Measurements of Gaseous *PVTx* Properties and Saturated Vapor Densities of Refrigerant Mixture R-125 + R-143a[1]

H. Uchida[2], H. Sato[2], and K. Watanabe[2,3]

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2. Department of System Design Engineering, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223, Japan
3. Author to whom correspondence should be addressed.

ABSTRACT

The experimental 136 *PVTx* properties of an binary refrigerant mixture, R-125 (pentafluoroethane) + R-143a (1,1,1-trifluoroethane), have been measured for a composition 50 mass % R-125, by a constant-mass-method coupled with expansion procedure in a range of temperatures from 300 to 400 K, pressures from 1.3 to 6.1 MPa, and densities from 98 to 301 kg·m^{-3}. The experimental uncertainties of the present measurements are estimated to be within ± 7.2 mK in temperature, ± 3.0 kPa in pressure, ± 0.30 kg·m^{-3} in density and ± 0.040 mass % in composition, respectively. The sample purities are 99.96 area % for R-125 and 99.94 area % for R-143a. Eight saturated-vapor densities of the R-125 + R-143a system have been determined, on the basis of rather detailed *PVTx* properties measured in the vicinity of the saturation boundary as well as the thermodynamic behavior of isochores near the saturation. The second and third virial coefficients for temperatures from 330 to 400 K have also been determined and discussed.

KEY WORDS: alternative refrigerant; binary refrigerant mixtures; HFC-125 + HFC-143a system; *PVTx* properties; saturated vapor densities; thermodynamic properties; virial coefficients

1. INTRODUCTION

One of the urgent issues to be solved in the refrigeration industries is to identify the optimum alternative refrigerant to replace the conventional refrigerant R-502 (an azeotropic refrigerant mixture of R-22 (chlorodifluoromethane) + R-115 (monochloropentafluoroethane)), which is dominantly being used in the refrigeration equipments for low temperature applications. One of the candidates to replace R-502 is a refrigerant mixture of R-125 (pentafluoroethane) + R-143a (1,1,1-trifluoroethane). R-125 and R-143a include no chlorine atom, so the ozone depletion potential (ODP) is null.

Reliable information about the thermodynamic properties of this blend is significantly important for the research & development of the advanced refrigeration equipments with binary R-125 + R-143a system. This paper deals with the experimental study of *PVTx* properties, saturated vapor densities, second and third virial coefficients for this refrigerant mixture.

2. MEASUREMENTS

The constant-mass-method coupled with expansion procedures was used for the present measurements of *PVTx* properties. The apparatus and procedure have been reported by Takaishi et al.[1] and Kiyoura et al.[2] in detail.

The apparatus shown in Fig. 1 consists of a sample cell (A), an expansion cell (B), a differential pressure detector (M), a platinum resistance thermometer (G) calibrated against ITS-90, a thermostated fluid bath (L), temperature control/measuring devices, and pressure measuring instruments. The inner volumes of the sample cell and expansion cell were carefully calibrated with pure water; they were (283.368 ± 0.027) cm^3 and (55.583 ± 0.007) cm^3, respectively, at 273.15 K. The temperature in the silicone oil-filled thermostated fluid bath was controlled within ± 2 mK. When thermal equilibrium was reached with the pressure remaining unchanged over several

hours, temperature and pressure of the sample fluid were measured. After a series of measurements along a prescribed isochore was completed, we expanded a part of the sample fluid into the expansion cell in the single gaseous phase to obtain another isochore, with composition unchanged.

The experimental uncertainties of the present measurements are estimated to be within ± 7.2 mK in temperature, ± 3.0 kPa in pressure, ± 0.30 kg•m^{-3} in density, and ± 0.040 mass % in composition, respectively. The sample purities are 99.96 area % for R-125 and 99.99 area % for R-143a for series 1 (50.026 mass % R-125), and 99.96 area % for R-125 and 99.94 area % for R-143a for series 2 (50.005 mass % R-125), which all are analyzed by the chemical manufacturers.

3. RESULTS

Measurements of *PVTx* properties of refrigerant mixture R-125 + R-143a were made along 8 isochores at temperatures from 300 to 400 K, pressures up to 6.3 MPa, and densities from 98 to 301 kg·m^{-3}, for compositions 50.026 and 50.005 mass % R-125, as shown in Fig. 2 which shows the distribution of the *PVTx* data on a pressure-temperature plane. The vapor pressure curves are calculated from the correlations of both pure components [3] and the critical temperatures are adopted from the earlier studies of our laboratory [4,5].

4. DISCUSSION

4.1. Saturated vapor densities

In this study, eight saturated-vapor densities of the R-125 + R-143a system for a composition 50 mass % R-125 have been determined, on the basis of rather detailed *PVTx* properties measured in the vicinity of the saturation boundary as well as the thermodynamic behavior of gaseous isochores near the saturation, as shown typically in Fig.3 where an isochore in two-phase region is correlated to a following relation:

$$\ln P_r = A - B / T_r \tag{1}$$

and a gaseous isochore near the saturation is correlated to a following relation:

$$Z = \mathrm{C} + \mathrm{D}/T_\mathrm{r} + \mathrm{E}/T_\mathrm{r}^{\,2} + \mathrm{F} \cdot \exp(1/T_\mathrm{r}) \tag{2}$$

where P_r, T_r, and Z denote reduced pressure, reduced temperature, and the compressibility factor. A, B, C, D, E, and F are numerical constants of the correlations. The *PVTx* measurements which were used to correlate are those within 10 K below the saturation temperature for Eq. (1), while those within 5 K above the saturation temperature for Eq. (2). Critical pressure and critical temperature for this refrigerant mixture R-125 + R-143a (50/50 mass %), which are reported by Higashi [6], are used for the correlations of Eq. (1) and Eq. (2). Each correlation expresses the *PVTx* measurements of this work within our experimental uncertainty.

After determining these numerical constants A through F along each isochore, saturated vapor densities were calculated with an aid of the Newton-Raphson method. Saturated vapor density values thus determined are shown in Table I. The uncertainties of these values are estimated to be within ± 0.10 K in temperature, ± 4.2 kPa in pressure, ± 0.30 kg·m^{-3} in density, respectively

Figure 4 shows the vapor-liquid saturation curve for R-125 + R-143a (50/50 mass %). This figure includes several studies reported by Ikeda et al. [7], Widiatmo et al. [8], Fujimine et al [9], and Kishizawa et al. [10]. Among those reported measurements, Ikeda et al. [7] and Kishizawa et al. [10] reported the measurements of the saturated vapor densities. The present results agree pretty better with those by Kishizawa et al.

4.2. Second and third virial coefficients

The compressibility factors, Z, of the present binary R-125 + R-143a mixtures with a composition 50 mass % R-125 were derived from the measurements by using the following relations:

$$Z = \mathrm{M}P / \rho \mathrm{R}T \tag{3}$$

and

$$\mathrm{M} = \sum_{\mathrm{i}=1}^{n} x_{\mathrm{i}} \mathrm{M}_{\mathrm{i}} \tag{4}$$

where P, ρ, and T denote pressure, mass density, and temperature, respectively. R is the universal gas constant R=8.31451 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, while $\mathrm{M_i}$ and x_i are the molar mass and respective mole fraction of each component.

The *PVTx* property measurements were represented within the estimated experimental uncertainty by the following truncated virial expression:

$$(Z-1)/\rho = \mathrm{B} + \mathrm{C}\rho \tag{5}$$

Straight lines can be drawn by plotting the values $(Z\text{-}1)/\rho$ vs ρ along isotherms, as shown in Fig. 5. The intersection with the ordinate corresponds to the second virial coefficient B, while the slope of each isotherm represents the third virial coefficient C. The second and third virial coefficients thus determined from the present measurements are listed in Table II. In this analysis, all of the measurements in gaseous phase are used to normalize the virial coefficients for the 50.0 mass % R-125 mixture, although they have been measured at two slightly-different compositions, 50.026 mass % R-125 and 50.005 mass % R-125. Note that difference in composition are small enough well within the uncertainties to determine these virial coefficients.

Figures 6 and 7 show the temperature dependence of B and C. Note that the solid and the dashed curves in Figs. 6 and 7 are the calculated results from correlation by Zhang et al. [11] developed for each mixture and pure component. The solid curves

denote the correlation for the pure components, whereas the dashed line for the mixture. Figure 6 includes the second virial coefficients for pure refrigerants reported by Zhang et al. [12]. This correlation represents the virial coefficient values by the present work within ± 0.7 % for B and ± 10.0 % for C satisfactorily.

ACKNOWLEDGMENTS

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Table I Saturated Vapor Densities of the R-125 + R-143a System

ρ'' (kg·m^{-3})	T'' (K)	P'' (MPa)
(a) 50.026 mass % R-125		
98.48	310.37	1.7432
119.57	317.14	2.0373
145.18	323.13	2.3383
176.27	328.86	2.6510
(b) 50.005 mass % R-125		
167.82	327.19	2.5792
203.76	332.47	2.8987
247.41	337.14	3.2082
300.43	340.77	3.4640

Table II Second and Third Virial Coefficients of the R-125 + R-143a System

T (K)	B (L•mol^{-1})	C (L^2•mol^{-2})
50.0 mass % R-125		
330	-0.308	0.031_3
340	-0.285	0.028_9
350	-0.265	0.026_8
360	-0.246	0.025_0
370	-0.230	0.023_3
380	-0.215	0.022_0
390	-0.201	0.020_6
400	-0.188	0.019_3

FIGURE CAPTIONS

Fig. 1 Experimental apparatus

[A] sample cell; [B] expansion cell; [C] vacuum pump;

[D] main heater; [E] sub heater; [F] cooler;

[G] platinum resistance thermometer; [H] thermometer bridge;

[I] PID controller; [J] DC power supply; [J1,J2] joints; [K] stirrer;

[L] thermostated fluid bath; [M] differential pressure detector;

[N] tester; [O] nitrogen cylinder; [P] precise pressure controller;

[Q] digital quartz pressure transducer;

[R] digital quartz pressure computer; [V1-V10] valves;

Fig. 2 Distribution of the *PVTx* measurements of R-125 + R-143a (50/50 mass %)

(×) this work (50.026 mass % R-125) ; (○) this work (50.005 mass % R-125) ;

(- - - -) vapor pressure curve of R-125 [3] ;

(— — —) vapor pressure curve of R-143a [3] ;

(▲) critical point of R-125 [4] ; (◆) critical point of R-143a [5] ;

Fig. 3 Determination of the saturated vapor densities

(○) present measurement ; (●) saturated vapor determined ;

(——) Eq. (1) ; (— — —) Eq. (2) ;

Fig. 4 Saturation curve for R-125 + R-143a (50/50 mass %)

(●) this work ; (×) Ikeda et al. [7] ; (△) Widiatmo et al. [8] ;

(+) Fujimine et al. [9] ; (□) Kishizawa et al. [10] ;

Fig. 5 Relation of $(Z-1)/\rho$ vs ρ for R-125 + R-143a (50/50 mass %)

Fig. 6 Temperature dependence of second virial coefficients for R-125 + R-143a (50/50 mass %)

(●) this work (50/50 mass %) ; (×) Zhang et al. (R-125) [11] ;

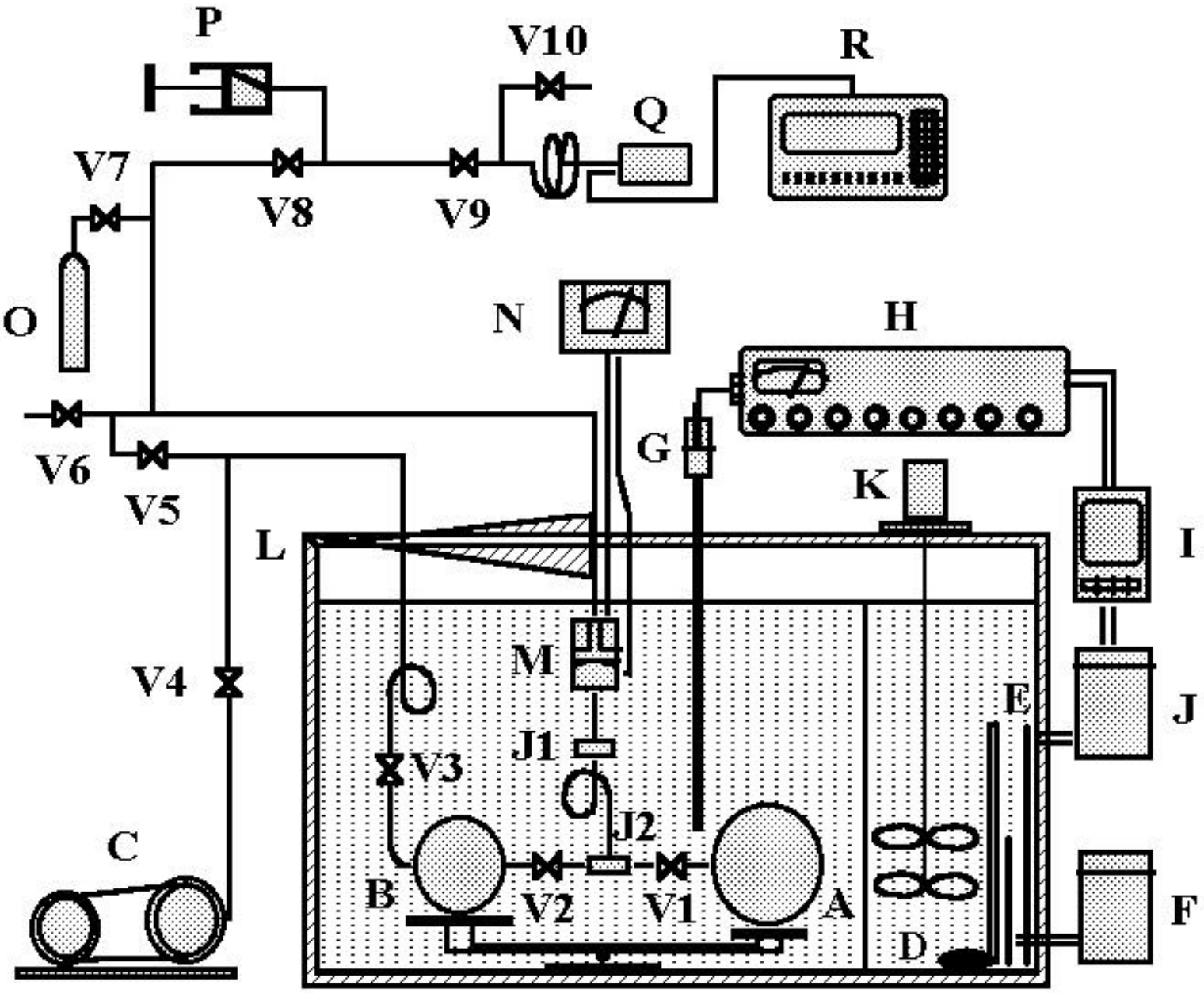
(✱) Zhang et al. (R-143a) [11] ; (- - - - -) B, Zhang (50/50 mass %) [12] ;

(——) B, Zhang (R-125) [12] ; (——) B, Zhang (R-143a) [12] ;

Fig. 7 Temperature dependence of third virial coefficients for R-125 + R-143a (50/50 mass %)

(●) this work (50/50 mass %) ; (- - - - -) B, Zhang (50/50 mass %) [12] ;

(——) B, Zhang (R-125) [12] ; (——) B, Zhang (R-143a) [12] ;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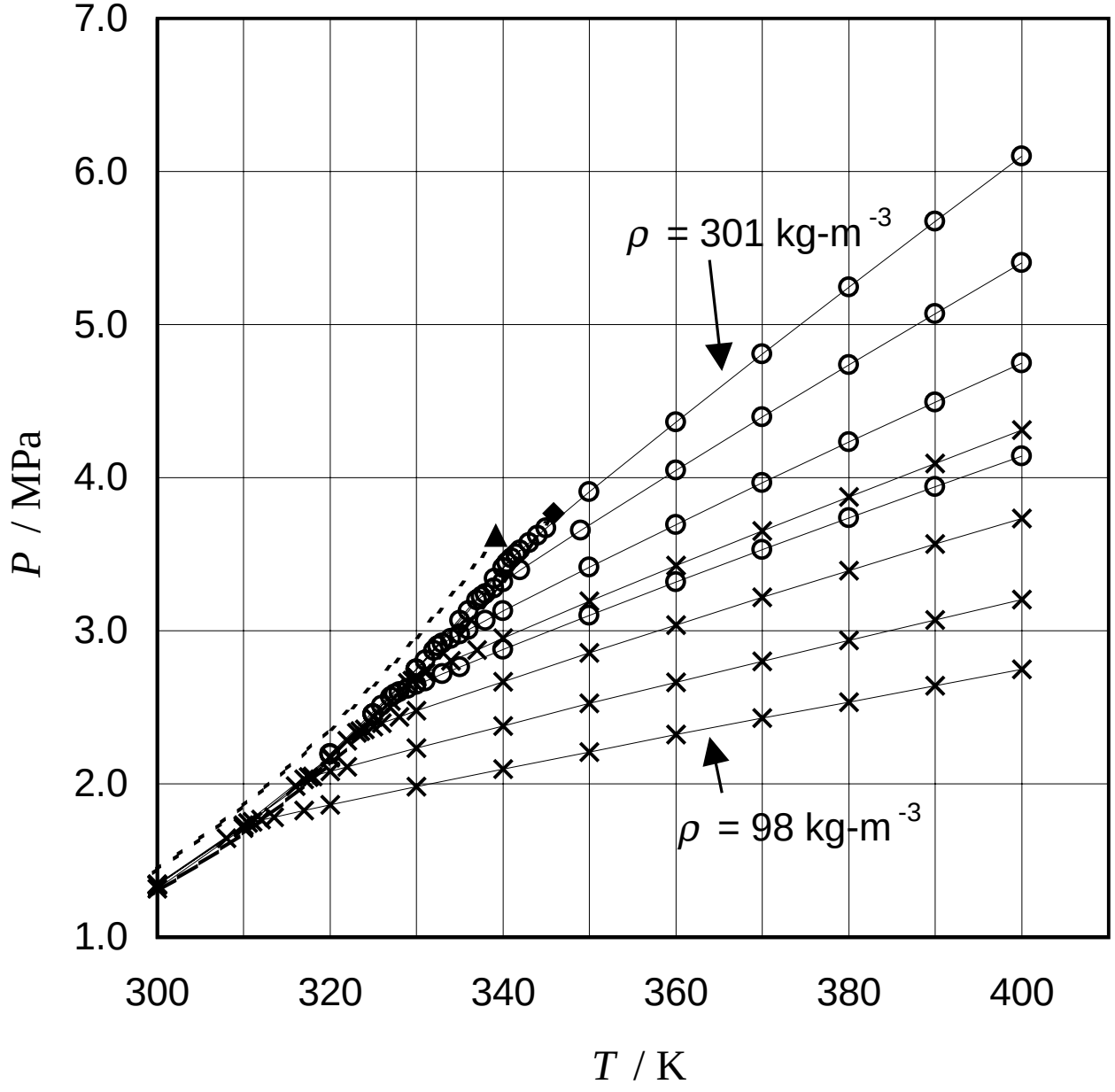
7.0
6.0
5.0
4.0
3.0
2.0
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P / MPa
300
320
340
360
380
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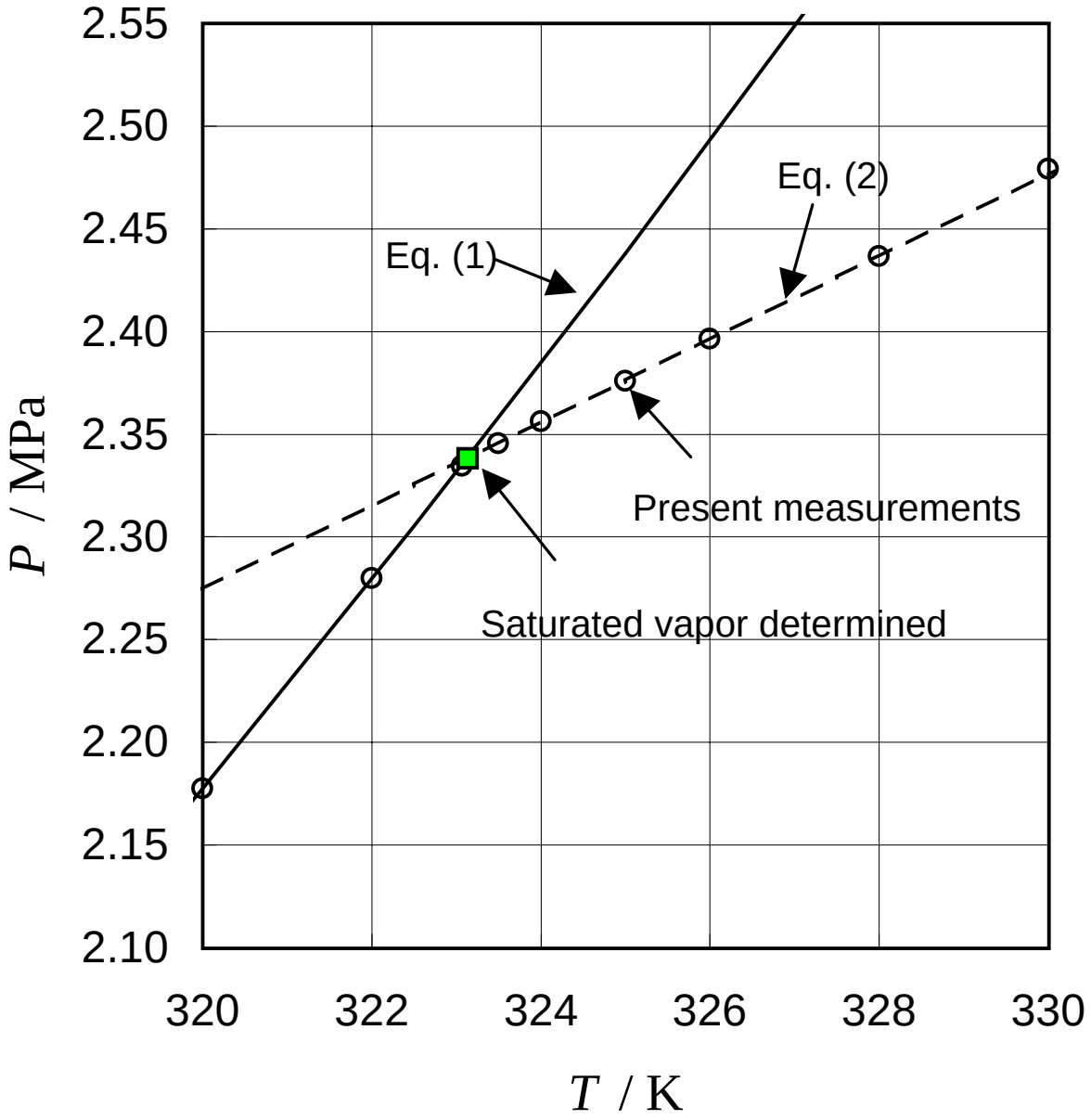
T / K
ρ = 301 kg-m -3
ρ = 98 kg-m -3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2.50
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2.30
2.25
2.20
2.15
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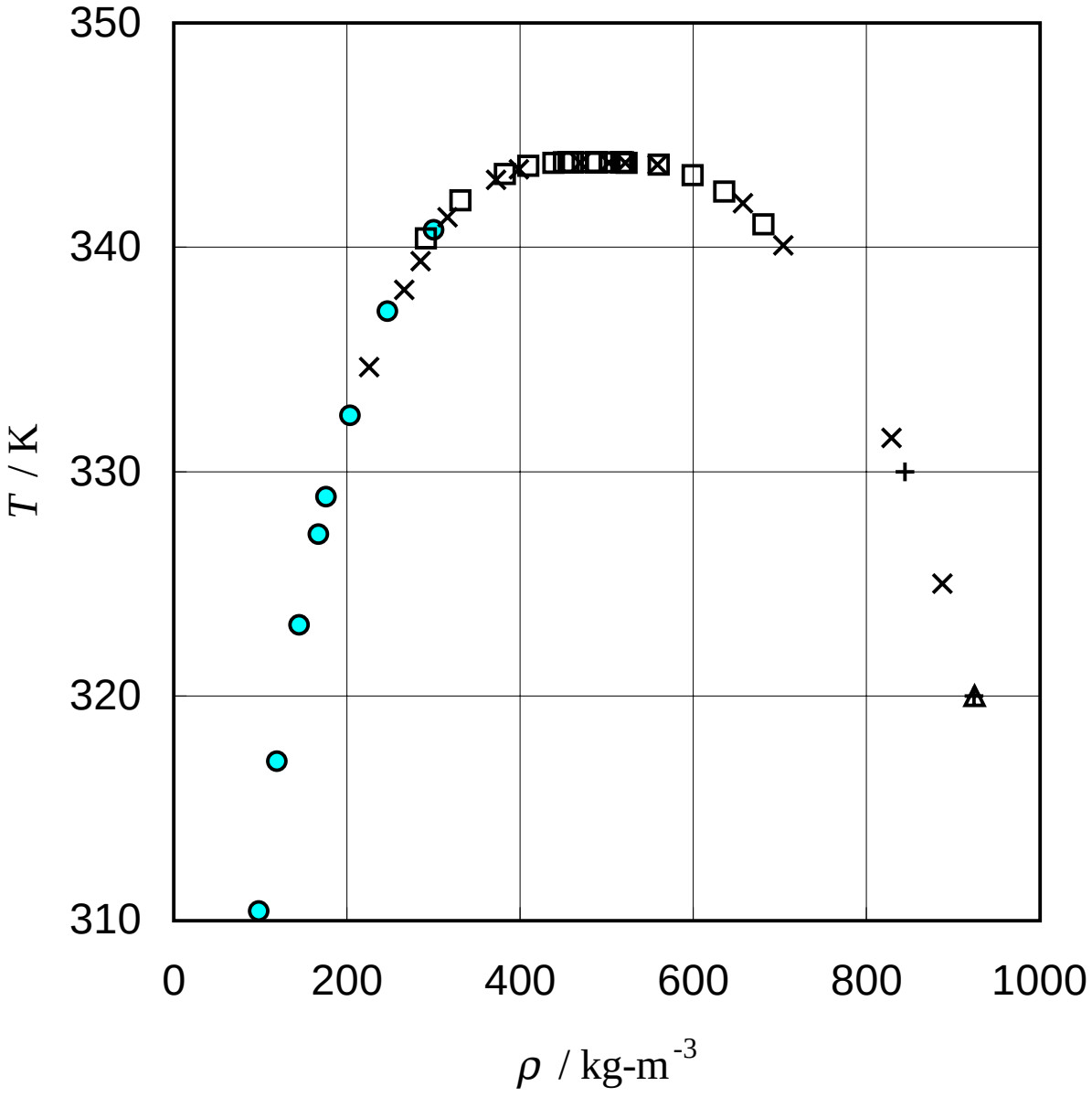
P / MPa
320
322
324
326
328
330
T / K
Eq. (1)
Eq. (2)
Present measurements
Saturated vapor determined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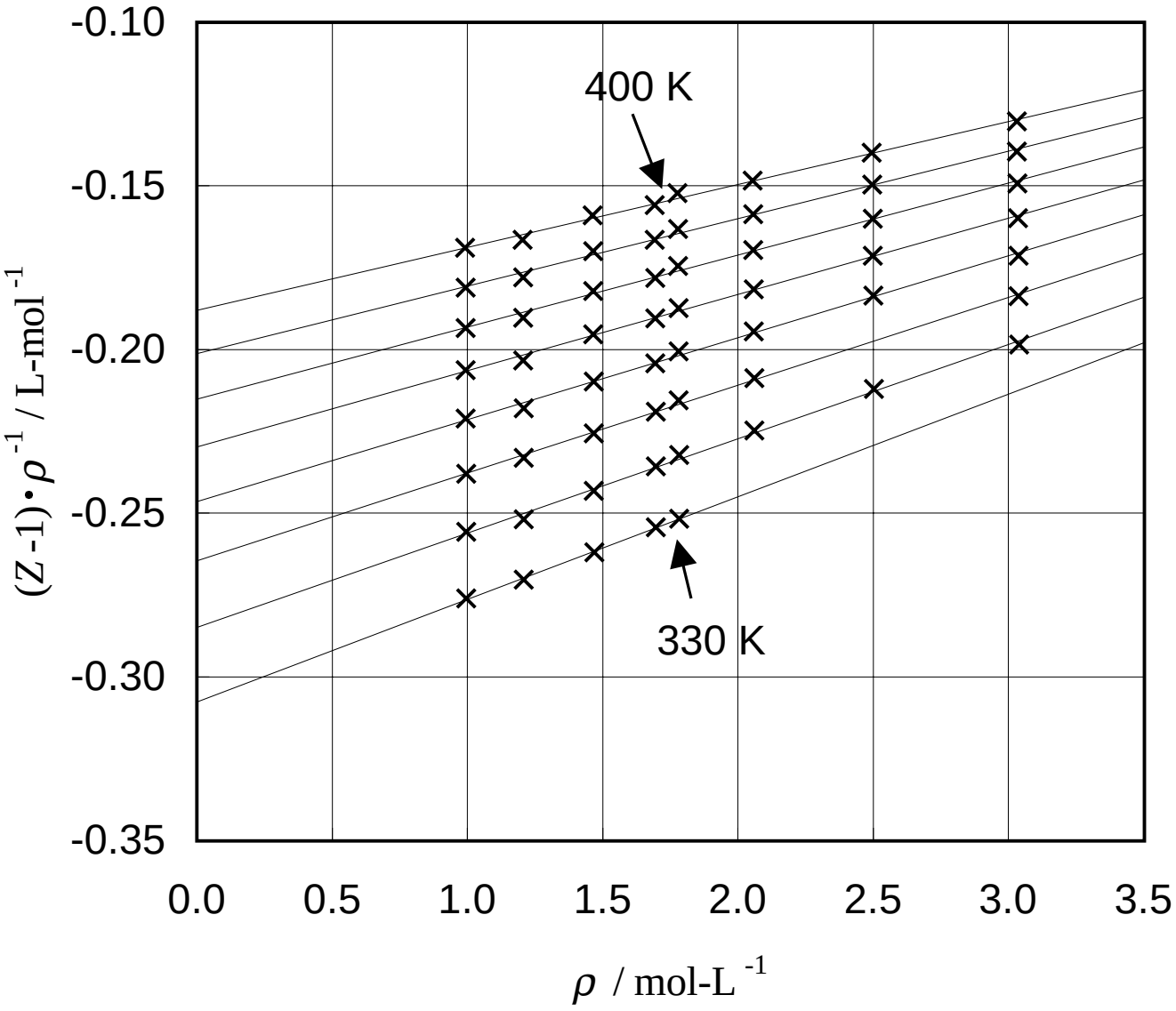
320
310
T / K
0
200
400
600
800
1000
ρ / kg-m-3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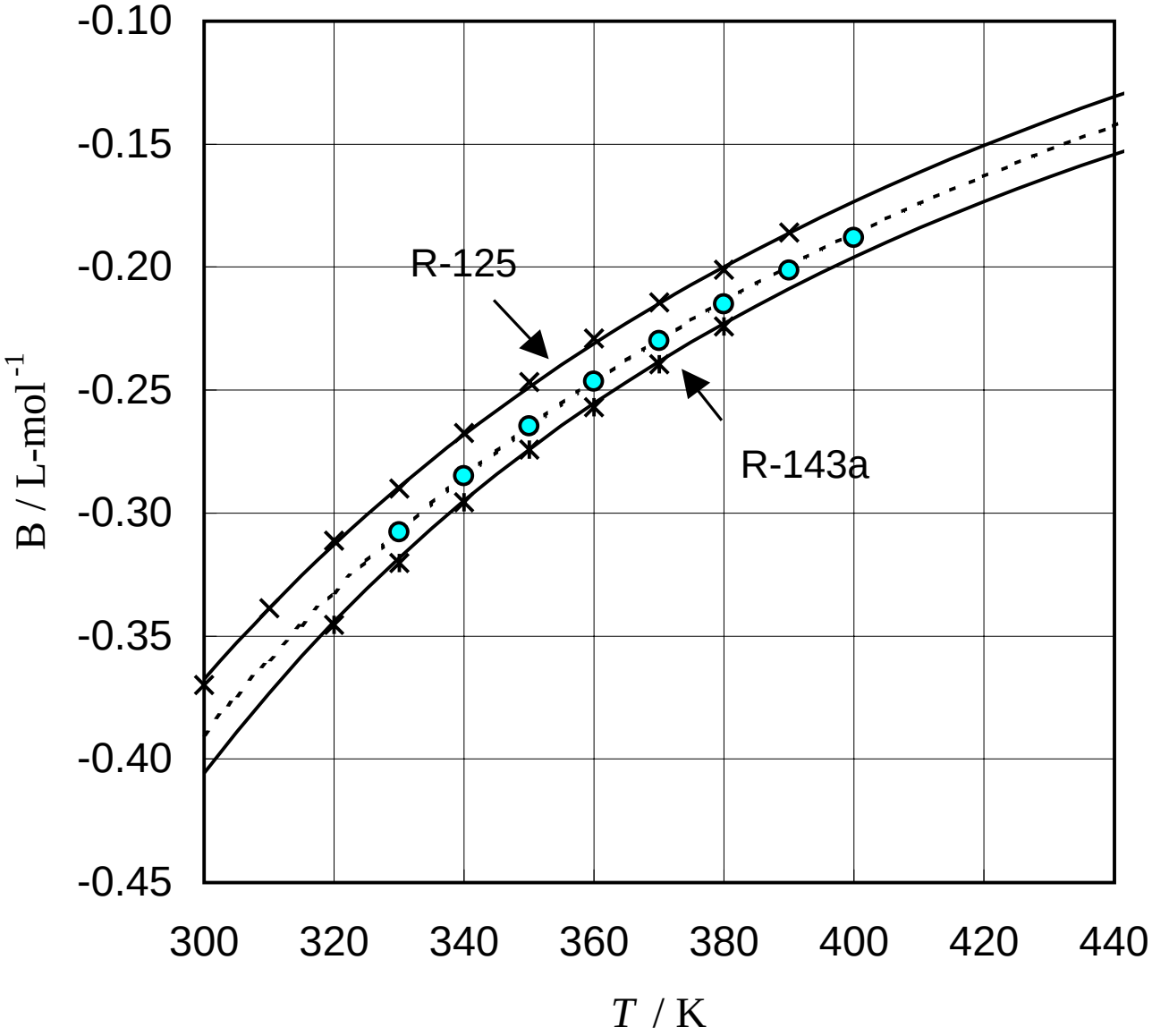
-0.15
-0.20
-0.25
-0.30
-0.35
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
400 K
330 K
(Z -1)• ρ -1 / L-mol -1
ρ / mol-L -1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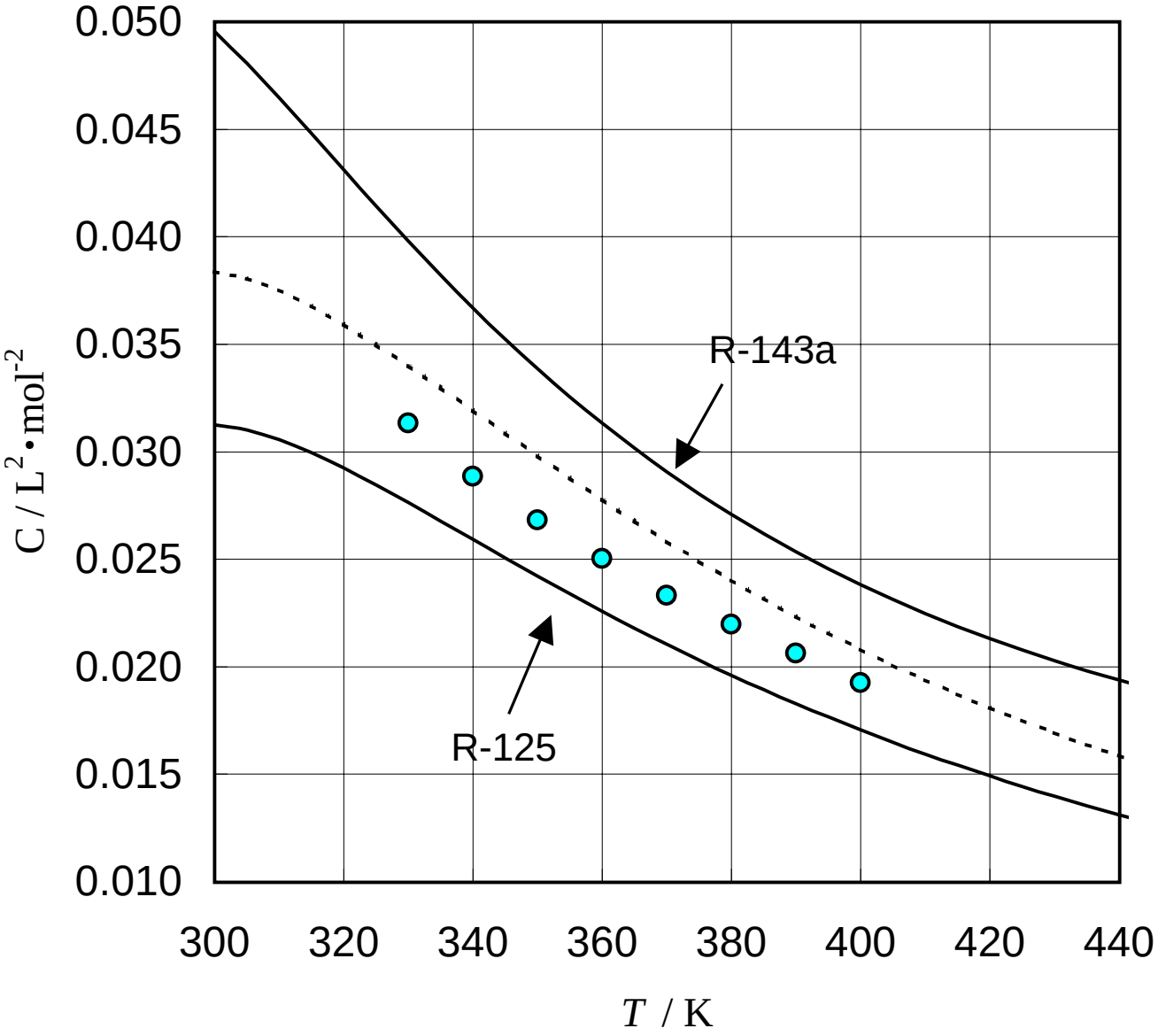
B / L-mol-1
R-125
R-143a
300
320
340
360
380
400
420
440
T / K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C / L2•mol-2
R-143a
R-125
300
320
340
360
380
400
420
440
T / K