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Predicting the Virial Coefficients and Thermodynamic Properties of a Multicomponent Mixture with Application to the Ternary Mixture of $CH_2F_2 + CF_3CHF_2 + CF_3CH_2F$

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A model for estimating second and third virial coefficients, which has been used successfully to represent the behavior of pure gases and binary mixtures, was applied to a ternary mixture. An estimate for the ternary third virial coefficient, C_{123}, was added to the model. Three experimentally determined binary interaction parameters were also used. The model has been applied to the ternary mixture $CH_2F_2 + CF_3CHF_2 + CF_3CH_2F$ (R32 + R125 + R134a). The results are useful for calculating gas-phase densities, thermodynamic properties, and fugacities for phase equilibrium calculations. The use of such models leads to a considerable economy of effort in the case of multicomponent mixtures. Examples of the thermodynamic properties are given for the equimolar ternary mixture in the range from the dew-point temperature to 400 K at pressures of 0.5, 1, and 2 MPa. Calculated densities and speeds of sound are compared with new experimental values for a near-equimolar composition.

KEY WORDS: density; R134a; R32; R125; refrigerants; ternary mixture; thermodynamic properties; virial coefficients.

1. INTRODUCTION

It is generally agreed that many refrigeration systems designed for the future will use, as working fluids, binary and multicomponent mixtures whose compositions can be tailored to produce properties appropriate for the required application. Relatively few experimental results have been reported for binary refrigerant mixtures, however, and almost none have

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been reported for multicomponent mixtures. Therefore, thermophysical properties calculations for these systems, produced at present by available computerized properties software, can only be considered to be approximate. Furthermore, since those properties packages generally rely on global equations of state which are semiempirical and thus have only weak theoretical foundations, the approximations may not be reliable.

The virial equation of state for the gas phase, on the other hand, does have a firm theoretical foundation. It also uses theoretically based mixing rules, which can be applied to multicomponent mixtures. It therefore offers obvious advantages, at least for gas-phase calculations. However, considerable experimental effort is required to produce the virial coefficient data necessary to characterize a mixture of arbitrary composition. For a binary mixture, sufficient *PVT* data are required for a minimum of four compositions (including the pure components). Data for more compositions would provide the desired overdetermination and thus better accuracy. For a ternary mixture, this minimum experimental effort increases to 10 compositions; for a quaternary mixture, 20 compositions are required; etc. It is obvious that the experimental effort quickly becomes overwhelming. In addition, unless some guidelines are available, more than a minimal amount of *PVT* data would be required for each composition. If, instead of a virial equation, one of the cubic equations of state were used, somewhat less experimental effort would be required (6 compositions instead of 10 for a ternary), albeit at the cost of some accuracy (especially for these polar gases). In the light of these considerations, it is not surprising that so few experimental studies are available for ternary and higher-order mixtures, with the exception of some data for specific compositions.

With the above-mentioned difficulties in mind, we present here model-calculated second and third virial coefficients for a ternary mixture of refrigerant candidates. The mixture of $CH_2F_2 + CHF_2CF_3 + CF_3CH_2F$ (R32 + R125 + R134a) is considered to be an important candidate for use in some future refrigeration systems. The model, described recently by Weber [1], allows estimation of all of the necessary interaction virial coefficients so that the properties at any composition can be calculated. This model has been used successfully to calculate the properties of pure fluids and binary mixtures [1–3]. For pure fluids it has good predictive capability. For each binary system a binary interaction parameter is necessary. For the ternary system of interest here, the necessary binary interaction parameters were obtained from a minimum amount of *PVT* data on equimolar binary mixtures of the constituents [2].

The next section briefly summarizes the calculation of the virial coefficients and gives some examples. Comparisons are made with some recently obtained experimental data at one composition. Appendix A provides the necessary mixing rules, and Appendix B tabulates the equations necessary to calculate the commonly used thermodynamic properties.

2. THE MODEL

2.1. Second Virial Coefficient

The model used for the second virial coefficient is based on the one given by Pitzer and Curl [4] and improved by Tsonopoulos [5],

$$BP_c/RT_c = f_1(T_r) + \omega f_2(T_r) + f_3(T_r) \tag{1}$$

where B is the second virial coefficient, P_c and T_c are critical parameters, ω is the Pitzer acentric factor, R is the gas constant, and $T_r = T/T_c$. The f's are considered to be universal functions of T_r. The f's used are the ones given by Tsonopoulos, as modified by Weber,

$$f_1 = 0.1445 - 0.33/T_r - 0.1385/T_r^2 - 0.0121/T_r^3 - 0.000608/T_r^8 \tag{2a}$$

$$f_2 = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 \tag{2b}$$

$$f_3 = a/T_r^6 \tag{2c}$$

where $a = -9 \times 10^{-7}\mu_R^2$, and μ_R is the reduced dipole moment,

$$\mu_R = 0.9896 \times 10^5 \mu^2 P_c/T_c^2 \tag{3}$$

with μ being the dipole moment of the molecule in debyes and T_c and P_c are in kelvins and bars. The properties needed for each of the three components are given in Table I. This formulation for $B(T_r)$ has been compared with the best available experimental data for polar halocarbons and other fluids in Refs. 1–3, and in general the agreement is within about 1–2% of B.

2.2. Third Virial Coefficient

The third virial coefficient used here is a development of the form proposed by Van Nhu et al. [6], who related it to the second virial coefficient,

$$C = C_h + (B - B_h)^2 \mathfrak{F}_c \mathcal{F}(T_r) \tag{4}$$

where B_h and C_h are the virial coefficients of the hard-sphere molecule, $\mathfrak{F}_c$ is a coefficient which sets the value at the critical temperature, and $\mathcal{F}(T_r)$

Table I. Parameters for Calculating Virial Coefficients and Thermodynamic Properties; $T_0 = 233.15$ K (Dipole Moments Were Taken from Refs. 18 and 19)[a]

	R32(1)	R125(2)	R134a(3)
Ref. Nos.	14, 15	14, 16	14, 17
T_c (K)	351.36	339.3	374.2
P_c (MPa)	5.793	3.629	4.055
v_c ($L \cdot mol^{-1}$)	0.122	0.210	0.201
μ (D)	1.98	1.56	2.06
ω	0.277	0.304	0.323
$H^0(T_0)$ ($J \cdot mol^{-1}$)	19686	20668	23235
$S^0(T_0)$ ($J \cdot mol^{-1} \cdot K^{-1}$)	88.596	91.349	93.757

[a] $k_{12} = 0.028$; $k_{13} = 0.030$; $k_{23} = 0.023$ (given incorrectly in Ref. 2).

is a simple function of temperature which, for nonassociating molecules, takes the value unity at T_c. We use the simplification $B_h = 0.36v_c$, where v_c is the critical molar volume and, from the hard-sphere model, $C_h = 0.625B_h^2$. The quantities $\mathfrak{F}_c$ and $\mathcal{F}(T_r)$ are functions of μ_R,

$$\mathfrak{F}_c = c_1 + c_2\mu_R^3 \tag{5a}$$

$$\mathcal{F}(T_r) = \mathcal{C} + (1 - \mathcal{C})/T_r^4 \tag{5b}$$

where

$$\mathcal{C} = c_3 + c_4\mu_R^3 \tag{5c}$$

The c's are taken to be universal constants and have the values, $c_1 = 0.17$, $c_2 = 1.85 \times 10^{-8}$, $c_3 = 1.584$, and $c_4 = -4.9 \times 10^{-8}$. The form of Eq. (5a) gives a dependence on μ which approximates the behavior of C calculated with the Stockmayer potential [7]. The dependence given in Eq. (5c) allows the location of the maximum value of C to vary as a function of the dipole moment. The form of Eqs. (4) and (5) shows that, once B has been calculated, calculation of C requires only one additional substance-specific parameter, v_c.

2.3. Mixtures

Mixing rules for B and C in multicomponent mixtures have a firm foundation in statistical mechanics. Mixture virial coefficients are given by [8]

$$B_m = \sum_{i=1}^{n} \sum_{j=1}^{n} B_{ij} x_i x_j \tag{6a}$$

and

$$C_{\mathrm{m}} = \sum_{i=1}^{n} \sum_{j=1}^{n} \sum_{k=1}^{n} C_{ijk} x_i x_j x_k \tag{6b}$$

for an n-component mixture, where the x's are the component mole fractions. For a virial equation of state terminated after two coefficients, it is necessary to consider only two- and three-molecule interactions (e.g., B_{ij} and C_{ijk}) in a mixture of any number of components. Equations (1) and (4) apply to the interaction virial coefficients as well as the pure fluid virials. They require mixing rules for the substance-specific parameters. The rules used were given in Refs. 1–3, and they are repeated here in Appendix A.

As shown in the appendix, calculation of B_{ij} also requires a set of binary interaction parameters, k_{ij}, for each binary pair in the mixture. In principle, these can be determined from one reliable PVT datum for each binary mixture at some convenient temperature. In practice, it is generally preferable to have some minimal set of data, such as a set of Burnett expansion data on one isotherm. Such data and binary parameters for the mixture considered here were measured in Ref. 2. Due to a calculation error, the binary parameters given in Ref. 2 were incorrect. The correct values for these three binaries are given in Table I. Binary parameters obtained from application of cubic equations of state to binary vapor–liquid equilibrium data on non polar or weakly polar systems often have similar values, and they can be used here. However, such parameters found for strongly polar systems (e.g., R32 + R134a) have very different values. This difference appears to be due to the fact that the cubic equations of state do not represent the overall behavior of strongly polar fluids very well.

The mixing rules given have been used successfully to reproduce the best available data for binary mixtures. Application to a ternary mixture requires only one new quantity, C_{ijk}, the ternary third virial coefficient. This quantity was estimated with simple extensions of the mixing rules used in the past, and given in Appendix A,

$$T_{\mathrm{c}123} = (T_{\mathrm{c}12} T_{\mathrm{c}23} T_{\mathrm{c}13})^{1/3} \tag{7a}$$

$$\mu_{\mathrm{R}_{123}} = (\mu_{\mathrm{R}_{12}} + \mu_{\mathrm{R}_{23}} + \mu_{\mathrm{R}_{13}})/3 \tag{7b}$$

$$C_{\mathrm{h}123} = 0.625(B_{\mathrm{h}12}^2 + B_{\mathrm{h}13}^2 + B_{\mathrm{h}23}^2)/3 \tag{7c}$$

and the replacement,

$$(B - B_{\mathrm{h}})^2 \rightarrow ((B_{11} - B_{\mathrm{h}11})(B_{22} - B_{\mathrm{h}22})(B_{33} - B_{\mathrm{h}33}))^{2/3} \tag{7d}$$

in Eq. (4). The quantities on the right-hand side of Eqs. (7) are defined in Appendix A. Then, for example,

$$C_{123} = C_{\mathrm{h}123} + \{(B_{11} - B_{\mathrm{h}11})(B_{22} - B_{\mathrm{h}22})(B_{33} - B_{\mathrm{h}33})\}^{2/3} \times \mathfrak{F}_{\mathrm{c}}(\mathscr{C} + (1 - \mathscr{C})/T^{4}_{\mathrm{r}123}) \tag{8}$$

with

$$\mathfrak{F}_{\mathrm{c}} = c_1 + c_2 \mu^3_{\mathrm{R}123}$$

$$\mathscr{C} = c_3 + c_4 \mu^3_{\mathrm{R}123}$$

$$T_{\mathrm{r}123} = T/T_{\mathrm{c}123}$$

Similar forms would be applicable for the interaction coefficients C_{iij} and C_{ijj} with the mixing rules and definitions from Appendix A. These simple additional rules allow the model to be applied to a mixture of any number of components.

3. RESULTS AND COMPARISONS

The second and third virial coefficients for the equimolar ternary mixture have been calculated with the above equations, and they are tabulated in Table II between 240 and 400 K. Experience with similar pure fluids and binary systems indicates that the best results are obtained

Table II. Model-Estimated Second and Third Virial Coefficients of the Equimolar Ternary Mixture of R32 + R125 + R134a

T (K)	$10^3 B$ $(\mathrm{L \cdot mol^{-1}})$	$10^6 C$ $(\mathrm{L \cdot mol^{-1}})^2$
240	−663.7	−67.503
260	−528.7	−1.890
280	−432.3	19.328
300	−360.4	24.901
320	−305.1	24.844
340	−261.3	22.876
360	−225.8	20.423
380	−196.4	18.023
400	−171.8	15.864

when these coefficients are used at densities less than about 1.5 mol · L^{-1} (or P $\simeq$ 2.5 MPa), where they can be used to calculate a pressure with an uncertainty equal to about 1–2% of the nonideality of the gas. They should be useful for calculating saturated vapor densities up to a reduced temperature of about 0.9. Uncertainties begin to increase rapidly when the gas nonideality reaches about 40%, i.e., $|B\rho + C\rho^2| \geqslant 0.4$, where ρ is the molar density. The above guidelines apply to polar gases. For a light, nonpolar gas, such as methane at 275 K, the present estimation method would produce good results to pressures as high as 10 MPa.

Results of the present work have been compared with the preliminary results from two recent sets of experimental measurements for this ternary mixture. Hurly [12] has made speed-of-sound measurements in the temperature range 240–400 K at pressures to 1 MPa or 80% of the dew-point pressure, whichever is less. Schmidt [13] has made *PVT* measurements with a Burnett/isochoric apparatus in the range 313–453 K. In both cases, results were obtained for the mixture composition R32(0.346) + R125(0.300) + R134a(0.354). Figures 1 and 2 compare model-generated values for that composition with those two sets of results at the experimental temperatures. The figure shows that the model agrees with the experimental results within the uncertainty estimates given above, i.e., within 1–2% of the nonideality for pressures up to the dew point or 2.5 MPa, whichever is less.

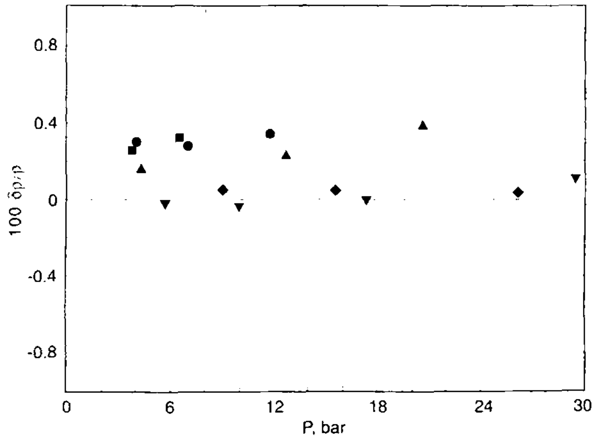

Fig. 1. Relative differences between the model-calculated densities and experimental values from Schmidt [13] for the ternary mixture, R32(0.346) + R125(0.300) + R134a(0.354): ■, 313 K; ●, 333 K; ▲, 353 K; ◆, 413 K; ▼, 453 K.

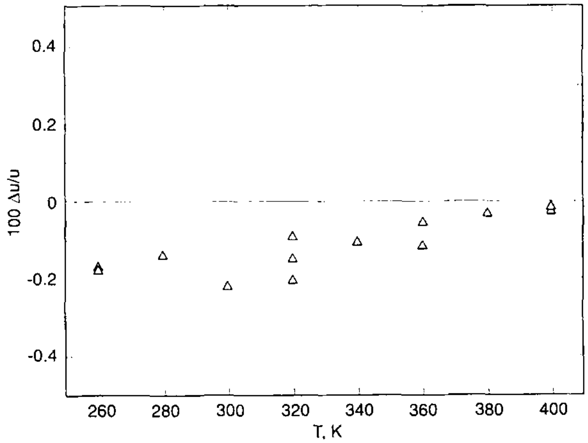

Fig. 2. Relative differences between the model-calculated speed of sound and the experimental values from Hurly [12] for the ternary mixture, R32(0.346) + R125(0.300) + R134a(0.354).

Virial coefficient formulations are also useful for calculating the thermodynamic properties of the mixture. Sample calculations for p, H, S, and C_p of the equimolar mixture at 0.5, 1, and 2 MPa from near the estimated dew curve to 400 K are given in Table III. The temperature dependence of the properties was calculated with the constant-pressure heat capacity of the ideal gas. For the mixture, this can be expressed as

$$C^0_{pm} = x_1 C^0_{p1} + x_2 C^0_{p2} + x_3 C^0_{p3} \tag{9}$$

where the heat capacities are understood to be functions of temperature. The ideal-gas heat capacity of R134a was taken from Goodwin and Moldover [9], that of R125 from Gillis [10], and that of R32 from the Thermodynamics Research Center tables [11]. Then changes of the ideal-gas properties with temperature are given by $\Delta H^0 = \int C^0_{pm}\, dT$ and $\Delta S^0 = \int (C^0_{pm}/T)\, dT$. The limits of the integration are from a reference temperature, T_0, to T. In order to avoid negative numbers in the table and to conform to convention, the values of the enthalpy and entropy for each pure component were made consistent with $H_L = S_L = 0$ for the saturated liquid at $T_0 = 233.15$ K. The corresponding starting values for the ideal gas, $H^0(T_0)$ and $S^0(T_0)$ (at $P = 0.101325$ MPa), are given in Table I. The relationships used for calculating the density dependence of the properties are summarized in Appendix B. With those relationships, the real-gas H, S, and C_p at temperature, T, were calculated at the density corresponding to the required pressure.

Table III. Calculated Thermodynamic Properties of the Equimolar Ternary Mixture of R32 + R125 + R134a

T (K)	ρ $(\mathrm{mol \cdot L^{-1}})$	H $(\mathrm{J \cdot mol^{-1}})$	S $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$	C_p $(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$
		$P = 0.5$ MPa		
280	0.23914	23,486	87.999	82.9
300	0.21715	25,129	93.668	81.9
320	0.19989	26,772	98.968	82.6
340	0.18572	28,437	104.017	84.1
360	0.17374	30,138	108.877	86.0
380	0.16341	31,880	113.586	88.2
400	0.15437	33,666	118.167	90.5
		$P = 1.0$ MPa		
300	0.48139	24,283	85.750	94.6
320	0.43020	26,121	91.683	90.1
340	0.39253	27,910	97.108	89.2
360	0.36276	29,697	102.213	89.7
380	0.33823	31,502	107.094	90.9
400	0.31745	33,337	111.800	92.6
		$P = 2.0$ MPa		
320	1.06886	24,374	81.589	126.4
340	0.90330	26,655	88.510	106.2
360	0.80281	28,706	94.374	100.1
380	0.73063	30,683	99.718	98.0
400	0.67449	32,639	104.737	97.9

4. SUMMARY

A model for estimating the second and third virial coefficients of fluids has been extended to multicomponent mixtures. As an example, sample results are given for the thermodynamic properties of the equimolar ternary mixture of R32 + R125 + R134a at three pressures. In addition, the calculated gas-phase densities and speeds of sound in a ternary mixture of these refrigerants at one composition have been compared with the only experimental values available for that mixture; they are found to be in relatively good agreement. The model provides a fast, economical means of estimating the properties of a mixture of any composition.

APPENDIX A

The model is extended to binary mixtures with the assumption that the interaction second virial coefficient, B_{12}, has the same corresponding-states temperature dependence as the pure-component coefficients. Mixing rules are necessary for the substance-specific parameters. We used the rules most often employed,

$$T_{c12} = (T_{c1} T_{c2})^{1/2} (1 - k_{12}) \tag{A1}$$

$$\omega_{12} = (\omega_1 + \omega_2)/2 \tag{A2}$$

$$P_{c12} = 4T_{c12}(P_{c1} v_{c1}/T_{c1} + P_{c2} v_{c2}/T_{c2})/(v_{c1}^{1/3} + v_{c2}^{1/3})^3 \tag{A3}$$

$$\mu_{R_{12}} = 0.9869 \times 10^5 \mu_1 \mu_2 P_{c12}/T_{c12}^2 \tag{A4}$$

where T_c and P_c are understood to be in units of kelvin and bar, respectively, and v_c is the critical molar volume. Values of the binary interaction parameters, k_{ij}, are given in Table I.

For the third virial coefficients of mixtures, no new parameters are needed, but additional mixing rules are required. We use the definitions

$$\mu_{Riij} = (\mu_{Rii} + 2\mu_{Rij})/3 \tag{A5}$$

$$\mu_{Rijj} = (\mu_{Rjj} + 2\mu_{Rij})/3 \tag{A6}$$

$$B_{hij} = (B_{hi} + B_{hj})/2 \tag{A7}$$

$$C_{hiij} = 0.625(B_{hi}^2 + 2B_{hij}^2)/3 \tag{A8}$$

$$C_{hijj} = 0.625(B_{hj}^2 + 2B_{hij}^2)/3 \tag{A9}$$

and in place of $(B_{ij} - B_{hij})^2$ in Eq. (4), we substitute

$$[(B_{jj} - B_{hjj})(B_{ij} - B_{hij})^2]^{2/3} \tag{A10}$$

or

$$[(B_{ii} - B_{hii})(B_{ij} - B_{hij})^2]^{2/3} \tag{A11}$$

In constructing a cross virial, such as C_{ijj}, we use Eqs. (4) and (5) calculated with μ_{Rijj}, with Eq. (A10), and with $T_{c_{ij}}$. It should be noted here that Eqs. (A5) and (A6) above are different from the formulation for these quantities given in Refs. 1–3. The present formulation is more appropriate, although the numerical differences in the value of C are quite small.

APPENDIX B

Calculation of the gas-phase thermodynamic properties began with the calculation of the properties of the ideal gas at the desired temperature and a pressure $P = 0.101325$ MPa, as shown in Section 3. Then, since calculations are more easily performed in terms of density, the mixture virial coefficients were used to determine the molar density, ρ, at the desired pressure. Then, enthalpy and entropy were calculated along isotherms from

$$H(T, \rho) = H^0(T) + \int_0^{\rho} [P/\rho^2 - (T/\rho^2)(\partial P/\partial T)_\rho]\, d\rho + (P/\rho - RT) \qquad \text{(B1)}$$

$$S(T, \rho) = S^0(T) - R \ln(RT\rho/P_0) + \int_0^{\rho} [R/\rho - (1/\rho^2)(\partial P/\partial T)_\rho]\, d\rho \qquad \text{(B2)}$$

where $P_0 = 0.101325$ MPa. These equations can be written in terms of the virial coefficients,

$$H(T, \rho) = H^0(T) - RT^2\rho B' - RT^2\rho^2 C'/2 + (P/\rho - RT) \qquad \text{(B1a)}$$

$$S(T, \rho) = S^0(T) - R \ln(RT\rho/P_0) - R\rho(B + TB') - R\rho^2(C + TC')/2 \qquad \text{(B2a)}$$

where B' and C' refer to the temperature derivatives of B and C, respectively. For the heat capacity, we use

$$C_v^0(T) = C_p^0(T) - R \qquad \text{(B3)}$$

$$C_v(T, \rho) = C_v^0(T) - RT\rho(2B' + \rho C' + TB'' + T\rho C''/2) \qquad \text{(B4)}$$

$$C_p(T, \rho) = C_v(T, \rho) + (T/\rho^2)(\mathcal{A}^2/\mathcal{B}) \qquad \text{(B5)}$$

where

$$\mathcal{A} = P/T + RT\rho^2(B' + \rho C') \qquad \text{(B6)}$$

$$\mathcal{B} = RT(1 + 2B\rho + 3C\rho^2) \qquad \text{(B7)}$$

For the purpose of comparison with the experimental results of Hurly [12], the speed of sound, u, was calculated from,

$$u = ((C_p/C_v)(\mathcal{B}/M))^{1/2} \qquad \text{(B8)}$$

where M is the molecular weight of the mixture.

The required first and second temperature derivatives of the virial coefficients can be calculated relatively easily for pure fluids; they can also be calculated for mixtures, but they are more easily obtained numerically.

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