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A Generalized Model for the Thermodynamic Properties of Mixtures[1]

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A mixture model explicit in Helmholtz energy has been developed which is capable of predicting thermodynamic properties of mixtures containing nitrogen, argon, oxygen, carbon dioxide, methane, ethane, propane, *n*-butane, *i*-butane, R-32, R-125, R-134a, and R-152a within the estimated accuracy of available experimental data. 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 generalized equation which is applied to all mixtures studied in this work. The independent variables are the density, temperature, and composition. The model may be used to calculate the thermodynamic properties of mixtures at various compositions including dew and bubble point properties and critical points. It incorporates accurate published equations of state for each pure fluid. The estimated accuracy of calculated properties is ±0.2% in density, ±0.1% in the speed of sound at pressures below 10 MPa, ±0.5% in the speed of sound for pressures above 10 MPa, and ±1% in heat capacities. In the region from 250 to 350 K at pressures up to 30 MPa, calculated densities are within ±0.1% for most gaseous phase mixtures. For binary mixtures where the critical point temperatures of the pure fluid constituents are within 100 K of each other, calculated bubble point pressures are generally accurate to within ±1 to 2%. For mixtures with critical points further apart, calculated bubble point pressures are generally accurate to within ±5 to 10%.

KEY WORDS: cryogens; equation of state; hydrocarbons; mixtures; refrigerants; thermodynamic properties.

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1. INTRODUCTION

A new approach has been used in the application of equations of state to fluid mixtures. This work, which began in 1992, is an extension of an excess property model which accounts for the difference between an ideal solution and the real property value at constant pressure and temperature. The model used to calculate properties of mixtures was developed by Lemmon [1] based on a modified excess, or excess-like, Helmholtz energy equation, and corresponding states theory. It follows to some extent the multifluid model for mixtures given by Leland and Chappelear [2] and is similar to the concurrent but independent work of Tillner-Roth [3]. The model reported here is largely empirical in nature.

The generalized model presented here may be used for mixtures of cryogens and hydrocarbons, including mixtures of the natural refrigerants propane/*n*-butane and propane/*i*-butane. Comparisons to experimental data for mixtures of nitrogen, argon, and oxygen, including air, are given by Lemmon and Jacobsen [4], although the parameters for mixtures containing these fluids are given here. For mixtures of the refrigerants R-32, R-125, R-134a, and R-152a, Lemmon and Jacobsen [5] present comparisons to experimental data and describe additional parameters required to implement the model.

The Helmholtz energy for an ideal mixture is determined at the reduced density and temperature of the mixture using accurate pure fluid equations of state for the mixture components. The Helmholtz energy contribution from mixing (the modified excess function) is calculated from the model given by Lemmon [1]. The reducing parameters for density and temperature are calculated using the critical points of the pure fluids. The model represents most of the available measured data within their estimated experimental accuracy.

An advantage of the approach used here is that the function describing the Helmholtz energy contribution to mixing is 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, speed of sound, vapor–liquid equilibrium (VLE), and the mixture critical temperature, pressure, and density can be calculated accurately using this approach. As the pure-fluid limits of concentration are approached, the model defaults to the pure fluid equations of state.

2. THE MIXTURE EQUATION

An excess property of a mixture is defined as the actual mixture property at a given condition minus the value for an ideal solution at the same condition. In most other work dealing with excess properties, the equilibrium condition is defined at constant pressure and temperature. Because the independent variables for the pure fluid Helmholtz energy equations are density and temperature, properties are calculated here at the density and temperature of the mixture. Since this model deals with the entire fluid surface, reduced values of density and temperature are used rather than absolute values to ensure that properties of the constituents are calculated for the same phase as the mixture. While this approach is arbitrary and different from the usual excess property format, it results in an accurate representation of the thermodynamic properties of mixtures.

The Helmholtz energy contribution to mixing is small in comparison to the ideal mixture Helmholtz energy. Equations could be developed to account for the Helmholtz energy contribution for every binary mixture of interest. However, this would require data that cover the entire surface, including p–ρ–T, heat capacity, and speed of sound data for each binary mixture. Such a database exists for the methane/ethane and methane/nitrogen mixtures. However, for most other mixtures such an extensive and highly accurate database is not available. A practical approach is to develop a relatively short generalized equation which can be used to calculate the properties of all binary mixtures. In addition, properties of ternary and higher order mixtures might also be calculated with these equations.

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

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

The Helmholtz energy for an ideal mixture is

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

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.

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

Fluid	Authors	Temperature range (K)	Maximum pressure (MPa)
Methane	Setzmann and Wagner [6]	90.694–625	1000
Ethane	Friend et al. [7]	90.352–623	69
Propane	Younglove and Ely [8]	85.47–600	100
n-Butane	Younglove and Ely [8]	134.86–500	70
i-Butane	Younglove and Ely [8]	113.55–600	35
Ethylene	Jahangiri et al. [9]	103.986–450	260
Nitrogen	Span et al. [10]	63.151–1000	2200
Argon	Stewart and Jacobsen [11]	83.804–1200	1000
Oxygen	Schmidt and Wagner [12]	54.361–300	82
Carbon dioxide	Span and Wagner [13]	216.58–1000	100

The contribution to the Helmholtz energy from mixing is calculated using

$$\frac{A^E}{RT} = \alpha^E(\delta, \tau, \mathbf{x}) = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} x_i x_j F_{ij} \sum_{k=1}^{10} N_k \delta^{d_k} \tau^{t_k} \tag{3}$$

The reduced density and temperature for the mixture are

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

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

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

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

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

The parameters ζ_{ij}, ξ_{ij}, β_{ij}, and ϕ_{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. For the methane/ethane system, ζ_{ij} and ξ_{ij} were set to zero. The value of ϕ_{ij} is 1 except for the propane/carbon dioxide system, where $\phi_{ij} = 1.235228$.

Table II. Coefficients and Exponents of the Mixture Equation, Eq. (3)

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

The values of the coefficients and exponents in Eq. (3) are given in Table II. The generalized factors and mixture parameters are given in Table III. The subscript i in Eqs. (3), (6), and (7) refers to the first component listed in Table III and the subscript j refers to the second component.

Table III. Parameters of the Mixture Equation

Binary mixture	F_{ij}	ξ_{ij} (dm^3/mol)	ζ_{ij} (K)	β_{ij}
Methane/ethane	1.	0.	0.	1.
Methane/propane	1.556 361	−0.002 669 06	19.390 289	1.882 266
Methane/*n*-butane	2.445 415	0.	41.132 992	2.006 673
Methane/*i*-butane	2.661 664	0.	40.039 217	2.544 409
Methane/nitrogen	0.634 182	0.003 810 45	−17.818 676	1.
Methane/carbon dioxide	0.808 546	0.	−37.271 180	1.
Methane/ethylene	0.742 836	0.	−11.071 005	1.
Ethane/propane	0.106 842	−0.001 546 38	3.745 019	1.
Ethane/*n*-butane	0.759 528	0.	0.	1.
Ethane/nitrogen	1.021 463	0.009 648 61	−17.864 694	1.233 477
Ethane/carbon dioxide	−0.154 127	0.009 519 99	−63.629 672	1.
Propane/*n*-butane	0.166 690	0.	0.	1.
Propane/*i*-butane	0.037 811	0.	4.774 913	1.
Propane/nitrogen	1.894 961	0.009 528 04	−22.339 155	4.367 740
Propane/carbon dioxide	−0.445 428	0.	−68.540 138	1.
n-Butane/*i*-butane	0.036 329	0.	0.	1.
n-Butane/nitrogen	−2.310 096	−0.025 061 25	112.809 220	1.194 089
Nitrogen/carbon dioxide	2.780 647	0.006 599 78	−31.149 300	1.
Nitrogen/argon	0.050 461	0.000 226 31	−3.952 992	1.
Nitrogen/oxygen	0.109 037	−0.000 144 04	−2.780 735	1.
Argon/oxygen	−0.243 919	0.000 488 30	−1.079 299	1.
Argon/carbon dioxide	−0.138 173	0.	0.	1.

A linear regression of the available data for each binary mixture was performed to determine the consistency among different data sets and to remove individual data points which were not consistent with the other points. The global fitting of these data sets began with the methane/ethane database in order to establish a preliminary set of coefficients (N_k) by linear regression. Other binary mixtures were then added to the fitting procedure one at a time to ensure a consistent fit in the generalization by nonlinearly fitting a small set of p–ρ–T data to obtain the generalizing parameters, F_{ij}, and the parameters ζ_{ij} and ξ_{ij}. This set was made up of 20 to 100 data points selected from the available data to cover the entire fluid surface. Generally, only the F_{ij}, ζ_{ij}, and ξ_{ij} parameters were needed to fit the p–ρ–T data. However, accurate representation of VLE data often required the use of either the β_{ij} or the ϕ_{ij} parameter.

Maintaining the parameters from the nonlinear fit, the linear regression was again performed including data for these other binary mixtures along with the data for the methane/ethane system. The output of the linear regression was the coefficients N_k for Eq. (3). The nonlinear fit was then repeated to improve the values of F_{ij}, ζ_{ij}, ξ_{ij}, β_{ij}, and ϕ_{ij}. This procedure of performing a linear regression and a nonlinear fit continued until the differences between values calculated from the equation and experimental data were less than the experimental error in the measurements, at which point data for another binary mixture were added to the regression.

3. PROPERTY CALCULATIONS

The functions used for calculating pressure, fugacity of component i, enthalpy, entropy, isochoric heat capacity, isobaric heat capacity, and speed of sound from the Helmholtz energy, Eq. (1), are given as Eqs. (8)–(14). 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, 14].

$$p = \rho RT\left[1 + \delta\left(\frac{\partial \alpha^r}{\partial \delta}\right)_\tau\right] \tag{8}$$

$$f_i = x_i \rho RT \exp\left(\frac{\partial(n\alpha^r)}{\partial n_i}\right)_{T,V,n_j} \tag{9}$$

$$\frac{h}{RT} = \tau\left[\left(\frac{\partial \alpha^0}{\partial \tau}\right) + \left(\frac{\partial \alpha^r}{\partial \tau}\right)_\delta\right] + \delta\left(\frac{\partial \alpha^r}{\partial \delta}\right)_\tau + 1 \tag{10}$$

$$\frac{s}{R} = \tau\left[\left(\frac{\partial \alpha^0}{\partial \tau}\right) + \left(\frac{\partial \alpha^r}{\partial \tau}\right)_\delta\right] - \alpha^0 - \alpha^r \tag{11}$$

$$\frac{c_v}{R} = -\tau^2 \left[\left(\frac{\partial^2 \alpha^0}{\partial \tau^2} \right) + \left(\frac{\partial^2 \alpha^r}{\partial \tau^2} \right)_\delta \right] \tag{12}$$

$$\frac{c_p}{R} = \frac{c_v}{R} + \frac{[1 + \delta(\partial \alpha^r/\partial \delta)_\tau - \delta\tau(\partial^2 \alpha^r/\partial \delta\, \partial \tau)]^2}{[1 + 2\delta(\partial \alpha^r/\partial \delta)_\tau + \delta^2(\partial^2 \alpha^r/\partial \delta^2)_\tau]} \tag{13}$$

$$\frac{w^2 M}{RT} = \frac{c_p}{c_v} \left[1 + 2\delta \left(\frac{\partial \alpha^r}{\partial \delta} \right)_\tau + \delta^2 \left(\frac{\partial^2 \alpha^r}{\partial \delta^2} \right)_\tau \right] \tag{14}$$

In these equations, the term α^0 is the contribution of the ideal gas,

$$\alpha^0 = \sum_{i=1}^{n} x_i \left[\frac{A_i^0(\rho, T)}{RT} + \ln x_i \right] \tag{15}$$

and the term α^r is the contribution from the residual Helmholtz energy of the pure fluids and from the Helmholtz energy contribution to mixing

$$\alpha^r = \alpha^E(\delta, \tau, \mathbf{x}) + \sum_{i=1}^{n} x_i \frac{A_i^r(\delta, \tau)}{RT} \tag{16}$$

The parameter n in Eq. (9) is the number of moles in the mixture, and the nomenclature n_j assumes that the number of moles of each component in the mixture is held constant except that for component i. The partial derivative in this equation is generally evaluated numerically. Additional details are given by Lemmon [1].

4. COMPARISONS OF CALCULATED MIXTURE PROPERTIES TO EXPERIMENTAL DATA

The accuracies of calculated values of various properties are determined by comparing them to measured values. Comparisons of selected data are given here. Comprehensive comparisons of all the mixtures are given by Lemmon [1]. Table IV shows the average absolute deviation (AAD) in density calculated from the mixture model for selected experimental data for the methane/ethane binary mixture. Table V gives the overall average absolute deviations in density calculated from the model for the binary mixtures studied in this work. Some of the older data sets which were not consistent with newer, more reliable data were eliminated for these calculations. Comparisons of the model to experimental data for refrigerant mixtures are given in Ref. 5.

Table IV. Comparisons of Mixture Properties for the Methane/Ethane Binary Mixture Calculated from the Model to Mixture Data

Author(s)	Data type[a]	No. points	Temp. range (K)	Comp. range (mol fract.)	AAD[b]	Bias
GERG TM4 [15]	p-ρ-T	807	270–330	0.70–0.96	0.033	0.021
Haynes et al. [16]	p-ρ-T	414	100–320	0.35–0.69	0.201	−0.042
Hiza et al. [17]	p-ρ-T	20	105–140	0.35–0.68	0.051	0.028
Hoover [18]	p-ρ-T	130	215–273	0.20–0.68	0.159	−0.031
Rodosevich and Miller [19]	p-ρ-T	19	91–155	0.69–0.95	0.076	0.072
Mayrath and Magee [20]	c_v	626	101–328	0.35–0.69	1.098	−0.124
Boyes [21]	w	74	250–349	0.85	0.082	−0.068
Younglove et al. [22]	w	392	250–350	0.35–0.95	0.210	−0.012
Bloomer et al. [23]	VLE	224	139–302	0.05–0.97	1.936	0.253
Ellington et al. [24]	VLE	248	142–300	0.05–0.98	1.753	0.103
Miller et al. [25]	VLE	25	160–180	0.03–0.90	2.998	2.534
Wichterle and Kobayashi [26]	VLE	135	130–200	0.02–1.00	1.273	0.788

[a] c_v, isochoric heat capacity; w, speed of sound; VLE, vapor–liquid equilibrium.

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

As part of the model evaluation, several equations of state were used to determine the effect of changing the equation for a pure fluid. For carbon dioxide, the equation of Span and Wagner [13] was replaced with the equation of Ely et al. [27]. For nitrogen, the equation of Span et al. [10] was replaced with the equation of Jacobsen et al. [28]. For ethane, the equation of Friend et al. [7] was exchanged with a preliminary equation developed in the initial work on this model. In all cases, except for nitrogen at temperatures below its triple point, there was not a noticeable difference in comparisons of calculated properties.

5. ACCURACY ASSESSMENT

An assessment has been made to determine the validity and accuracy of the mixture model reported here. In general, the equation is accurate to ±0.2% in density where binary data exist, ±0.1% in the speed of sound at pressures below 10 MPa, ±0.5% in the speed of sound for pressures above 10 MPa, and ±1% in heat capacities. In the region from 250 to 350 K at pressures up to 30 MPa, calculated densities are within ±0.1%

Table V. Regions of Stated Accuracy of the Mixture Model

Mixture	Temperature range (K)	Maximum pressure (MPa)	AAD[a]
Methane/ethane	90–400	40	0.09
Methane/propane	90–500	70	0.07
Methane/*n*-butane	95–575	70	0.36
Methane/*i*-butane[b]	110–510	40	0.50
Methane/nitrogen	80–350	500	0.11
Methane/carbon dioxide	200–400	40, vapor and supercritical states only	0.18
Methane/ethylene[b]	290–340	100	0.57
Ethane/propane	100–400	35	0.09
Ethane/*n*-butane[b]	260–400	12	0.60
Ethane/nitrogen	100–470	30	0.23
Ethane/carbon dioxide	270–400	10, vapor and supercritical states only	0.16
Propane/*n*-butane	240–400	35	0.10
Propane/*i*-butane	200–400	35	0.03
Propane/nitrogen	100–330	12	0.03
Propane/carbon dioxide[b]	270–510	70	0.60
n-Butane/*i*-butane[b]	280–320	1	0.02
n-Butane/nitrogen	270–330	12	0.03
Nitrogen/carbon dioxide	200–470	60	0.13
Nitrogen/argon	70–420	800	0.18
Nitrogen/oxygen and air	60–870	300	0.12
Argon/oxygen[b]	70–400	60	0.21
Argon/carbon dioxide[b]	280–370	100	0.36

[a] Average absolute deviation in density for data sets used in developing the mixture model.
[b] Estimated accuracy in density is 0.5%.

for most gaseous phase mixtures away from the critical region. For binary mixtures where the critical point temperatures of the pure fluid constituents are within 100 K of each other, calculated bubble point pressures are generally accurate to within ±1 to 2%. For mixtures with critical points further apart, calculated bubble point pressures are generally accurate to within ±5 to 10%. The mixtures and ranges for which calculated properties have been verified by experimental data to be within these accuracies are listed in Table V. In regions where there are no binary mixture data, the accuracy is estimated to be of the same magnitude. 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 can be used to calculate the properties of mixtures with three or more constituents based upon comparisons of calculated values to available data for the nitrogen/argon/oxygen and R-32/125/134a systems which are reported elsewhere [4, 5].

The extrapolation behavior of pure fluid equations of state beyond the limits of the formulation may not be correct, and the use of calculated properties outside the limits should be verified by comparison to experimental data. In this work, errors resulting from short extrapolations of the equations of state for p–ρ–T properties were less than 0.4%. However, errors may be much larger for VLE calculations.

This generalized mixture model is expected to be useful in the prediction of properties for engineering system design and analysis. New measurements are continuously being made, and these 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. These data will enable continued evaluation and development of the model. In addition, new data will soon be available for calculating the thermodynamic properties of mixtures of hydrocarbons and refrigerants, including the systems propane/R-32 and propane/R-134a.

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