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Vapor Pressure, Speed of Sound, and *PVT*-Properties of R-404a in the Vapor Phase

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Abstract The density (300–363 K, up to 3.5 MPa) and speed of sound (293–373 K, 7.5–480 kPa) in gaseous R-404a have been studied by an isochoric piezometer method and an ultrasonic interferometer, respectively. The pressures of the saturated vapor along the dew line were measured from 298 to 330 K. The experimental uncertainties of the temperature, pressure, density, and speed-of-sound measurements were estimated to be within ±20 mK, ±1.5 kPa, ±0.15%, and ±(0.1–0.2)%, respectively. On the basis of the obtained data, the isobaric molar heat capacity of R-404a was calculated for the ideal-gas state. An eight-coefficient Benedict–Webb–Rubin equation of state has been developed for the gaseous phase of R-404a.

Keywords Density · Ideal-gas heat capacity · Isochoric piezometer · Pressure · R-404a · Speed of sound · Ultrasonic interferometer · Vapor

1 Introduction

Freon R-404a, a ternary HFC mixture of R-125 (44% by mass), R-143a (52% by mass), and R-134a (4% by mass) has been considered as an alternative to R-502, which has appreciable ozone-depletion potential [1]. Effective use of working fluids is possible if their thermophysical properties are reliably known. However, for refrigerant mixtures it is difficult to perform the detailed experimental investigations because measurements should be carried out over a wide range of composition. For this reason and to obtain new compositions with given properties, it is necessary to

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develop new methods and check existing methods of property predictions using the theory of thermodynamic similarity [2].

In the present article, we report measurements for the vapor pressure on the dew line, the density, and the speed of sound in gaseous R-404a (Suva R-404a, DuPont) from 300 to 363 K and at pressures up to 3.5 MPa. On the basis of the obtained data, the isobaric molar heat capacity of R-404a was calculated for the ideal-gas state, and the accuracy in prediction in the volumetric properties with the help of the Lee-Kesler equation was considered.

2 Experimental

A cylindrical stainless-steel isochoric piezometer of $(438.86 \pm 0.15)\,cm^3$ capacity was used for measurements of the vapor density and the saturated vapor pressure. The cell was immersed in a thermostated bath. The temperature in the bath was maintained to within ±10 mK throughout the measurements. The temperature of the piezometer was measured on ITS-90 with a 10-Ω platinum resistance thermometer calibrated at the Siberian Scientific Research Institute of Metrology, Novosibirsk. The pressure was measured by a quartz manometer, calibrated initially by a piston gauge. A membrane null indicator made of stainless steel was used. The instrumental error in the pressure measurement in the range of up to 0.2 MPa did not exceed 0.2 kPa, and at 3.5 MPa, it was about 1.5 kPa. The main contribution to the error of the vapor-density determination gives an uncertainty in the sample mass of $(0.01–0.05) \times 10^{-3}$ kg. It results from adsorption and residual vapor in the piezometer after freezing of R-404a in a vessel for weighing.

The speed of sound was measured by an ultrasonic interferometer fabricated from stainless steel with lithium niobate transducers operated at a frequency of 1 MHz. Instrumental errors of the pressure and temperature measurements were the same as in the vapor-density experiments. A detailed description of the measurement method and the experimental setup has been given in the previous publications [3,4]. To estimate the instrumental error in the measurements of the speed of sound, we made performance test measurements on pure argon. The results obtained during these experiments differ from the most reliable data by no more than 0.06%.

Care was taken to retain the initial composition of R-404a during filling of the measuring cells. The piezometer was filled by a liquid phase of R-404a. The connecting tubes and null indicator were always overheated relative to the piezometer temperature.

3 Results and Discussion

3.1 Vapor Density

PVT-properties of R-404a in the vapor phase were measured on quasi-isochores (at constant mass of the substance in the piezometer) over the temperature range from 300 to 363 K and at pressures from the dew line to 3.5 MPa. The uncertainties of the specific volume did not exceed ±0.15%. The experimental data are given in Table 1.

Table 1 Experimental vapor densities of R-404a

T (K)	P (MPa)	ρ (kg·m^{-3})
300.65	1.26901	65.913
303.15	1.28863	65.904
308.15	1.32718	65.888
312.35	1.77645	99.171
318.15	1.85195	99.142
318.15	1.40334	65.854
323.15	2.26492	133.302
323.15	1.91437	99.117
323.15	1.43994	65.838
328.15	1.47682	65.821
328.15	1.97608	99.091
328.15	2.35681	133.268
333.15	2.44593	133.235
333.15	1.51300	65.804
333.15	2.03645	99.066
333.15	2.77015	174.129
338.15	1.54902	65.787
338.15	2.53587	133.201
338.15	2.89620	174.084
338.15	2.09656	99.041
343.15	3.01981	174.040
343.15	2.62189	133.166
343.23	1.58533	65.770
348.15	2.21491	98.990
348.15	2.70692	133.132
348.15	1.62013	65.754
348.15	3.14012	173.995
353.15	1.65478	65.737
353.15	2.79153	133.098
353.15	3.25932	173.951
353.15	2.27259	98.965
358.15	3.37592	173.906
358.15	1.68951	65.720
358.15	2.87475	133.064
358.15	2.32956	98.939
363.15	2.38618	98.914
363.15	3.49223	173.861
363.15	2.95778	133.030
363.15	1.72405	65.703

Corrections to the measured vapor density are due to a thermal expansion and pressure deformation of the piezometer and do not exceed $\pm 0.2\%$.

The relation between the pressure (P) and temperature (T) in the vapor phase was measured for four isomasses: 28.969, 43.612, 58.654, and 76.657 g. The $P(T)$ curves were obtained for both increasing and decreasing temperatures. The results were reproducible at the limits of the estimated measurement errors. It is necessary to note that equilibrium in the piezometer was stabilized over a long period, especially near the dew line. This time reached 8–10 h. The beginning of vapor-phase condensation was marked by a bend of the temperature–pressure curve (Fig. 1).

Experimental data for the density of superheated vapor were fitted by an eight-parameter equation of state of Benedict–Webb–Rubin:

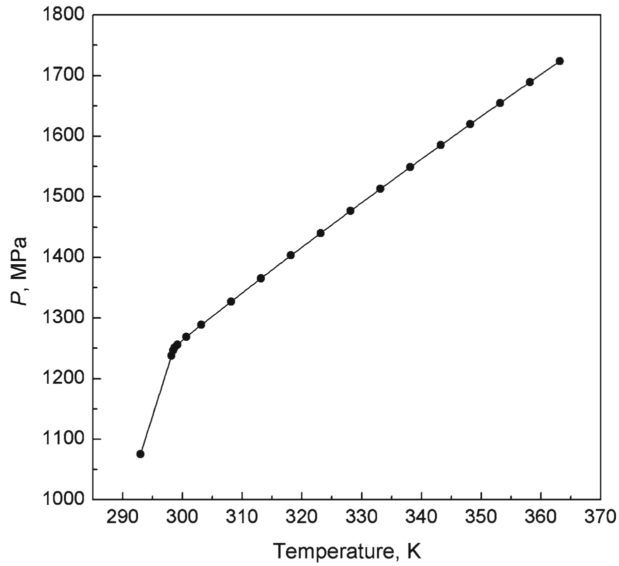

Fig. 1 Temperature dependence of the vapor pressure of R-404a at constant mass

Table 2 Coefficients of Eq. 1

Coefficient	Value
a_1	0.045503
a_2	0.397207
a_3	60381.7
a_4	0.02595
a_5	0.172366
a_6	−0.02011
a_7	−5730.17
a_8	1.14506

$$P = RTd + \left(a_1 RT - a_2 - \frac{a_3}{T^2}\right) d^2 - (a_4 RT - a_5) d^3 + a_5 a_6 d^6 + \frac{a_7 d^3}{T^2}\left(1 + a_8 d^2\right) \exp\left(-a_8 d^2\right) \quad (1)$$

where P is the vapor pressure in MPa, T is the temperature in K, d ($\mathrm{mol \cdot L^{-1}}$) is the vapor density, and $R = 8.314472 \times 10^{-3}\,\mathrm{MPa \cdot L \cdot mol^{-1} \cdot K^{-1}}$ is the universal gas constant. The values of the coefficients a_i are given in Table 2. The standard deviation of the experimental points from Eq. 1 does not exceed 0.4 kPa or 0.03% (Fig. 2). Comparisons between our results and Refs. [5–7] are shown in Fig. 3. As seen from the figure, the discrepancies in density are less than the experimental errors; however, they increase at pressures higher than 2.6 MPa.

Experimental data for the vapor density of R-404a make it possible to estimate the accuracy of *PVT*-properties of this class of refrigerant mixtures using the theory of thermodynamic similarity. The Lee-Kesler method [8] is used for this purpose.

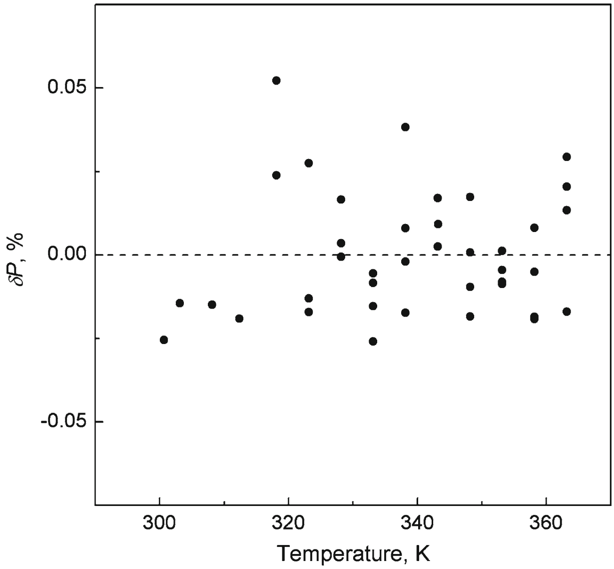

Fig. 2 Deviations of the experimental vapor pressures (P) from Eq. 1, as a function of temperature: $\delta P = 100[P/P(\text{Eq. }1) - 1]$

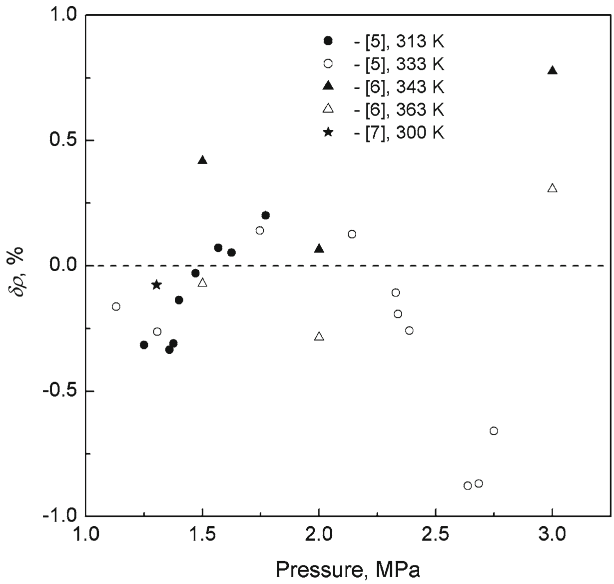

Fig. 3 Deviations of the experimental vapor densities (ρ) from Eq. 1 as a function of pressure: $\delta\rho = 100[\rho(\text{Ref.})/\rho\ (\text{Eq. }1) - 1]$

Initial data [9,10] for these calculations are given in Table 3. Relative deviations of the R-404a vapor density calculated by the Lee-Kesler equation from the experimental data (Table 1) are presented in Fig. 4. It is shown that the calculated and measured

Table 3 Critical parameters [9] and normal boiling temperatures [10] of R-125, R-143a, and R-134a

Freon	T_C (K)	P_C (MPa)	ρ_C (kg·m^{-3})	T_b (K)
R-125	339.23	3.593	567.5	224.65
R-143a	345.90	3.764	431.8	225.55
R-134a	374.211	4.055	512.9	246.65

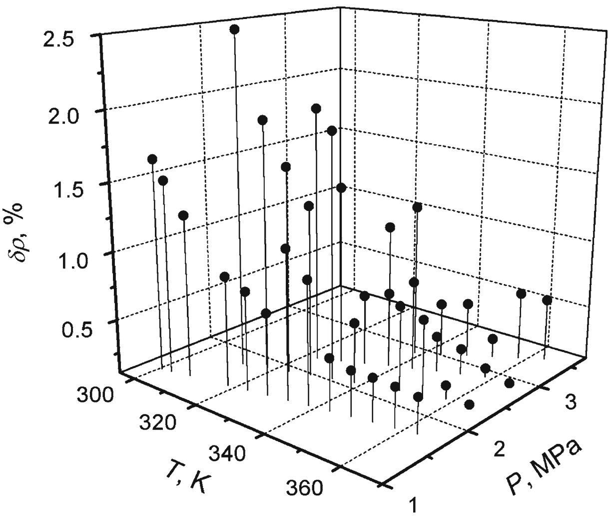

Fig. 4 Comparison of the experimental vapor densities (ρ) and data calculated by the Lee-Kesler model (ρ_{LC}); $\delta\rho = 100[\rho/\rho_{LC} - 1]$

values practically coincide at high temperatures. The root-mean-square deviation of 1% is a good result, if we take into account that only data for pure components were used in the calculations. It can be expected that even for different mixture compositions of this system, the Lee-Kesler equation will provide relatively reliable data on *PVT*-properties.

3.2 Vapor Pressure and Vapor Density along the Dew Line

The experimental data for vapor pressure along the dew line (Table 4) were fitted by the following equation [11]:

$$\ln\left(\frac{P_S}{P_C}\right) = \frac{T_C}{T}\left[b_1\tau + b_2\tau^{1.5} + b_3\tau^3 + b_4\tau^6\right], \tag{2}$$

where $\tau = \left(1 - \frac{T}{T_C}\right)$, $T_C = 345.15$ K, and $P_C = 3.726$ MPa are the critical temperature and the critical pressure, respectively [11], $b_1 = -7.78398$, $b_2 = 2.95713$, $b_3 = -22.096$, and $b_4 = 2324.2$. Equation 2 describes the experimental data with

Table 4 Experimental vapor pressures of R-404a on dew line

T (K)	P (MPa)
298.15	1.23780
298.45	1.24638
312.15	1.76784
312.35	1.77645
322.15	2.24168
330.15	2.68545

a standard deviation of ±0.25 kPa. The deviations of our experimental data, as well of literature values [5,7,12] from Eq. 2 are shown in Fig. 5. Our data are in good agreement with the correlation of Fujiwara et al. [11].

The temperature dependence of the vapor density on the dew line was determined using Eqs. 1 and 2. The obtained data were fitted by the following equation [3]:

$$\frac{\rho}{\rho_C} = 1 - c_1\tau^{0.338} + c_2\tau^{2/3} + c_3\tau + c_4\tau^{4/3}, \quad (3)$$

where $\rho_C = 490\,\text{kg}\cdot\text{m}^{-3}$ is the critical density [11], $c_1 = 1.70525$, $c_2 = -2.38261$, $c_3 = 7.1823$, and $c_4 = -4.94522$. The standard deviation of the experimental points from Eq. 3 does not exceed 0.18%. Comparisons between our results and Refs. [5,7,11] are shown in Fig. 6. As seen from the figure, the discrepancies in density are less than 0.4% except for one point at 333 K [5] and a calculated value [7].

Smoothed values of the vapor pressure and vapor density along the dew line are given in Table 5.

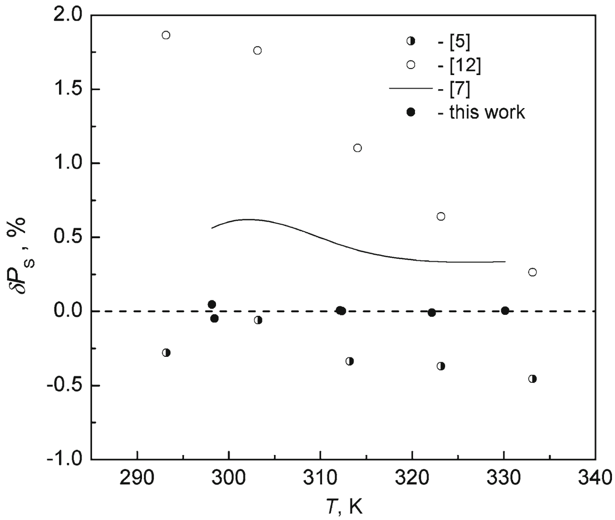

Fig. 5 Deviations of the experimental vapor pressures (P_S) along the dew line from Eq. 2, as a function of temperature: $\delta P = 100[P_S(\text{Ref.})/P_S(\text{Eq. 2}) - 1]$

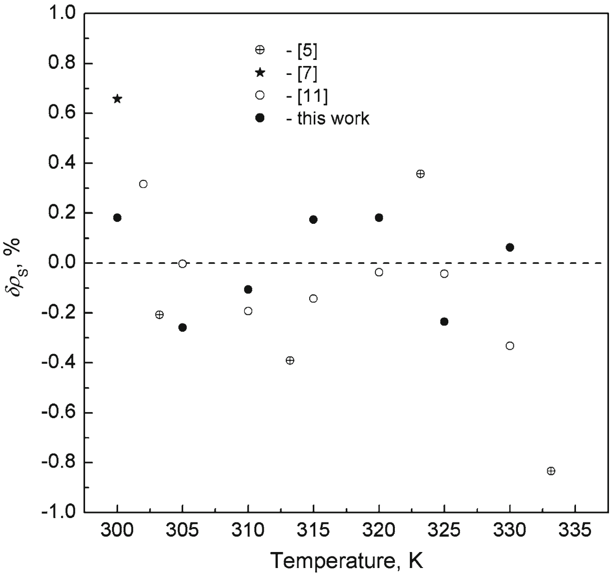

Fig. 6 Deviations of the experimental vapor densities (ρ_S) along the dew line from Eq. 3, as a function of temperature: $\delta\rho_S = 100[\rho_S(\text{Ref.})/\rho_S\ (\text{Eq. }3) - 1]$

Table 5 Properties of R-404a along the dew line

T (K)	P (MPa)	ρ (kg · m^{-3})
300	1.29862	68.46
305	1.47784	79.77
310	1.67638	92.50
315	1.89448	107.11
320	2.13284	124.26
325	2.39278	145.01
330	2.67643	171.20

3.3 Speed of Sound

The speed of sound (U) was measured along isotherms from 293 to 373 K at 20 K increments at pressures from 7.5 to 510 kPa. The results are given in Table 6 and Fig. 7. There was no dispersion within the range of the thermodynamic parameters studied. To determine the speed of sound (U_0) in the ideal-gas state (as $P \to 0$), the P-dependence of the speed of sound was approximated by polynomials of the second order. The errors in the obtained data did not exceed 0.1% at pressures above 50 kPa, and they increase up to 0.25% at lower pressures.

To estimate the molar ideal-gas heat capacity $C_P^0(T)$ of R-404a with the help of a well-known thermodynamic ratio [3], the values of the ideal-gas sound speed $U_0(T)$ were used;

$$C_P^0(T) = \frac{R}{\left(1 - \frac{RT}{MU_0^2}\right)}, \tag{4}$$

Table 6 Experimental speeds of sound in gaseous R-404a

T (K)	P (kPa)	U ($\mathrm{m \cdot s^{-1}}$)	P (kPa)	U ($\mathrm{m \cdot s^{-1}}$)
293.15	7.6	166.7	102.1	164.7
293.15	20.8	166.4	102.5	164.6
293.15	35.1	166.1	192.8	162.4
293.15	66.6	165.3	250.5	161.1
293.15	101.5	164.5	285.1	160.2
293.15	102.0	164.5	368.1	158.2
313.15	12.6	171.6	293.1	166.3
313.15	28.0	171.4	397.1	164.2
313.15	62.5	170.9	398.3	164.3
313.15	104.1	170.2	398.9	164.3
313.15	110.2	169.8	478.4	162.7
333.15	15.6	176.8	115.3	175.2
333.15	48.5	176.2	215.1	173.5
333.15	71.6	175.8	342.8	171.3
333.15	106.5	175.4	425.4	170.0
333.15	111.0	175.0	–	–
353.15	24.5	181.6	147.5	179.9
353.15	45.4	181.2	207.8	179.1
353.15	45.8	181.1	308.7	177.6
353.15	51.9	181.3	394.5	176.6
353.15	76.8	180.9	479.4	175.4
353.15	99.8	180.6	–	–
373.15	9.3	186.4	105.8	185.3
373.15	17.5	186.5	105.8	185.4
373.15	20.9	186.5	208.3	184.1
373.15	46.3	186.1	263.6	183.5
373.15	50.1	186.0	384.0	182.1
373.15	99.6	185.2	483.2	180.9

where R is the universal gas constant and $M = 97.604\,\mathrm{kg \cdot kmol^{-1}}$ is the molar mass of R-404a. The results are given in Table 7. The obtained data are correlated by the equation,

$$C_P^0/R = 0.106 + 0.0417\ T - 3.045 \times 10^{-5} T^2 \tag{5}$$

The standard deviation of the experimental points from Eq. 5 does not exceed 0.35%. Comparisons between our results and Ref. [11] are shown in Fig. 8. Taking into account that the calculation of the heat capacity of polyatomic gases using speed-of-sound data with uncertainties of 0.1–0.25% leads to errors in the molar heat capacity of 4–8%, our data and those from [11] are in reasonable agreement.

4 Conclusion

New experimental data for the density (39 points) and speed of sound (54 points) in the vapor phase as well as the vapor pressure on the dew line (6 points) have been obtained for R-404a. The density of the saturated vapor on the dew line and the molar

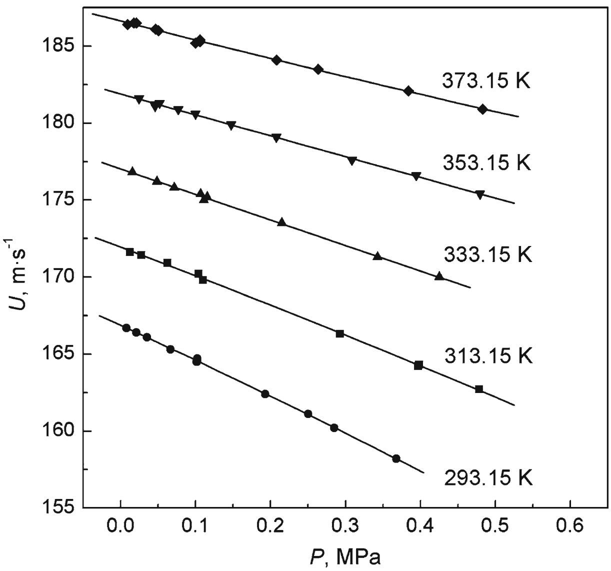

Fig. 7 Experimental sound-speed isotherms for R-404a vapor

Table 7 Ideal-gas heat capacity of R-404a

T (K)	C_P^0/R
293.15	9.69
313.15	10.23
333.15	10.59
353.15	11.02
373.15	11.44

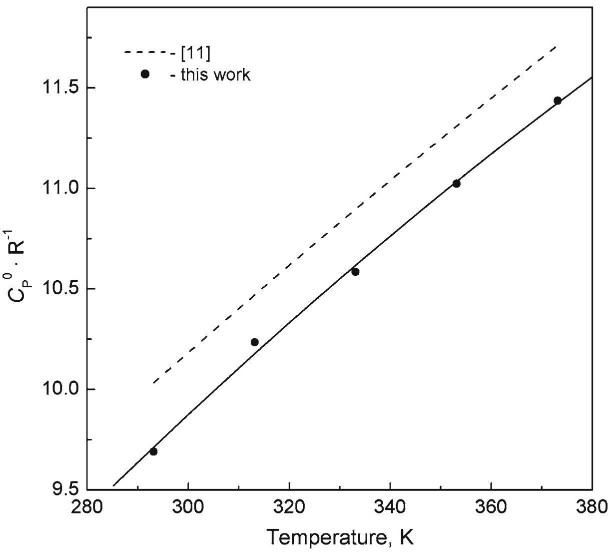

Fig. 8 Ideal-gas heat capacity of R-404a

ideal-gas heat capacity have been determined. It is shown that the equation of state of Lee-Kesler can be used to estimate the vapor density of R-404a with satisfactory accuracy.

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