International Journal of Thermophysics, Vol. 22, No. 5, September 2001 (© 2001)

Thermodynamic Modeling of Gas-Phase *PVTx* Properties for the Ternary R-32/125/143a System[1]

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Experimental *PVTx* property data have been used to develop a thermodynamic model of the gas-phase *PVTx* properties for R-32/125/143a in terms of a truncated virial equation of state. It is developed on the basis of the experimental *PVTx* property data which were obtained by a group of the present authors. The present model represents the input data with a high reproducibility, i.e., within ±0.2% in pressure for each pure component, ±0.25% for binary mixtures except for R-32/143a, and ±0.3% for ternary mixtures. The present model covers a temperature range of 300 to 380 K, pressures up to 4.5 MPa, and densities up to 2.5 $\mathrm{mol \cdot dm^{-3}}$ at any composition of the present ternary system. The uncertainty of the present model is considered being within ±0.3% in pressure and ±0.3% in the second virial coefficient. The thermodynamic behaviors of the specific isobaric heat capacity, isochoric heat capacity, and speed of sound are also discussed, in addition to the examination of the temperature dependence of the second and third virial coefficients.

KEY WORDS: gas phase; *PVTx*; R-32/125/143a mixture; thermodynamic properties; virial equation.

1. INTRODUCTION

Study of the fundamental thermodynamic properties of promising refrigerant mixtures which are expected to replace CFCs and HCFCs is a pressing subject. The azeotropic refrigerant mixture, R-502 [R-22/115 (63/37 mass%)], has been used widely in low-temperature applications, and its replacement is now in progress. Among the candidates to substitute for R-502, essential thermodynamic properties of typical HFC blended mixtures such as R-507A [R-125/143a (50/50 mass%)] and R-404A

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[1] Paper presented at the Fourteenth Symposium on Thermophysical Properties, June 25–30, 2000, Boulder, Colorado, U.S.A.

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0195-928X/01/0900-1475/0 © 2001 Plenum Publishing Corporation

[R-125/143a/134a (44/52/4 mass%)] have been studied rather extensively. For the ternary R-32/125/143a system, however, there exist only a very limited number of reliable sets of measured data; only the vapor–liquid equilibrium (VLE) properties [1, 2] and *PVTx* properties in the liquid phase [2] are available.

In the present study, therefore, we have developed a thermodynamic model which represents the gas-phase *PVTx* properties of this important ternary system on the basis of the experimental data over the entire range of compositions, including each pure component, and their binary mixtures, which were obtained by a group of the present authors. Namely, the experimental *PVT* properties were measured for R-32 by Qian et al. [3], for R-125 by Ye et al. [4], and for R-143a by Zhang et al. [5]. The *PVTx* properties for the binary R-32/125 and R-125/143a systems were reported by Zhang et al. [6, 7] and those for R-32/143a by Mizote and Watanabe [8], whereas those for the ternary R-32/125/143a system were reported by Tada et al. [9] and Kayukawa et al. [10]

2. FUNCTIONAL FORM

The model is a form of the truncated virial equation of state, where Z is the compressibility factor, ρ is the molar density, x is the mole fraction, and the subscripts i, j, and k indicate the pure components. The subscripts 1, 2, and 3 represent the pure components R-32, R-125, and R-143a, respectively.

$$Z = 1 + \sum_{\mathrm{i}}^{3} \sum_{\mathrm{j}}^{3} x_{\mathrm{i}} x_{\mathrm{j}} B_{\mathrm{ij}} \rho + \sum_{\mathrm{i}}^{3} \sum_{\mathrm{j}}^{3} \sum_{\mathrm{k}}^{3} x_{\mathrm{i}} x_{\mathrm{j}} x_{\mathrm{k}} C_{\mathrm{ijk}} \rho^2 + \sum_{\mathrm{i}}^{3} x_{\mathrm{i}} D_{\mathrm{i}} \rho^3 \tag{1}$$

B and C denote the second and third virial coefficients expressed in terms of the reduced temperature, $T_{\mathrm{r}} = T/T^*$, where T^* is equivalent to the critical temperature for a pure component. The characteristic temperature, T^*, used for the binary and ternary mixtures is defined by

$$T^* = \sqrt{T_{\mathrm{C,i}} T_{\mathrm{C,j}}} \tag{2}$$

$$T^* = \sqrt[3]{T_{\mathrm{C,i}} T_{\mathrm{C,j}} T_{\mathrm{C,k}}} \tag{3}$$

where the subscript C denotes the critical point of a pure refrigerant.

The cross second virial coefficient, B_{ij}, and the third one, C_{ijk}, are expressed by the following correlations.

$$B_{\mathrm{ij}} = b_{1,\mathrm{ij}} + b_{2,\mathrm{ij}} T_{\mathrm{r,ij}}^{-1} + b_{3,\mathrm{ij}} \exp(T_{\mathrm{r,ij}}^{-1}) \tag{4}$$

$$C_{\mathrm{ijk}} = c_{1,\mathrm{ijk}} + c_{2,\mathrm{ijk}} T_{\mathrm{r,ijk}}^{-k_{1,\mathrm{ijk}}} + c_{3,\mathrm{ijk}} T_{\mathrm{r,ijk}}^{-k_{2,\mathrm{ijk}}} \tag{5}$$

For the cross virial coefficients such as B_{23} and C_{112}, the critical temperature values used for the reduced temperature conversion are substituted by the pseudocritial temperatures given in Eqs. (2) and (3).

Note that for each subscript, the relation ij=ji or ijk=ikj=jik=jki=kij=kji holds. It should also be noted that i=j or i=j=k denotes a pure component, while i, j ≠ k, i ≠ j, k, and i, k ≠ j represent either the cross second or the third virial coefficients in Eqs. (4) and (5).

Since the applicable density range of the present model is up to 2.5 $\text{mol} \cdot \text{dm}^{-3}$, the fourth and higher virial terms are truncated except for each pure component. The fourth virial coefficient for the pure component, D_i, is expressed as a simple cubic function of the reduced temperature, T_r as follows:

$$D_i = d_i T_{r,i}^{-3} \tag{6}$$

3. DETERMINATION OF NUMERICAL CONSTANTS

The numerical constants of Eqs. (4)–(6) were obtained by least-squares fitting to the gas-phase *PVT* and/or *PVTx* data for the pure components or the binary and the ternary mixtures for the R-32/125/143a system. Since the temperature range of the present model is subject to that of *PVTx* data available for the ternary R-32/125/143a mixtures [9, 10], i.e., 305 to 380 K, we selected the input *PVTx* property data from those obtained with the same Burnett apparatus as used by our group. For determination of the numerical constants for the second, third, and fourth virial coefficients for pure components such as B_{11}, C_{222}, and D_3, 95 points of the gas-phase *PVT* properties for R-32 obtained by Qian et al. [3], 93 points for R-125 by Ye et al. [4], and 92 points for R-143a by Zhang et al. [5] were selected as input data. The numerical constants for the virial terms in Eqs. (4) through (6) for each pure component were determined by introducing these input data into our model and then applying our optimum least-squares fitting procedure.

By using these virial terms for pure components thus optimized, the cross second and third virial coefficients were correlated by the same fitting procedure to three different sets of input data for the binary mixtures. Namely, the numerical constants for the virial terms, B_{12}, C_{112}, and C_{122}, were obtained by employing 124 input data of the gas-phase *PVTx* properties for the binary R-32/125 system reported by Zhang et al. [6], together with the optimized virial terms for R-32 and R-125 as described above. B_{23}, C_{223}, and C_{233} correlations were optimized in a similar manner based on 220 points of gas-phase *PVTx* properties for R-125/143a obtained by Zhang et al. [7]. These input data for the binary R-32/125

Table I. Numerical Constants in Eqs. (4) through (6)

ij	$b_{1,\mathrm{ij}}$ ($\mathrm{dm}^3 \cdot \mathrm{mol}^{-1}$)	$b_{2,\mathrm{ij}}$ ($\mathrm{dm}^3 \cdot \mathrm{mol}^{-1}$)	$b_{3,\mathrm{ij}}$ ($\mathrm{dm}^3 \cdot \mathrm{mol}^{-1}$)		
11	2.953892×10^{-1}	7.115033×10^{-1}	-4.428261×10^{-1}		
22	4.180144×10^{-1}	2.628148×10^{-1}	-3.498170×10^{-1}		
33	4.324401×10^{-1}	9.356728×10^{-1}	-6.075998×10^{-1}		
12	3.904362×10^{-1}	5.307931×10^{-1}	-4.201338×10^{-1}		
23	4.476388×10^{-1}	1.199246×10^{-1}	-3.112357×10^{-1}		
13	3.574865×10^{-1}	-6.305227×10^{-2}	-1.923525×10^{-1}		
ijk	$c_{1,\mathrm{ijk}}$ ($\mathrm{dm}^6 \cdot \mathrm{mol}^{-2}$)	$c_{2,\mathrm{ijk}}$ ($\mathrm{dm}^6 \cdot \mathrm{mol}^{-2}$)	$c_{3,\mathrm{ijk}}$ ($\mathrm{dm}^6 \cdot \mathrm{mol}^{-2}$)	$k_{1,\mathrm{ijk}}$	$k_{2,\mathrm{ijk}}$
111	1.156706×10^{-2}	1.059520×10^{-2}	-2.468411×10^{-3}	7	10
222	1.203541×10^{-3}	2.593338×10^{-2}	-1.103833×10^{-3}	2.5	13
333	1.630541×10^{-2}	1.886313×10^{-2}	-8.411061×10^{-4}	5	12
112	1.300696×10^{-2}	7.128677×10^{-3}	-3.232567×10^{-4}	7	14
122	-8.097871×10^{-3}	3.451074×10^{-2}	-2.878990×10^{-4}	2.5	12
223	6.228510×10^{-3}	4.545076×10^{-2}	-2.183036×10^{-2}	5	7
233	6.538272×10^{-3}	7.530236×10^{-2}	-5.037317×10^{-2}	5	6
113	8.442775×10^{-4}	2.734839×10^{-2}	-4.804706×10^{-3}	4	8
133	4.398368×10^{-3}	2.606075×10^{-2}	-3.180763×10^{-4}	3	12
123	5.244248×10^{-3}	1.960900×10^{-2}	-7.896543×10^{-6}	3.5	7
i	$T_{\mathrm{C,i}}$ (K)	d_{i} ($\mathrm{dm}^9 \cdot \mathrm{mol}^{-3}$)			
1	351.255 [11]	-1.074352×10^{-3}			
2	339.165 [11]	-1.948749×10^{-4}			
3	345.860 [12]	-1.791378×10^{-3}			

and R-125/143a systems, and those for each single component, were obtained by Burnett measurements in our laboratory, whereas 123 $PVTx$ properties for the binary R-32/143a system, which were used for the present optimization of B_{13}, C_{113}, and C_{133}, were obtained by means of a constant-volume apparatus with isothermal expansion by Mizote and Watanabe [8].

By introducing these virial terms for each pure component and binary mixture into our model, the numerical constants for the cross third virial coefficient, C_{123}, were obtained by fitting the present model to a total of 220 data points of the input data at four compositions, i.e., 10/45/45, 20/30/50, 33/34/33, and 20/60/20 mass%, for the ternary R-32/125/143a system [9, 10]. All the numerical constants for Eqs. (4) through (6) are listed in Table I, together with the critical temperature values for each pure component [11, 12]. The range of validity of the present model is subject to the availability of the input data, i.e., 305 to 380 K for temperatures and densities up to 2.5 $\mathrm{mol \cdot dm^{-3}}$.

4. DISCUSSION

Figure 1 illustrates the relative pressure deviations of all the input data from the pressures calculated by the present model. It is apparent that the present model represents most of the pure component data with an excellent reproducibility, i.e., within $\pm 0.20\%$ in pressure, while the data for pure R-125 deviate by a maximum of $+0.26\%$. It is also found that the reproducibility of our model for the binary and ternary mixtures is within $\pm 0.3\%$ in pressure. These facts confirm that the present model has shown an excellent *PVTx* reproducibility over the entire range of compositions.

The temperature dependences of the second virial coefficients, B_{11}, B_{22}, B_{33}, B_{12}, B_{23}, and B_{13}, calculated from the present model are shown in Fig. 2 together with the recalculated "experimental" values and reported second virial coefficients for each pure component except those from earlier works [3–5]. It should be noted that the recalculated "experimental" values of the second and third virial coefficients are obtained in the present study by least-squares refitting of the right-hand side of Eq. (7) to a simple linear function of density along respective isotherms reported by the original works [3–5].

$$\frac{Z-1}{\rho} = B + C\rho \tag{7}$$

It is obvious that the second virial coefficients for pure components and the cross second virial coefficients show thermodynamically rational behavior. All the experimental values for the single components, B_{11}, B_{22}, and B_{33}, agree well with the curves calculated by the present model. These calculated curves for B_{22} and B_{33} also agree well with the values reported by Gillis [13] and Beckermann and Kohler [14] within the applicable range of temperatures from 300 to 380 K, although the deviations of the B_{33} values by Beckermann and Kohler become more significant at lower temperatures. To examine the reproducibility of the present model for the second virial coefficients, relative deviations of the experimental second virial coefficients from those calculated by the present model are illustrated

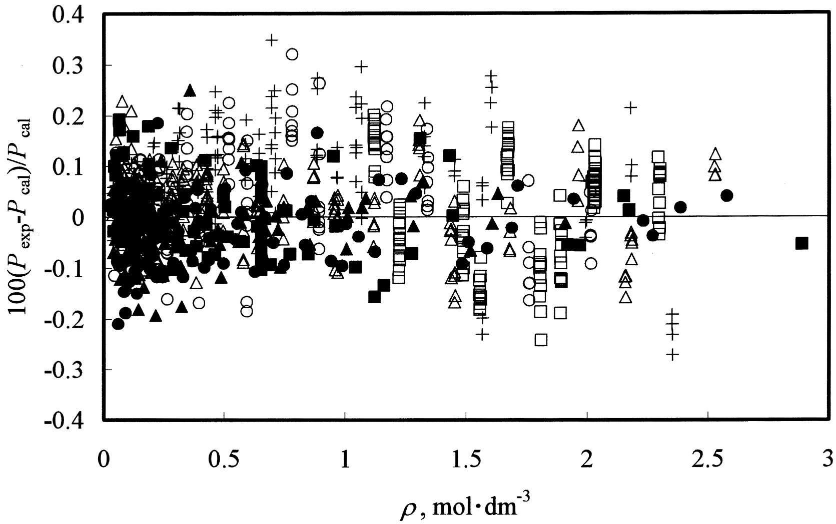

Fig. 1. Relative pressure deviations of input data from the present model for the ternary R-32/125/143a system: ●, R-32 [3]; ▲, R-125 [4]; ■, R-143a [5]; ○, R-32/125 [6]; △, R-125/143a [7]; □, R-32/143a [8]; +, R-32/125/143a [10].

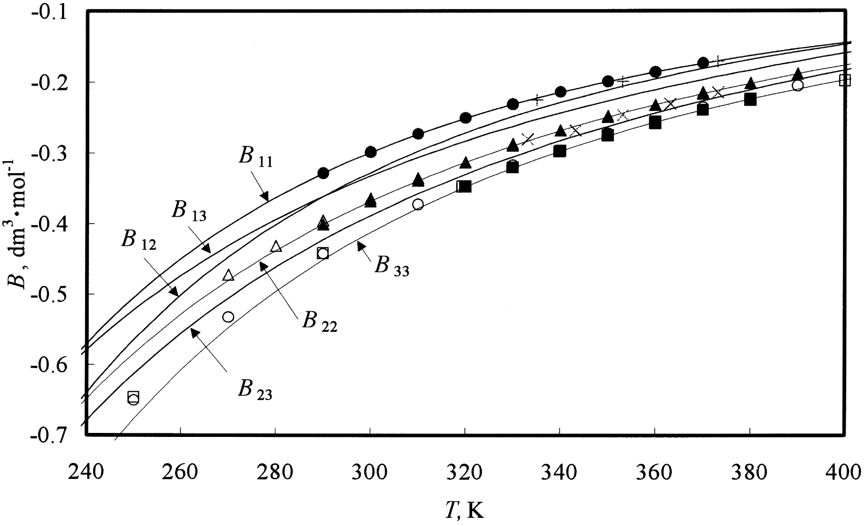

Fig. 2. Temperature dependence of the second virial coefficients: (●) B_{11}, this work; (▲) B_{22}, this work; (■) B_{33}, this work; (△) B_{22}, Gillis [13]; (□) B_{33}, Gillis [13]; (○) B_{33}, Beckermann and Kohler [14]; (+) B_{12}, Weber and Defibaugh [16]; (×) B_{23}, Weber and Defibaugh [16]; (——) curves calculated by the present model.

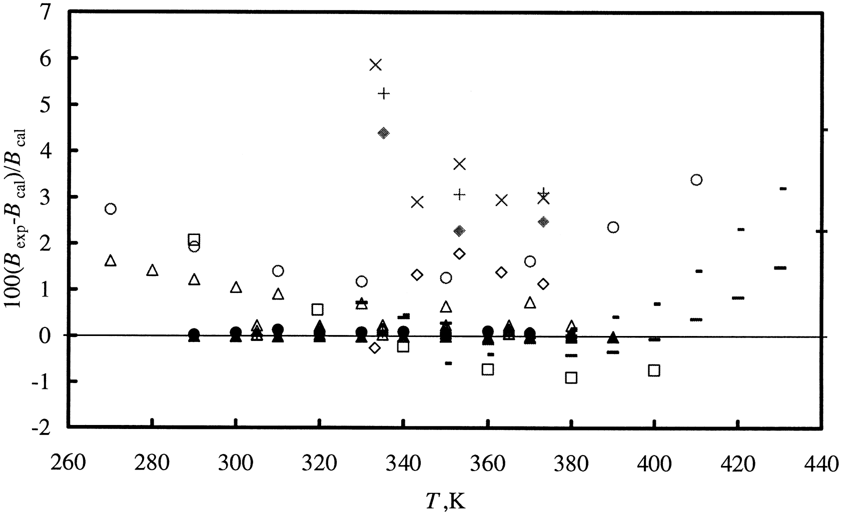

Fig. 3. Relative deviations of the second virial coefficients from the present model: (●) B_{11}, this work; (▲) B_{22}, this work; (■) B_{33}, this work; (△) B_{22}, Gillis [13]; (□) B_{33}, Gillis [13]; (○) B_{33}, Beckermann and Kohler [14]; (+) B_{12}, Weber and Defibaugh [16]; (×) B_{23}, Weber and Defibaugh [16]; (-) B_m (55/45/0 mol%), Weber and Defibaugh [16]; (◇) B_m (0/51/49 mol%), Weber and Defibaugh [16]; (—) B_m (20/80/0 mol%), Kiyoura et al. [15]; (■) B_m (40/60/0 mol%), Kiyoura et al. [15].

in Fig. 3, where the experimental values for R-32/125 (20/80 and 40/60 mass%) reported by Kiyoura et al. [15] are included. Although we have excluded the comparison of the present second virial coefficients for binary and ternary mixtures is simply due to its clarity, we have found that all the present second virial coefficients are excellently represented within ±0.15% for pure components, ±0.20% for binary mixtures, and ±0.25% for ternary mixtures.

The available experimental second virial coefficient values for R-32/125 of Kiyoura et al. [15] agree well with both the present model within ±0.7% at applicable temperatures of the present model from 330 to 400 K, although their deviations become more significant at higher temperatures. The deviations of the cross second virial coefficients, B_{12} and B_{23}, reported by Weber and Defibaugh [16] from the present model vary from 2.9 to 5.8%, which are recognized as being satisfactorily small, since the cross second virial coefficients were not obtained directly from the *PVTx* property measurements for the mixtures. The experimental second virial coefficients for the binary R-32/143a system were not obtained in this work, since there were only three or four data points along each isotherm, and these are not sufficient to determine the experimental second virial coefficient precisely.

Table II. Numerical Constants, $a_{k,i}$, in Eq. (2)

$i\backslash k$	0	1	2	3
1	4.4971	−2.8987	5.8251	−1.7477
2	3.0164	10.7918	1.2173	−0.3680
3	1.8567	10.14878	−1.4867	−0.1700

To confirm the thermodynamic consistency of the present model, derived properties such as isochoric heat capacities, c_v, isobaric heat capacities, c_P, and speeds of sound, w, calculated from the present model are examined. These properties are calculated by Eqs. (8) through (10), where R denotes the gas constant.

$$c_v = c_P^0 - R - \int_0^\rho \frac{T}{\rho^2}\left(\frac{\partial P}{\partial T^2}\right)_\rho d\rho \tag{8}$$

$$c_P = c_v + \frac{T(\partial P/\partial \rho)_\rho^2}{\rho^2(\partial P/\partial \rho)_T} \tag{9}$$

$$w = \sqrt{\frac{c_P}{c_v}\left(\frac{\partial P}{\partial \rho}\right)_T} \tag{10}$$

The ideal gas heat capacity, c_P^0, is given in Eq. (11), whose numerical constants were obtained by Ogawa and Sato [17] for each pure component and are given in Table II.

$$\frac{c_P^{0_\mathrm{i}}}{R} = \sum_{k=0}^{3} \mathbf{a}_{k,\mathrm{i}} T_\mathrm{r}^k \tag{11}$$

Figures 4, 5, and 6 illustrate the temperature dependence of c_v, c_P, and w for the ternary R-32/125/143a (10/45/45 mass%) system. It is apparent that the present model shows thermodynamically reasonable behavior for these derived properties not only in an applicable range but also in an extensive range of pressures up to 8 MPa and temperatures from 200 to 500 K. This fact confirms the thermodynamic consistency of our model not only in the input data range to develop the present model but also in the extended range of temperatures and pressures for the gas-phase R-32/125/143a mixture.

The present model also exhibits an excellent representation of the third virial coefficient with thermodynamically sound behavior as far as the temperature range of the input data is concerned.

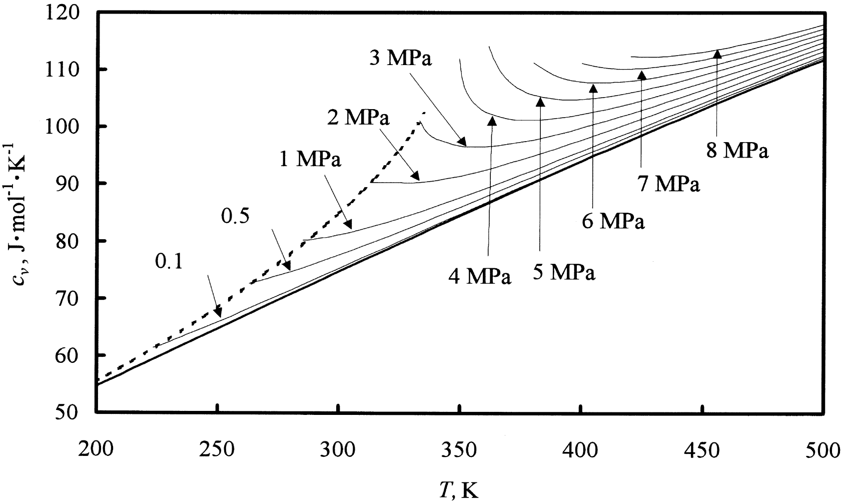

Fig. 4. Calculated isochoric heat capacities for the ternary R-32/125/143a (10/45/45 mass%) system: – – –, saturated vapor; ——, ideal gas.

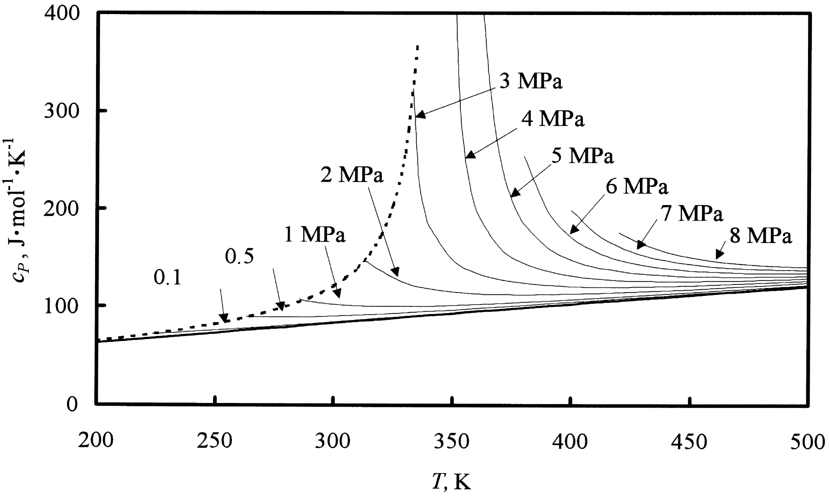

Fig. 5. Calculated isobaric heat capacities for the ternary R-32/125/143a (10/45/45 mass%) system: – – –, saturated vapor; ——, ideal gas.

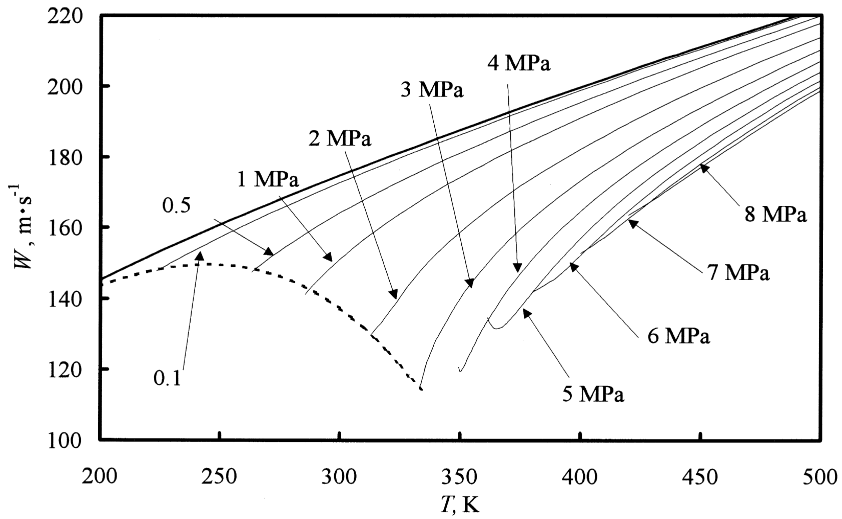

Fig. 6. Calculated speeds of sound for the ternary R-32/125/143a (10/45/45 mass%) system: – – –, saturated vapor; ——, ideal gas.

5. CONCLUSION

A thermodynamic model that represents the *PVTx* properties in the gaseous phase of the ternary R-32/125/143a system has been developed. The model has a form of a truncated virial equation of state, and the numerical constants for its virial terms were obtained on the basis of the experimental *PVTx* data in the entire range of compositions including each binary mixture and single component. The reproducibility of the present model has been confirmed to be satisfactory, within ±0.3% for both pressure and second virial coefficient. The range of validity of the present model was subject to the range of the input data available, i.e., densities up to 2.5 mol·dm^{-3}, pressures up to 4.5 MPa, and temperatures 300 to 380 K, over all compositions of the ternary R-32/125/143a system. The temperature dependence of the derived properties, c_v, c_P, and w, as well as that for the second and third virial coefficients, was also confirmed to behave in a thermodynamically rational fashion.

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