, S. J. van der Walt, M. Brett, J. Wilson, K. J. Millman, N. Mayorov, A. R. J. Nelson, E. Jones, R. Kern, E. Larson, C. J. Carey, İ. Polat, Y. Feng, E. W. Moore, J. VanderPlas, D. Laxalde, J. Perktold, R. Cimrman, I. Henriksen, E. A. Quintero, C. R. Harris, A. M. Archibald, A. H. Ribeiro, F. Pedregosa, P. van Mulbregt, and SciPy 1.0 Contributors, "SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python," Nature Methods 17, 261–272 (2020).
- <sup>46</sup>R. A. Perkins and M. O. McLinden, "Spherical resonator for vaporphase speed of sound and measurements of 1,1,1,2,2,3,3-heptafluoro-3-methoxypropane (RE347mcc) and trans-1,3,3,3-tetrafluoropropene [R1234ze(E)]," J. Chem. Thermodyn. **91**, 43–61 (2015).
- <sup>47</sup>Y. Kano, Y. Kayukawa, K. Fujii, and H. Sato, "Ideal gas heat capacity derived from speed of sound measurements in the gaseous phase for trans-

1,3,3,3-tetrafluoropropene," J. Chem. Eng. Data 58, 2966–2969 (2013).

- <sup>48</sup>U. K. Deiters and T. Kraska, *High-Pressure Fluid Phase Equilibria: Phenomenology and Computation*, edited by E. Kiran (Elsevier, 2012).
- <sup>49</sup>I. H. Bell and U. K. Deiters, "On the construction of binary mixture p-x and T-x diagrams from isochoric thermodynamics," AIChE J. **64**, 2745–2757 (2018).
- <sup>50</sup>I. H. Bell, "Effective hardness of interaction from thermodynamics and viscosity in dilute gases," J. Chem. Phys. **152**, 164508 (2020).
- <sup>51</sup>S. Polychroniadou, K. D. Antoniadis, M. J. Assael, and I. H. Bell, "A Reference Correlation for the Viscosity of Krypton From Entropy Scaling," Int. J. Thermophys. **43** (2021), 10.1007/s10765-021-02927-5.
- <sup>52</sup>G. Garberoglio, P. Jankowski, K. Szalewicz, and A. H. Harvey, "Fully quantum calculation of the second and third virial coefficients of water and its isotopologues from ab initio potentials," Faraday Discuss. **212**, 467–497 (2018).