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Determination of Second Virial Coefficients and Virial Equations of R-32 (Difluoromethane) and R-125 (Pentafluoroethane) Based on Speed-of-Sound Measurements[1]

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The second virial coefficients, B, for difluoromethane (R-32, CH_2F_2) and pentafluoroethane (R-125, CF_3CHF_2) are derived from speed-of-sound data measured at temperatures from 273 to 343 K with an experimental uncertainty of $\pm 0.0072\%$. Equations for the second virial coefficients were established, which are valid in the extensive temperature ranges from 200 to 400 K and from 240 to 440 K for R-32 and R-125, respectively. The equations were compared with theoretically derived second virial coefficient values by Yokozeki. A truncated virial equation of state was developed using the determined equation for the virial coefficients. The virial equation of state represents our speed-of-sound data and most of the vapor $P\rho T$ data measured by deVries and Tillner-Roth within ± 0.01 and $\pm 0.1\%$, respectively.

KEY WORDS: alternative refrigerant; equation of state; hydrofluorocarbon; R-32; R-125; second virial coefficient; speed of sound.

1. INTRODUCTION

Since the speed of sound in the dilute gas depends heavily on the ideal-gas heat capacity, the second virial coefficients can be accurately determined from speed-of-sound measurements. Hydrofluorocarbons, R-32, R-125, and

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1,1,1,2-tetrafluoroethane (R-134a, CH_2FCF_3) are components of promising binary and/or ternary refrigerant mixtures to replace chlorodifluoromethane (R-22, $CHClF_2$). The speed of sound in gaseous R-32 [1, 2], R-125 [3], and R-134a [2, 4] has been measured with an uncertainty of ±0.0072%.

The second virial coefficient is important to calculate thermodynamic properties at low temperatures and low pressures where experimental data are scarce. The virial coefficients for R-134a were determined recently [5, 6] by a new analytical method. In the present study, second virial coefficients are determined from this new analytical method based on experimental speed-of-sound values for R-32 and R-125. The determined values are compared with literature results. A simple virial equation of state is also developed based on the determined values. The experimental speed-of-sound and $P\rho T$ data are compared with calculated values from the equations of state.

2. DETERMINATION OF SECOND VIRIAL COEFFICIENTS FROM SPEED OF SOUND

Since a detailed explanation of the use of speed-of-sound measurements for the determination of second virial coeffiecients has been presented in previous papers [5, 6], only a brief explanation is given here. The speed-of-sound data were measured at various temperatures and pressures; however, the density was not measured. The second virial coeffiecients of the density-series virial equation are useful in the development of equations of state. The virial coefficients, B', C', D', and E', of a pressure-series virial equation (denoted by a prime) are related to the virial coefficients, B, C, and D of a density-series virial equation as follows:

$$B' = \frac{B}{RT} \tag{1}$$

$$C' = \frac{C - B^2}{(RT)^2} \tag{2}$$

$$D' = \frac{D + 2B^3 - 3BC}{(RT)^3} \tag{3}$$

$$E' = \frac{E - 5B^4 + 10B^2C - 4BD - 2C^2}{(RT)^4} \tag{4}$$

By using Eqs. (1)–(4), a pressure-series virial equation with the virial coefficients of a density-series virial equation is derived as expressed by Eq. (5).

$$Z = 1 + \frac{B}{RT} P + \frac{C - B^2}{(RT)^2} P^2 + \frac{D + 2B^3 - 3BC}{(RT)^3} P^3 + \frac{E - 5B^4 + 10B^2C - 4BD - 2C^2}{(RT)^4} P^4 \tag{5}$$

The Gibbs function is derived from Eq. (5) using ideal-gas heat capacities [2, 3], and the speed of sound is derived from the Gibbs function by using a general thermodynamic relation. The virial coefficients of a density-series virial equation can be derived by fitting the equation to the experimental speed-of-sound data with temperature and pressure values.

Before carrying out the procedure discussed above, we examined the number of terms of virial equations needed for representing the $P\rho T$ properties over the same range of the speed-of-sound data [1–3]. For almost the entire range of the gaseous phase, only a two-term density-series virial equation with the second and third virial coefficients is needed for the required accuracy, whereas a four-term pressure-series virial equation with the second to fifth virial coefficients is needed to represent the $P\rho T$ properties over the same range of the present speed-of-sound data with the same deviations as those of the density-series virial equation. The number of terms are the same for R-32, R-125, and R-134a.

We fitted Eq. (5), with the fourth and fifth virial coefficients of the density-series virial equation being zero ($D = 0$ and $E = 0$), to the speed-of-sound measurements, and then we determined the second and third virial coefficients. Because the fitting range is a very small region of the dilute gaseous phase, it is not possible to determine the third virial coefficient from the present speed-of-sound measurements. When we fitted Eq. (5) to the speed-of-sound measurements, we used the following temperature function:

$$B = \mathrm{b}_0 + \mathrm{b}_1 \exp\left(\frac{\mathrm{b}_2}{T}\right) \tag{6}$$

The determined coefficients of Eq. (6) are presented in Table I for both R-32 and R-125.

Table I. Coefficients of Eq. (6) for R-32 and R-125

	R-32	R-125
b_0 ($\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$)	75.183	194.42
b_1 ($\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$)	−40.088	−109.405
b_2 (K)	667.86	489.41

Table II. Coefficients of Eq. (8) for R-32 and R-125

	R-32	R-125
c_1 ($dm^6 \cdot mol^{-2}$)	2.357×10^{-2}	1.107×10^{-2}
c_2 (K)	310.94	489.41
c_3 ($dm^6 \cdot mol^{-2}$)	-1.50×10^{-4}	-1.46×10^{-5}
α	3.354	2.426
β	16.41	13.27

3. FORMULATION OF VIRIAL EQUATION OF STATE

A simple truncated virial equation of state is formulated by simply assigning functional forms to B and C.

$$Z = 1 + B\rho + C\rho^2 \tag{7}$$

The functional form for B is Eq. (6), and the coefficients of b_0, b_1, and b_2 are determined from the experimental speed-of-sound values. Since the contribution of C to the speed of sound at low pressure is very small, the C values are determined based on available experimental $P\rho T$ values [7, 8].

The functional form of C is taken as

$$C = c_1 \left(\frac{c_2}{T}\right)^{\alpha} + c_3 \left(\frac{c_2}{T}\right)^{\beta} \tag{8}$$

where c_1, c_2, c_3, α, and β are fitting parameters. Namely, the present virial equation of state, Eq. (7), consists of four temperature and density terms as shown in Eqs. (6) and (8).

The C values were determined with accurate experimental $P\rho T$ values by fitting the coefficients in Eq. (8). For the determination of the four-term virial equations of state, the experimental $P\rho T$ values of R-32 and R-125 reported by Zhang et al. [7] and by de Vries and Tillner-Roth [8] were used. The determined parameters in Eq. (8) are given in Table II for R-32 and R-125, while the ranges of validity of Eq. (7) for R-32 and R-125 are reported in Table III. The ranges include most of the gaseous phase region

Table III. Range of Eq. (7) for R-32 and R-125

	T (K)	P (MPa)	ρ ($kg \cdot m^{-3}$)
R-32	263-383	0-6.0	0-150
R-125	263-390	0-4.0	0-300

for these refrigerants. The present four-term virial equation can be used for prediction of thermodynamic properties at very low temperatures because of the reasonable behavior of the second virial coefficients as shown in Figs. 1 and 2 and explained in the following section.

4. RESULTS AND DISCUSSION

4.1. Second Virial Coefficients

The experimental speed-of-sound data at constant temperature are fitted by a quadratic speed-of-sound equation of the pressure series type, but the speed-of-sound data should be fitted by a more complicated equation as derived from Eq. (5). Figures 1 and 2 show the differences between the second virial coefficient derived by a previous method [1–4] and those by the present procedure for R-32 and R-125, respectively.

Figure 1 shows comparisons of the second virial coefficient for R-32. The values of Zhang et al. [9] and de Vries and Tillner-Roth [8] for R-32 agree with results from Eq. (6) within ±0.6 and ±1.8%, respectively. We plotted the theoretical values of Yokozeki et al. [10], which agree with the present results within ±2.0%, even at temperatures below 260 K and above 380 K. The previous values [1] agree with present results within ±2.0% over a limited temperature range, 273 to 343 K. However, the extrapolated second virials of the previous paper [1] deviate by −15% from the present values at 200 K. Since the thermodynamic state of R-32 is much closer to the ideal-gas condition than that of R-125, the second virial coefficient of R-32 is more difficult to be determined from experimental results.

For R-125, the second virials of Zhang et al. [9], Gillis [11], and Boyes and Weber [12] agree with calculated values from Eq. (6) within ±1.7, ±2.4, and ±0.7%, respectively, as shown in Fig. 2. The theoretical values of Yokozeki et al. [10] agree well with the present results, i.e., within ±0.6% over the range of validity of the present model. Even if Eq. (6) is extrapolated to temperatures below 260 K and to temperatures above 390 K, the present second virials agree with those of Yokozeki et al. [10] within ±3.0%. And we also show in Fig. 2 the previous second virials [3], which have been determined by using second acoustic virial coefficients. The previous values [3] agree with present values within ±1.6% from 240 to 440 K since the contribution of the second virials to the speed of sound is sufficiently large to allow accurate calculations of the second virials.

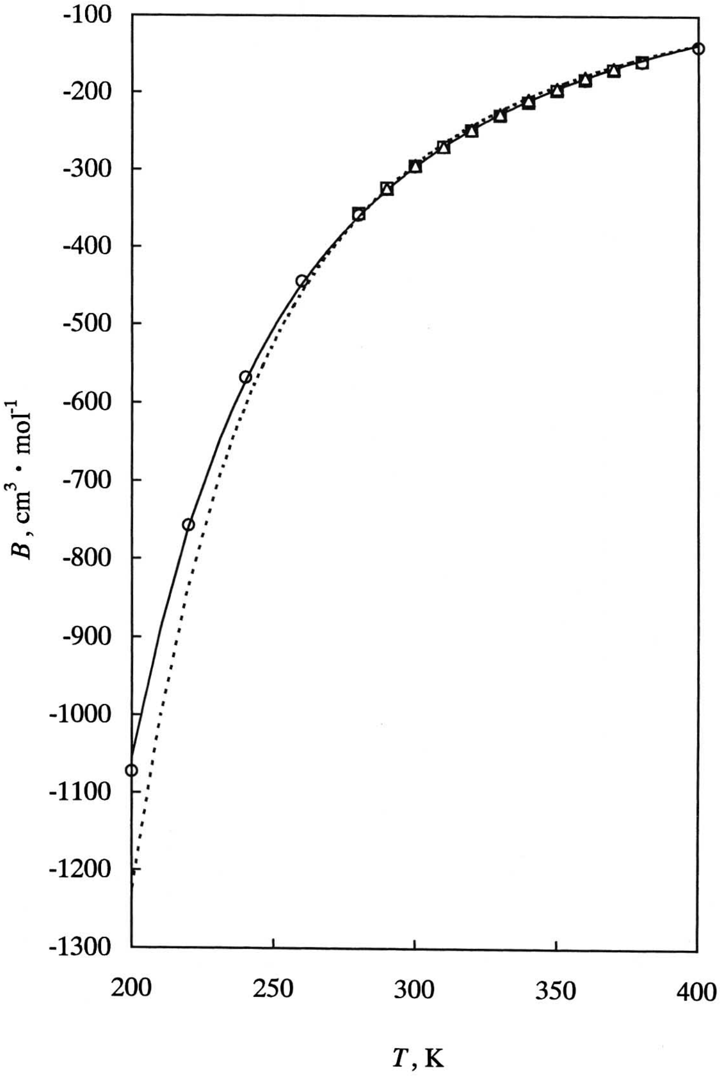

Fig. 1. Second virial coefficients for R-32. (△) Zhang et al. [9]; (□) de Vries and Tillner-Roth [8]; (○) Yokozeki et al. [10]; (- - - -) Hozumi et al. [1]; (——) calculated values from Eq. (6).

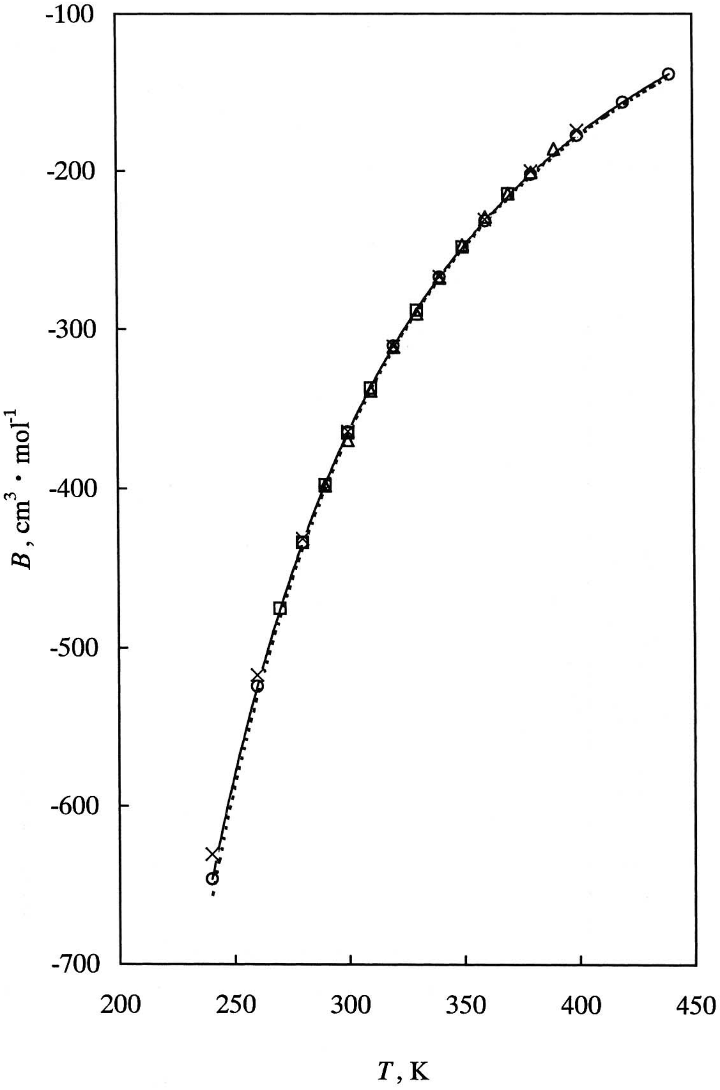

Fig. 2. Second virial coefficients for R-125. (△) Zhang et al. [9]; (×) Gillis [11]; (□) Boyes and Weber [12]; (○) Yokozeki et al. [10]; (- - - -) Hozumi et al. [3]; (——) calculated values from Eq. (6).

4.2. Virial Equation of State

Figures 3 and 4 show the deviations of the experimental speed-of-sound data from the calculated values using the four-term virial equations of state for R-32 and R-125, respectively. For R-32, the speed-of-sound data [1, 2] agree well within ±0.006% with the calculated values from Eq. (5), as shown in Fig. 3. The experimental speed-of-sound data [3] for R-125 agree with the calculated values from Eq. (5) within ±0.011% as shown in Fig. 4.

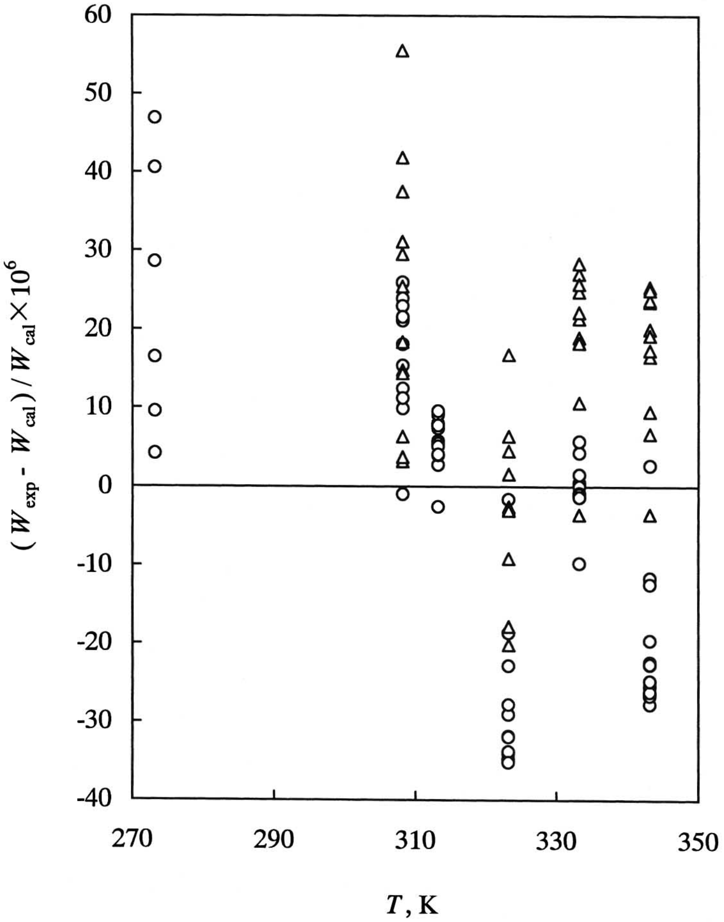

Fig. 3. Deviations of experimental speeds of sound from calculated values of Eq. (5) for R-32. (○) Hozumi et al. [1]; (△) Hozumi et al. [2]; (——) calculated values from Eq. (5).

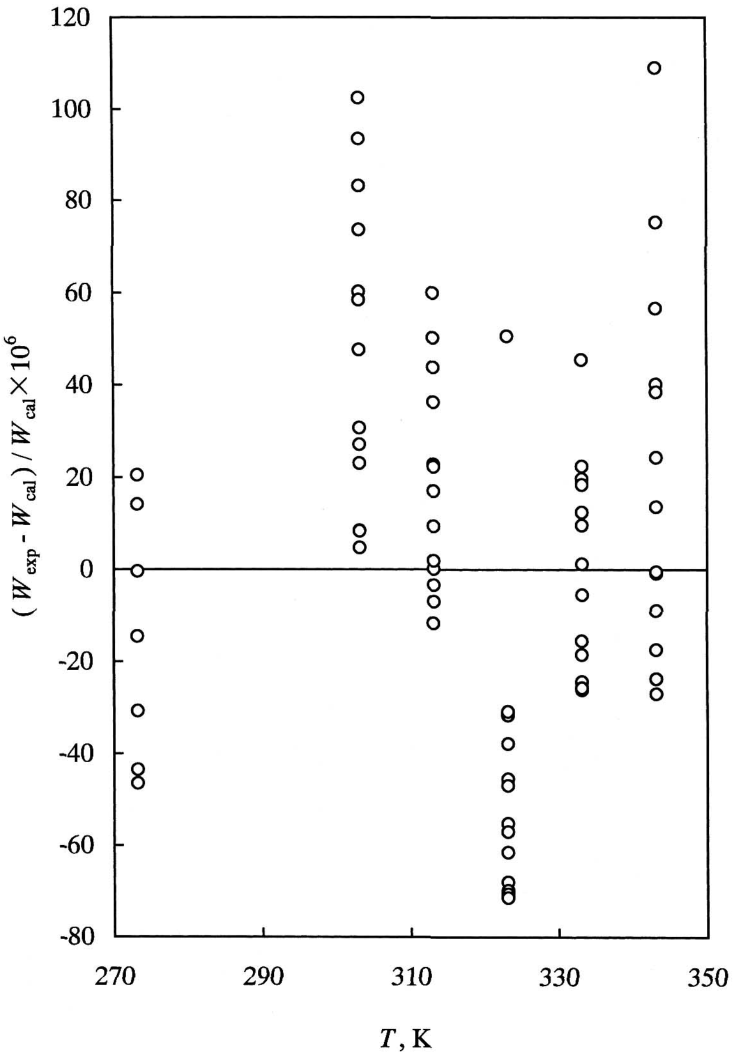

Fig. 4. Deviation of experimental speeds of sound from calculated values of Eq. (5) for R-125. (○) Hozumi et al. [3]; (——) calculated values from Eq. (5).

The deviations of experimental $P\rho T$ data from the present four-term virial equation of state are shown in Figs. 5 and 6. In Fig. 5, the experimental $P\rho T$ data reported by Zhang et al. [7] and by de Vries and Tillner-Roth [8] for R-32 agree with the calculated values from Eq. (7) within ±0.1% in pressure. In Fig. 6 the experimental $P\rho T$ data reported by de Vries and

Tillner-Roth [8] for R-125 agree very well with the calculated values from Eq. (7), within ±0.05% in pressure. On the other hand, the data reported by Zhang et al. [7] for R-125 agree with the calculated values from Eq. (7) within ±0.20% except for four data points at higher densities along the 290, 320, and 390 K isotherms.

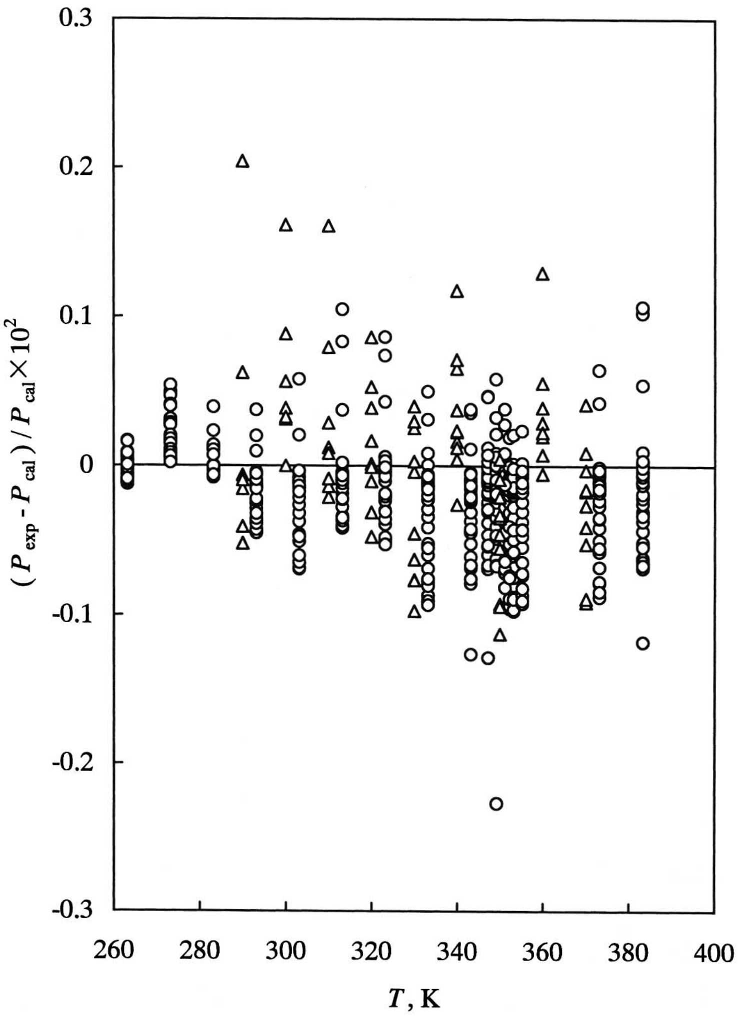

Fig. 5. Deviation of experimental $P\rho T$ data from calculated values of Eq. (7) for R-32. (△) Zhang et al. [7]; (○) de Vries and Tillner-Roth [8]; (——) calculated values from Eq. (7).

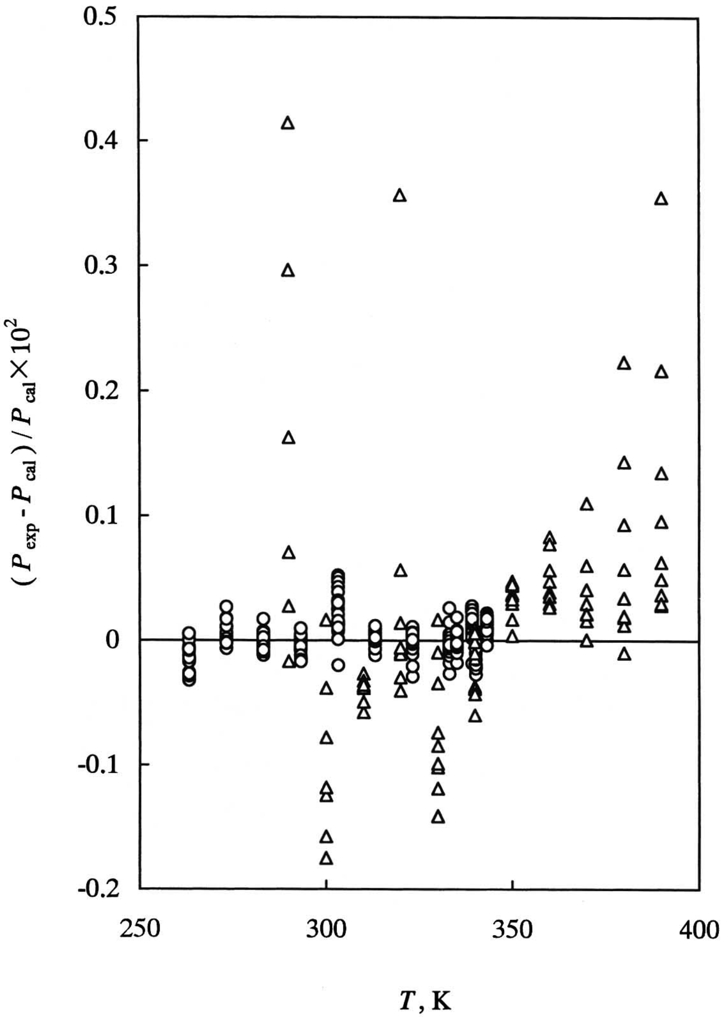

Fig. 6. Deviation of experimental $P\rho T$ data from calculated values of Eq. (7) for R-125. (△) Zhang et al. [7]; (○) de Vries and Tillner-Roth [8]; (——) calculated values from Eq. (7).

5. CONCLUSIONS

We determined the second virial coefficients from the experimental speed-of-sound data for R-32 and R-125 using a new method. The determined second virial coefficients agree well with the reported experimental data. The second virials for R-32 and R-125 agree well with theoretical values, even at temperatures far beyond the range of the speed-of-sound measurements, the temperature range is 200 to 400 K for R-32 and 240 to 440 K for R-125. The present four-term virial equation of state represents experimental speed-of-sound data and most $P\rho T$ data within ±0.01% and ±0.1% in pressure, respectively.

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