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Thermodynamic Properties of Mixtures of R-32, R-125, R-134a, and R-152a[1]

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A mixture model explicit in Helmholtz energy has been developed that is capable of predicting thermodynamic properties of refrigerant mixtures containing R-32, R-125, R-134a, and R-152a. The Helmholtz energy of the mixture is the sum of the ideal gas contribution, the compressibility (or real gas) contribution, and the contribution from mixing. The contribution from mixing is given by a single equation that is applied to all mixtures used in this work. The independent variables are the density, temperature, and composition. The model may be used to calculate thermodynamic properties of mixtures, including dew and bubble point properties and critical points, generally within the experimental uncertainties of the available measured properties. It incorporates the most accurate published equation of state for each pure fluid. The estimated uncertainties of calculated properties are ±0.25% in density, ±0.5% in the speed of sound, and ±1% in heat capacities. Calculated bubble point pressures are generally accurate to within ±1%.

KEY WORDS: equation of state; mixtures; R-32; R-125; R-134a; R-152a; thermodynamic properties.

1. INTRODUCTION

Applications increasingly require the use of equations of state capable of accurate prediction of thermodynamic properties of environmentally safe

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refrigerant mixtures. New refrigerants and mixtures of refrigerants are used as environmentally acceptable replacements for chlorofluorocarbons and hydrochlorofluorocarbons in refrigeration, heat pumps, foam-blowing, and other applications. Mixture equations are required to evaluate the performance of possible alternatives to the fully halogenated chlorofluorocarbons as working fluids. Many of the refrigerant mixtures form azeotropes. This is often desirable in vapor compression cycles because the mixture behaves as a pure fluid during phase changes.

The model presented here for mixtures of refrigerants is part of a more generalized model reported by Lemmon and Jacobsen [1] for mixtures of cryogens, hydrocarbons, and refrigerants. This model was initially reported by Lemmon [2] in a slightly different format. The model is based on corresponding states theory. Reducing parameters which are dependent on the mole fraction are used to modify absolute values of density and temperature. The Helmholtz energy for an ideal solution is determined at the reduced density and temperature of the mixture using accurate pure-fluid equations of state for the mixture components.

The part of the model describing the Helmholtz energy contribution due to mixing is nearly the same for all binary mixtures, and relatively simple scaling factors are used to determine its magnitude for a particular application. Experimental data from many different mixtures were used to determine the function. The model is capable of predicting mixture properties for fluids with limited experimental databases. In addition, all vapor and liquid thermodynamic properties, including density, energy, entropy, heat capacity, sound speed, vapor–liquid equilibrium (VLE), and the mixture critical temperature, pressure, and density, can be calculated accurately using this approach.

The mixtures studied in this work are

- R-32/R-125,
- R-32/R-134a,
- R-125/R-134a,
- R-32/R-125/R-134a, and
- R-134a/R-152a.

Data for these mixtures were used to evaluate the behavior of the model, to calculate the coefficients of the generalized refrigerant mixture equation, and to calculate the individual parameters for each binary mixture. Table I lists the pure fluid equations of state used in this work. For convenience, all equations were converted from the published format to a fundamental form widely used in system analysis and design.

Table I. Pure Fluid Equations of State for Refrigerants Used in the Mixture Model

Fluid	Reference	Temperature range (K)	Maximum pressure (MPa)
R-32	Tillner-Roth and Yokozeki [3]	136.34–435	70
R-125	Sunaga et al. [4]	172.52–500	60
R-134a	Tillner-Roth and Baehr [5]	169.85–455	70
R-152a	Tillner-Roth [6]	154.56–435	30

2. THE MIXTURE EQUATION

The equation for the mixture Helmholtz energy used in this work is

$$A = A^{\mathrm{idmix}} + A^{\mathrm{E}} \tag{1}$$

The Helmholtz energy for an ideal mixture is

$$A^{\mathrm{idmix}} = \sum_{i=1}^{n} x_i [A_i^0(\rho, T) + A_i^{\mathrm{r}}(\delta, \tau) + RT \ln x_i] \tag{2}$$

where ρ and T are the mixture density and temperature, δ and τ are the reduced mixture density and temperature, n is the number of components in the mixture, A_i^0 is the ideal gas Helmholtz energy of component i, A_i^{r} is the residual Helmholtz energy of component i, and the x_i are the mole fractions of the mixture constituents. References for the pure fluid ideal gas Helmholtz energy and residual Helmholtz energy equations are given in Table I.

The contribution to the Helmholtz energy from mixing is calculated using

$$\frac{A^{\mathrm{E}}}{RT} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j F_{ij} \sum_{k=1}^{10} N_k \delta^{d_k} \tau^{t_k} + x_{\mathrm{R\text{-}32}} x_{\mathrm{R\text{-}125}} (N_{11} \delta\tau + N_{12} \delta) + x_{\mathrm{R\text{-}32}} x_{\mathrm{R\text{-}134a}} N_{13} \delta \tag{3}$$

where the N_k, i_k, and j_k are coefficients and exponents obtained from linear regressions of experimental mixture data. The parameter F_{ij} relates the mixing contribution of one binary mixture to that of another. This value is determined with a nonlinear fitting procedure that minimizes the sum of squares of the deviations between the equation and the data for a small select set of measurements. All thermodynamic properties can be calculated from the Helmholtz energy using differentiation with respect to density or temperature as described by Lemmon et al. [1, 2, 7].

The reduced density and temperature for the mixture are

$$\delta = \rho/\rho_{\mathrm{red}} \tag{4}$$

$$\tau = T_{\mathrm{red}}/T \tag{5}$$

where ρ_{red} and T_{red} are the reducing values,

$$\rho_{\mathrm{red}} = \left[\sum_{i=1}^{n} \frac{x_i}{\rho_{c_i}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \xi_{ij} \right]^{-1} \tag{6}$$

$$T_{\mathrm{red}} = \sum_{i=1}^{n} x_i T_{c_i} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j \zeta_{ij} \tag{7}$$

The parameters ζ_{ij} and ξ_{ij} are used to define the shapes of the reducing parameter lines. The reducing parameters are not the same as the critical parameters of the mixture, and the use of these parameters allows the calculation of VLE properties above the reducing temperature where required. These parameters define the relationship between the critical lines of different binary mixtures and are determined simultaneously in the nonlinear fit with the generalizing factor F_{ij}. Details of the fitting procedures used to determine the generalizing factors and mixture parameters are given by Lemmon [2] and are not repeated here. The values of the coefficients and exponents in Eq. (3) are given in Table II. The generalizing factors and mixture parameters are given in Table III.

Table II. Coefficients and Exponents of the Mixture Equation

k	N_k	d_k	t_k
1	$-0.245\,476\,271\,425 \times 10^{-1}$	1	2
2	$-0.241\,206\,117\,483$	1	4
3	$-0.513\,801\,950\,309 \times 10^{-2}$	1	-2
4	$-0.239\,824\,834\,123 \times 10^{-1}$	2	1
5	$0.259\,772\,344\,008$	3	4
6	$-0.172\,014\,123\,104$	4	4
7	$0.429\,490\,028\,551 \times 10^{-1}$	5	4
8	$-0.202\,108\,593\,862 \times 10^{-3}$	6	0
9	$-0.382\,984\,234\,857 \times 10^{-2}$	6	4
10	$0.262\,992\,331\,354 \times 10^{-5}$	8	-2
11	$-0.198\,606\,229\,861 \times 10^{-1}$	1	1
12	$0.143\,226\,453\,485$	1	0
13	$0.369\,107\,330\,061 \times 10^{-1}$	1	0

Table III. Parameters of the Mixture Equation

Binary mixture	F_{ij}	ξ_{ij} ($dm^3 \cdot mol^{-1}$)	ζ_{ij} (K)
R-32/R-125	−0.789 585	−0.005 301 77	14.663 390
R-32/R-134a	−0.314 574	−0.003 920 17	5.737 916
R-125/R-134a	0.104 729	0.0	−2.736 948
R-134a/R-152a	0.125 997	0.004 879 24	−2.041 245

3. COMPARISONS OF CALCULATED REFRIGERANT MIXTURE PROPERTIES TO EXPERIMENTAL DATA

The accuracies of calculated values of various properties are determined by comparisons with measured values. Statistical analyses are used to determine the overall estimated accuracy of the model, and to define the ranges of estimated accuracies for various properties calculated with the formulation. Summary comparisons of values calculated using the mixture equation to p–ρ–T data, isochoric heat-capacity data (c_v), sound-speed data (w), and VLE data for refrigerant mixtures are given in Table IV, along with the temperature and composition range for the first component listed. Compositions for VLE data are bubble-point compositions, except where noted. Details of the property calculation methods, including those for VLE states, are given by Lemmon [2].

The statistics used to evaluate the equation are based on the percentage deviation for any property, X,

$$\%\Delta X = 100\left(\frac{X_{\text{data}} - X_{\text{calc}}}{X_{\text{data}}}\right) \tag{8}$$

Using this definition, the statistics in Table IV are defined as

$$\text{AAD} = \frac{1}{n}\sum_{i=1}^{n} |\%\Delta X_i| \tag{9}$$

$$\text{Bias} = \frac{1}{n}\sum_{i=1}^{n} (\%\Delta X_i) \tag{10}$$

Two of the terms listed in Eq. (3) are specific to the R-32/125 binary mixture, and another is specific to the R-32/134a binary mixture. The mixture model behavior is sensitive to the accuracy of the pure-fluid equations of state. The equation of Outcalt and McLinden [33] for R-32 was

Table IV. Comparisons of Mixture Properties Calculated from the Model to Refrigerant Mixture Data

Reference	No. points	Temp. range (K)	Comp. range (mol frac.)	AAD (%)[a]	Bias (%)
R-32/R-125: p-ρ-T					
Holcomb et al. [8]	45	279–341	0.24–0.96	0.907	0.285
Kiyoura et al. [9]	94	330–440	0.37–0.61	0.234	−0.233
Kleemiss [10]	415	243–413	0.50–0.51	0.163	−0.001
Magee [11]	228	200–400	0.50	0.104	0.019
Oguchi et al. [12]	6	355–430	0.87	0.392	−0.305
Piao et al. [13]	533	263–393	0.37–0.90	0.261	−0.130
Sato et al. [14]	156	320–440	0.70–0.90	0.261	−0.247
Weber and Defibaugh [15]	17	338–373	0.55	0.427	−0.427
Zhang et al. [16]	124	300–380	0.50–0.70	0.238	−0.228
Overall	1618	200–440	0.24–0.96	0.231	−0.093
R-32/R-125: VLE					
Defibaugh and Morrison [17]	10	249–338	0.76	0.148	0.019
Fujiwara et al. [18]	8	273	0.06–0.90	2.137	2.137
Higashi [19]	45	283–346	0.23–0.90	0.327	0.314
Holcomb et al. [8]	30	280–340	0.34–0.95	0.324	0.181
Kleemiss [10]	23	224–333	0.48–0.52	0.320	−0.149
Nagel and Bier [20]	34	205–345	0.24–0.95	0.554	0.061
Oguchi et al. [12]	11	250–350	0.87	0.525	0.525
Piao et al. [13]	10	263–283	0.37–0.90[b]	0.597	−0.564
Widiatmo et al. [21]	24	280–310	0.20–0.90	0.559	0.410
Overall	195	205–350	0.06–0.95	0.489	0.232
R-32/R-134a: p-ρ-T					
Holcomb et al. [8]	44	279–340	0.13–0.97	1.123	0.535
Kleemiss [10]	390	243–413	0.50–0.56	0.090	0.001
Magee [11]	461	200–400	0.50	0.116	−0.010
Oguchi et al. [12]	19	363–473	0.39	0.426	0.407
Piao et al. [13]	633	263–393	0.33–0.89	0.405	−0.225
Sato et al. [22]	220	320–440	0.33–0.89	0.147	−0.011
Weber and Defibaugh [15]	17	338–373	0.51	1.048	−1.048
Widiatmo et al. [23]	22	280–330	0.40	0.105	−0.003
Overall	1806	200–473	0.13–0.97	0.252	−0.075
R-32/R-134a: c_v					
Magee [11]	131	205–343	0.50	0.371	0.293

Table IV. *(Continued)*

Reference	No. points	Temp. range (K)	Comp. range (mol frac.)	AAD (%)[a]	Bias (%)
		R-32/R-134a: w			
Hozumi et al. [24]	193	303–343	0.16–0.90	0.030	0.030
		R-32/R-134a: VLE			
Defibaugh and Morrison [17]	25	253–358	0.50–0.55	0.403	0.270
Fujiwara et al. [18]	6	273–273	0.20–0.92	3.262	−3.262
Higashi [25]	39	283–365	0.12–0.67	0.903	0.798
Holcomb et al. [8]	48	280–340	0.16–0.78	0.400	0.127
Kleemiss [10]	16	223–343	0.42–0.52	0.229	0.117
Nagel and Bier [20]	50	203–369	0.21–0.77	0.500	0.134
Oguchi et al. [12]	34	238–301	0.27–0.71	0.868	0.776
Piao et al. [13]	10	261–283	0.33–0.89[b]	0.564	−0.564
Widiatmo et al. [26]	30	280–340	0.33–0.89	1.646	1.646
Overall	258	203–369	0.12–0.92	0.760	0.380
		R-125/R-134a: p–ρ–T			
Holcomb et al. [8]	17	280–342	0.35–0.72	0.332	−0.254
Kleemiss [10]	407	243–413	0.50–0.51	0.160	−0.130
Magee [11]	268	200–400	0.50	0.158	−0.150
Weber and Defibaugh [15]	18	303–373	0.50	0.305	−0.276
Widiatmo et al. [23]	110	280–350	0.09–0.92	0.125	−0.110
Overall	820	200–413	0.09–0.92	0.161	−0.140
		R-125/R-134a: VLE			
Higuchi and Higashi [27]	55	283–365	0.18–0.78	0.447	0.041
Holcomb et al. [8]	40	280–340	0.26–0.65	0.522	−0.031
Kleemiss [10]	24	224–343	0.46–0.51	0.363	−0.264
Nagel and Bier [20]	31	206–365	0.25–0.75	0.513	0.174
Widiatmo et al. [23]	75	280–350	0.09–0.92	0.708	0.708
Overall	225	206–365	0.09–0.92	0.553	0.248
		R-32/R-125/R-134a: p–ρ–T			
Holcomb et al. [8]	42	244–346	0.20–0.68	1.199	0.716
Kiyoura et al. [9]	105	315–440	0.38–0.52	0.385	0.230
Kleemiss [10]	369	243–413	0.33–0.35	0.075	−0.029
Oguchi et al. [12]	12	365–430	0.38–0.47	0.164	−0.159
Piao et al. [13]	994	263–393	0.19–0.47	0.311	−0.133
Widiatmo et al. [23]	53	280–340	0.38–0.46	0.190	−0.186
Overall	1575	243–440	0.19–0.68	0.277	−0.066

Table IV. *(Continued)*

Reference	No. points	Temp. range (K)	Comp. range (mol frac.)	AAD (%)[a]	Bias (%)
R-32/R-125/R-134a: VLE					
Higashi [28]	52	273–359	0.17–0.54	0.783	−0.265
Holcomb et al. [8]	58	221–345	0.05–0.60	0.905	0.059
Kleemiss [10]	44	222–353	0.14–0.66	0.347	−0.274
Nagel and Bier [20]	29	205–362	0.19–0.43	0.645	−0.085
Piao et al. [13]	31	270–326	0.32–0.38	0.679	0.195
Widiatmo et al. [23]	43	280–340	0.35–0.46	0.514	0.513
Overall	257	205–362	0.05–0.66	0.657	0.026
R-134a/R-152a: p–ρ–T					
Dressner and Bier [29]	139	333–423	0.49–0.54	0.221	−0.050
Tillner-Roth [30]	1679	243–433	0.25–0.75	0.097	0.014
Weber and Defibaugh [15]	11	353–373	0.50	0.087	0.019
Overall	1829	243–433	0.25–0.75	0.042	0.017
R-134a/R-152a: w					
Grebenkov et al. [31]	120	230–336	0.69	0.466	−0.446
R-134a/R-152a: VLE					
Defibaugh and Morrison [17]	13	248–368	0.78	0.284	0.009
Kleiber [32]	25	255–298	0.31–0.98	0.146	−0.134
Tillner-Roth [30]	65	243–378	0.23–0.75	0.071	−0.035
Overall	103	243–378	0.12–0.98	0.116	−0.054

[a] Average absolute deviation in density for p–ρ–T data and in bubble point pressure for VLE data.

[b] Dew-point composition.

used in place of the equation from Tillner-Roth and Yokozeki [3] to determine the sensitivity of the deviations of calculated properties to the selection of the R-32 equation. Replacing the equation increased the AAD for the critical region density data of Magee [11] (at temperatures greater than 350 K) from 0.17 to 0.20% for the R-32/134a binary mixture. The deviations for other data in the supercritical region increased as well. Additional details of this analysis are given by Lemmon [2]. This issue may be resolved by additional measurements and a revised correlation for R-32. Likewise, there are similar deficiencies in the R-125 database in the critical region.

4. ACCURACY ASSESSMENT

Based on comparisons to experimental data, the equation is generally accurate to ±0.25% for density, ±1% for heat capacity, ±0.5% for speed of sound, and ±1% for calculated bubble-point pressures. The model is valid from 200 to 450 K up to 60 MPa as verified by experimental data. In regions where there are no binary mixture data, the accuracy is estimated to be of the same magnitude through the use of the generalized mixing function. This mixing function is based on experimental data for many mixtures [1], including hydrocarbons, cryogens, and refrigerants, and should allow the extension of the model to other mixtures with limited databases with good confidence. However, this cannot be verified by the authors until experimental data are available to support these conclusions. Although the equation was developed using mostly binary data, it is accurate in calculating the properties of mixtures with three or more constituents. This conclusion is based upon comparisons of calculated values to the limited data available for multicomponent systems.

Future measurements will confirm whether the equation is valid for other mixtures and in regions not covered by the experimental data used in the development of this model. Such data will enable continued evaluation and development of the model.

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