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

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ABSTRACT

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 used in this work. The independent variables are the reduced density and reduced temperature. The model may be used to calculate 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 ±0.1% 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. 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.

1. INTRODUCTION

A new approach has been used in the application of equations of state to fluid mixtures. This approach is an extension of the excess property model which accounted for the difference between an ideal solution and the real property value at constant pressure and temperature. In this work, the model used to calculate properties of mixtures was developed by Lemmon [1] based on a modified excess, or excess-like property and corresponding states theory. 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 from the critical points of the pure fluids. The generalized model represents available measured data in all parts of the thermodynamic surface within their estimated experimental accuracy.

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 [2], 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 [3] give comparisons to experimental data and describe additional parameters required to implement the model.

An advantage of the approach used here is that the portion of the model 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, sound speed, vapor-liquid equilibrium, and

the mixture critical temperature, pressure, and density, can be calculated accurately using this approach.

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. Since this model deals with the entire fluid surface, reduced values are used rather than absolute values to ensure that pure fluid properties are calculated for the same phase as the mixture. The reducing parameters are functions of the critical parameters of the pure fluids. Because the independent variables for the Helmholtz energy equation are density and temperature, properties are calculated at the same reduced density and reduced temperature. While this approach is arbitrary and different from the usual excess property format, it results in an accurate representation of the phase boundaries for pure fluids and their mixtures.

The extrapolation behavior of equations of state beyond the limits of the formulation may not be correct, and 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 percent. However, errors may be much larger for VLE calculations.

As the pure-fluid limits of concentration are approached, the model defaults to the pure fluid equations of state. 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 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 generalized equations.

The Helmholtz energy for mixtures can be calculated using

$$\alpha_m(\delta,\tau,\mathbf{x}) = \alpha_m^i(\delta,\tau,\mathbf{x}) + \alpha^E(\delta,\tau,\mathbf{x}), \tag{1}$$

where the Helmholtz energy for an ideal mixture is

$$\alpha_m^i(\delta,\tau,\mathbf{x}) = \sum_{i=1}^{r} x_i\left[\alpha_i^0(\delta,\tau) + \alpha_i^r(\delta,\tau) + \ln x_i\right]. \tag{2}$$

In these equations, r is the number of fluids in the mixture, α_i^0 is the ideal gas Helmholtz energy of component i, and α_i^r is the residual Helmholtz energy of component i. Equations for the ideal gas Helmholtz energy and residual Helmholtz energy for the pure fluids are given in the references shown in Table I.

The Helmholtz energy contribution to mixing used in this work is

$$\alpha^E = \sum_{p=1}^{r} \sum_{q=p+1}^{r} x_p x_q F_{pq} \sum_{k=1}^{10} N_k \delta^{i_k} \tau^{j_k}, \tag{3}$$

where the N_k, i_k, and j_k are coefficients and exponents obtained from linear regression of experimental mixture data. The coefficients, N_k, of the equation are determined using a stepwise least-squares technique with a search and selection procedure which selects an optimum group of terms from a large comprehensive function based on statistical evaluation of the significance of individual terms. All thermodynamic properties can be calculated from the Helmholtz energy using differentiation with respect to density or temperature as described by Lemmon *et al.* [12].

The independent parameters of the Helmholtz energy equation given in this work are reduced density and temperature and mixture composition. In addition, one other parameter, F_{pq}, is required which relates the contribution to mixing of one binary mixture to those 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 selected set of measurements.

The reduced density and temperature for the mixture are

$$\delta = \rho / \rho_j \text{ and} \tag{4}$$

$$\tau = T_j / T \quad , \tag{5}$$

where T_j and ρ_j are the reducing values,

$$T_j = \sum_{p=1}^{r} x_p T_{c_p} + \sum_{p=1}^{r} \sum_{q=p+1}^{r} x_p^{\beta_{pq}} x_q \zeta_{pq} \ , \tag{6}$$

$$\rho_j = \left[\sum_{p=1}^{r} \frac{x_p}{\rho_{c_p}} + \sum_{p=1}^{r} \sum_{q=p+1}^{r} x_p x_q \xi_{pq} \right]^{-1} , \tag{7}$$

and where ζ_{pq}, ξ_{pq}, and β_{pq} are used to define the shapes of the reducing parameter lines as defined by Eqs. (6) and (7). The units for temperature and density are kelvins and mol·dm^{-3}. 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. For the methane/ethane system, ζ_{pq} and ξ_{pq} were arbitrarily set to zero. These parameters were determined simultaneously with the generalized factor in the nonlinear fit.

A linear regression of the available data for each binary mixture was performed to determine the consistency among different datasets and to remove individual data points which were not consistent with the other points. The global fitting of these datasets began with the methane/ethane database. Other binaries were added to the fitting procedure one at a time to ensure a consistent fit in the generalization. First, a nonlinear fit of a small set of P-ρ-T data was performed to obtain the generalized parameter, F_{pq}, and the parameters ζ_{pq} and ξ_{pq}. This set was made up of 20 to 100 data points selected to cover the entire surface. Generally, only the F_{pq}, ζ_{pq}, and ξ_{pq} parameters were needed to fit the P-ρ-T data. However, accurate representation of VLE data often required the use of the β_{pq} parameter as well.

Next, maintaining the parameters from the nonlinear fit, a linear regression was performed including selected data for individual binary mixtures along with the methane/ethane set. The output of the linear regression was the coefficients N_k for Eq (3). The nonlinear fit was repeated to improve the values of F_{pq}, ζ_{pq}, ξ_{pq}, and β_{pq}. 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.

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 *p* in Eqs. (3), (6), and (7) refers to the first component listed in Table III and the subscript *q* refers to the second component.

3. VAPOR-LIQUID EQUILIBRIUM

In a two-phase non-reacting mixture, the thermodynamic constraints for vapor-liquid equilibrium (VLE) are

$$T' = T'' = T\,, \tag{8}$$

$$P' = P'' = P\,, \text{ and} \tag{9}$$

$$\mu'_i = \mu''_i\,, \quad i = 1,2,\Lambda\ ,r\,, \tag{10}$$

where the superscripts ' and " refer to the liquid and vapor phases, respectively, and *r* is the number of fluids in the mixture. Often, the criterion of equal chemical potentials is replaced with

$$f'_i = f''_i\,, \quad i = 1,2,\Lambda\ ,r\,, \tag{11}$$

where *f* is the fugacity which can be calculated from the Helmholtz energy using

$$f_i = x_i \rho RT \exp\left(\frac{\partial\left(n\alpha^r\right)}{\partial n_i}\right)_{T,V,n_j}\,, \tag{12}$$

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

$$\alpha^r = \alpha^E\left(\delta,\tau,\mathbf{x}\right) + \sum_{i=1}^{r} x_i \alpha_i^r\left(\delta,\tau\right). \tag{13}$$

The partial derivative in Eq. (12) can be evaluated numerically or analytically as 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) and bias for selected experimental data for the methane/ethane binary mixture.

As part of the model evaluation, several different equations of state were used to determine the effect of changing the equation for a pure fluid. For carbon dioxide, the equation of Ely *et al.* [11] was replaced with the equation of Span and Wagner [25]. For nitrogen, the equation of Jacobsen *et al.* [8] was replaced with the preliminary equation of Span [26]. For ethane, the equation of Friend *et al.* [5] 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 improvement 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. The equation is accurate to ±0.1% 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. 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 appears to be accurate in calculating 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/R-125/R-134a systems which are reported elsewhere [2, 3].

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

Fluid	Author	Temperature Range (K)	Maximum Pressure (MPa)
Methane	Setzmann and Wagner [4]	90.694 - 625	1000
Ethane	Friend *et al.* [5]	90.352 - 623	69
Propane	Younglove and Ely [6]	85.47 - 600	100
n-Butane	Younglove and Ely [6]	134.86 - 500	70
i-Butane	Younglove and Ely [6]	113.55 - 600	35
Ethylene	Jahangiri *et al.* [7]	103.986 - 450	260
Nitrogen	Jacobsen *et al.* [8]	63.148 - 2000	1000
Argon	Stewart and Jacobsen [9]	83.804 - 1200	1000
Oxygen	Schmidt and Wagner [10]	54.361 - 300	82
Carbon Dioxide	Ely *et al.* [11]	216.58 - 1000	100

Table II. Coefficients and Exponents of the Mixture Equation

k	N_k	i_k	j_k
1	$-0.245476271425\times10^{-1}$	1	2
2	-0.241206117483	1	4
3	$-0.513801950309\times10^{-2}$	1	-2
4	$-0.239824834123\times10^{-1}$	2	1
5	0.259772344008	3	4
6	-0.172014123104	4	4
7	$0.429490028551\times10^{-1}$	5	4
8	$-0.202108593862\times10^{-3}$	6	0
9	$-0.382984234857\times10^{-2}$	6	4
10	$0.262992331354\times10^{-5}$	8	-2

Table III. Parameters of the Mixture Equation

Binary Mixture	F_{pq}	ξ_{pq}	ζ_{pq}	β_{pq}
Methane/Ethane	1.	0.	0.	1.
Methane/Propane	1.556361	-0.00266906	19.390289	1.882266
Methane/*n*-Butane	2.445415	0.	41.132992	2.006673
Methane/*i*-Butane	2.661664	0.	40.039217	2.544409
Methane/Nitrogen	0.634182	0.00381045	-17.818676	1.
Methane/Carbon Dioxide	0.808546	0.	-37.271180	1.
Methane/Ethylene	0.742836	0.	-11.071005	1.
Ethane/Propane	-0.030997	-0.00656221	2.721297	1.
Ethane/*n*-Butane	0.759528	0.	0.	1.
Ethane/Nitrogen	1.021055	0.00975023	-17.779863	1.233539
Ethane/Carbon Dioxide	-0.154127	0.00951999	-63.629672	1.
Propane/*n*-Butane	0.268056	0.	0.	1.
Propane/*i*-Butane	0.131521	0.	0.	1.
Propane/Nitrogen	1.894961	0.00952804	-22.339155	4.367740
Propane/Carbon Dioxide	-0.435617	0.	-48.820556	0.726976
n-Butane/*i*-Butane	0.036329	0.	0.	1.
n-Butane/Nitrogen	-2.310096	-0.02506125	112.809220	1.194089
Nitrogen/Carbon Dioxide	2.780647	0.00659978	-31.149300	1.
Nitrogen/Argon	-0.028542	0.	-3.106041	1.
Nitrogen/Oxygen	0.116000	0.	-2.325382	1.
Argon/Oxygen	-0.360385	0.	0.	1.
Argon/Carbon Dioxide	-0.138173	0.	0.	1.

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

Author	**Data Type**	**No. Points**	**Temp. Range (K)**	**Comp. Range**	**AAD**	**Bias**
GERG TM4 [13]	P-ρ-T	807	270-330	0.70-0.96	0.033	0.021
Haynes *et al.* [14]	P-ρ-T	414	100-320	0.35-0.69	0.201	-0.042
Hiza *et al.* [15]	P-ρ-T	20	105-140	0.35-0.68	0.051	0.028
Hoover [16]	P-ρ-T	130	215-273	0.20-0.68	0.159	-0.031
Rodosevich and Miller [17]	P-ρ-T	19	91-155	0.69-0.95	0.076	0.072
Mayrath and Magee [18]	c_v	626	101-328	0.35-0.69	1.098	-0.124
Boyes [19]	w	74	250-349	0.85	0.082	-0.068
Younglove *et al.* [20]	w	392	250-350	0.35-0.95	0.210	-0.012
Bloomer *et al.* [21]	VLE	224	139-302	0.05-0.97	1.936	0.253
Ellington *et al.* [22]	VLE	248	142-300	0.05-0.98	1.753	0.103
Miller *et al.* [23]	VLE	25	160-180	0.03-0.90	2.998	2.534
Wichterle and Kobayashi [24]	VLE	135	130-200	0.02-1.00	1.273	0.788

Table V. Regions of Stated Accuracy of the Mixture Model

Mixture	Temperature Range (K)	Maximum Pressure (MPa)
Methane/Ethane	90-350	40
Methane/Propane	90-500	70
Methane/*n*-Butane	270-330	12
Methane/*i*-Butane†	110-510	40
Methane/Nitrogen	80-350	500
Methane/Carbon Dioxide	200-330	40 MPa, Vapor and Supercritical States Only
Methane/Ethylene†	290-340	100
Ethane/Propane*	100-320	20
Ethane/*n*-Butane†	260-400	12
Ethane/Nitrogen	100-350	30
Ethane/Carbon Dioxide	270-400	10 MPa, Vapor and Supercritical States Only
Propane/*n*-Butane*	280-330	10
Propane/*i*-Butane†	280-320	2
Propane/Nitrogen	100-330	12
Propane/Carbon Dioxide†	270-510	70
n-Butane/*i*-Butane*	280-320	1
n-Butane/Nitrogen	270-330	12
Nitrogen/Carbon Dioxide	200-470	60
Nitrogen/Argon	70-420	800
Nitrogen/Oxygen and Air	60-870	300
Argon/Oxygen	70-90	0.2
Argon/Carbon Dioxide†	280-370	100

*Based on less reliable data, estimated accuracy in density may be greater than 0.1%
†Estimated accuracy in density is 0.5%