ELDATA: Int. Electron. J. Phys.-Chem. Data 1998, 4, 39-48

Gas phase isochores and vapor pressures of pure refrigerants: difluoromethane (R 32), pentafluoroethane (R 125), 1,1,1,2-tetrafluoroethane (R 134a), and 1,1,1,2,3,3,3-heptafluoropropane (R 227ea)

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Experimental pressure-temperature (P-T) data at several constant densities were obtained for gaseous non-chlorinated refrigerant fluids, difluoromethane (R 32), pentafluoroethane (R 125), 1,1,1,2-tetrafluoroethane (R 134a), and 1,1,1,2,3,3,3-heptafluoropropane (R 227ea), by using of a new constant-volume cell constructed to work at high pressures at temperatures from 273.15 K to 353.15 K. The vapor pressures were estimated graphically at the break point of the measured P-T curves. The vapor pressure values were correlated using Antoine and Wagner equations. These data, and the derived acentric factors and enthalpies of vaporization, agree within 2 to 5 % with literature values.

# 1. INTRODUCTION

The knowledge of precise vapor pressure data and the corresponding saturation curve of refrigerant fluids is important for the design of process equipment, especially heat exchangers and compressors. At present time, the non-chlorinated refrigerants difluoromethane (R 125),1,1,1,2-tetra (R 32),pentafluoroethane fluoroethane (R 134a), and 1,1,1,2,3,3,3-hepta fluoropropane (R 227ea) and mixtures thereof, are predestinated to substitute the partially or totally chlorinated refrigerants (HCFC or CFC) having a high Ozone Depletion Potential (ODP) and Global Warming Potential (GWP), like trichlorofluoromethane (R 11), dichlorodifluoromethane (R 12), 1,2-dichlorotetrafluoro ethane (R 114), or the chlorodifluoromethane (R 22) + chloropentafluoroethane (R 115) azeotrope (R 502).

Experimental pressure-temperature (P-T) data and correlations are available in the literature for several of the fluids considered in this work. Data were reported by [BOUC1970; MCLM1900; SATT1941] for R 32, by [BOYS0950; DUAH0970; TSV00950] for R 125, and by [BLAW0950; TILR0940] for R 134a.

For R 227ea we have found saturated liquid density values [DEFD0970] and unpublished vapor pressure measurements [WEBL0980].

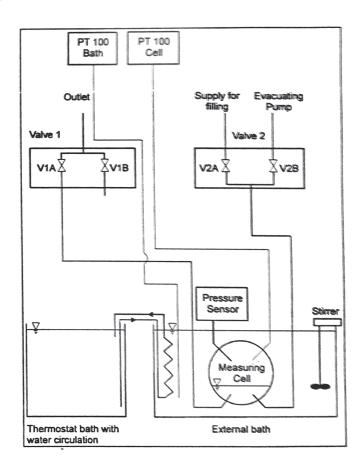


Figure 1. Schematic representation of the experimental equipment

The data from all references mentioned above were used for comparison with our experimental results obtained using a new high-pressure cell.

TABLE 1 Antoine coefficients, A, B, and C, Eq.(1), and Wagner coefficients,  $a_1$ ,  $a_2$ ,  $a_3$ , and  $a_4$ , Eq.(2), valid in the temperature range  $\Delta T$ 

Refrigerant	A	В	<i>C</i>	$a_1$	<i>a</i> <sub>2</sub>	<i>a</i> <sub>3</sub>	<i>a</i> <sub>4</sub>	$\Delta T/K$
R 32	15.0984	2105.3	-24.60	- 7.929	3.494	-7.999	0.529	250-385
R 125	12.8429	1186.9	-86.76	-8.642	5.328	-9.521	0.477	250-360
R 134a	14.8115	2239.9	-30.18	-6.916	-1.431	3.516	1.322	250-390
R 227ea	14.5994	2338.4	-23.87	-7.840	0.471	2.392	1.192	255-380

#### 2. EXPERIMENTAL SECTION

## 2.1. Apparatus and Procedure

A constant volume (ca.  $0.98 \text{ dm}^3$ ) cell for P-T and vapor-liquid equilibrium (VLE) measurements was constructed to work at pressures up to  $20 \cdot 10^6 \text{Pa}$  and temperatures up to 623.15 K. The cell, as well as all the parts of the suspension, were made of austenitic stainless-steel (Materials No. 1.4571 and 1.4301, respectively). The cell was immersed in a  $300 \times 400 \times 300$  mm external thermostat bath with water circulation. A schematic diagram of the apparatus is shown in Figure 1.

The estimated uncertainty in the volume determination is 0.01~%. The temperature T in the measuring the cell and the temperature of the external bath were measured by means of Pt100 resistance thermometers (MWT 603/B, SAB, Goettingen, Germany), previously calibrated with a high precision thermometer unit (ASL, model F25, Bradville, UK) against ITS-90.

The pressure P inside the cell was measured with a digital pressure sensor, calibrated by the manufacturer (Type 892.23.520, WIKA Instruments, Klingenberg, Germany). However, that transducer was also calibrated against a high accuracy pressure controller/calibrator, Desgranges & Huot (Aubervillier, France), model PPC2, and the pertinent corrections were taken into consideration. After calibration, the estimated uncertainties in T and P were less than, respectively, 0.3 K and 0.02  $10^6$ Pa (both in the working range).

In this work the P-T measurements were carried out by loading a known quantity of sample into the cell to obtain different isochoric lines. The mass of refrigerant was measured with an electronic balance COBOS, type C600SX (Barcelona, Spain) with an accuracy of 0.2  $10^{-4}$ kg, corresponding to 0.3 kg m<sup>-3</sup> overall accuracy in the densities  $\rho$ . The vapor pressure values were obtained by varying the cell temperature, in the range from ca. 353 K to 273 K, along 4 to 6 isochores, and measuring

the pressure of the gaseous refrigerants from ca. max. 6  $10^6$ Pa, until the dew points were reached (Figure 2). After the isochore determination the fluid was evacuated into a small tared vessel and reweighed.

#### 2.2. Materials

CH<sub>2</sub>F<sub>2</sub>, Difluoromethane (R 32). DuPont (Wilmington, USA) material of stated purity 99.95 wt. % was used as received. Characteristic properties: Flammability, Yes; ODP (R 11, 1),0; GWP (CO<sub>2</sub>, 100), 580; Substitutes, R 502.

C<sub>2</sub>HF<sub>5</sub>, Pentafluoroethane (R 125). DuPont (Wilmington, USA) material of stated purity 99.9 wt. % was used as received. Characteristic properties: Flammability, No; ODP (R 11, 1), 0; GWP (CO<sub>2</sub>, 100), 3200; Substitutes, R 502.

C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>, 1,1,1,2-Tetrafluoroethane (R 134a). ICI (Barcelona, Spain) material of stated purity 99.99 wt. % was used as received. Characteristic properties: Flammability, No; ODP (R 11, 1), 0; GWP (CO<sub>2</sub>, 100), 1300; Substitutes, R 12.

C<sub>3</sub>HF<sub>7</sub>, 1,1,1,2,3,3,3-Heptafluoropropane (R 227ea). Solvay (Hannover, Germany) material of stated purity 99.99 wt. % was used as received. Characteristic properties: Flammability, No; ODP (R 11, 1), 0; GWP (CO<sub>2</sub>, 100), 3300; Substitutes, R 114.

#### 3. RESULTS

The direct experimental P-T values at 4 to 6 constant densities  $\rho$  are all tabulated and graphed in the Appendix and saved on disk as Standard ELDATA Files **RAUJ0980.001** through **RAUJ0980.004**.

The vapor pressures, estimated graphically at the break point of the measured *P-T* curves, are all tabulated and graphed in the Appendix and saved on disk as Standard ELDATA Files RAUJ0980.005 through RAUJ0980.008.

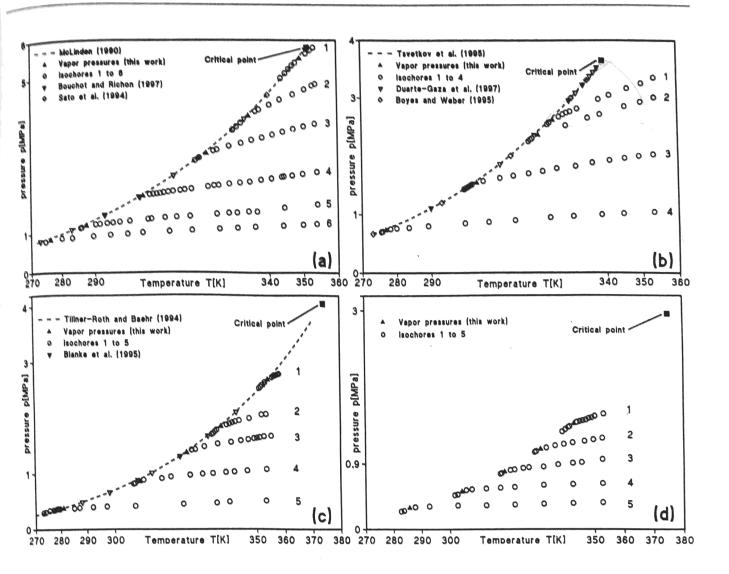


Figure 2. Pressure P — temperature T diagrams at various constant densities  $\rho/kg$  m 3 (given in parentheses) for gaseous refrigerants and derived vapor pressure curves. (a) R 32: 1 — (282.5), 2 — (184.5), 3 — (141.8), 4 — (107.6), 5 — (88.5), 6 — (82.6); (b) R 125: 1 — (222.2), 2 — (197.6), 3 — (123.3), 4 — (62.1); (c) R 134a: 1 — (161.8), 2 — (111.3), 3 — (87.70), 4 — (61.7), 5 — (42.0); (d) R 227ea: 1 — (167.8), 2 — (135.3), 3 — (111.5), 4 — (89.3), 5 — (80.0).

The vapor pressure data were fitted to two classical equations, the Antoine equation, Eq. (1):

$$\ln(P/10^{3}\text{Pa}) = A - B/[(T/\text{K}) + C]$$
 (1)

and the Wagner equation [BLAW0950], Eq. (2):

$$\ln P_r = (a_1 \tau + a_2 \tau^{1.5} + a_3 \tau^{2.5} + a_4 \tau^5) / T_r \tag{2}$$

where  $\tau = 1 - T_r$ ,  $P_r = P/P_c$  is the reduced pressure,  $T_r = T/T_c$  is the reduced temperature,  $P_c$  is the critical pressure, and  $T_c$  is the critical temperature.

The objective function Q was the sum of the squared relative deviations in pressure:

$$Q = \Sigma [(P_{\text{calc}} - P_{\text{exp}})/P_{\text{exp}}]^2$$
 (3)

The coefficients are listed in Table 1.

#### 4. DISCUSSION AND CONCLUSIONS

The vapor pressures calculated with the Antoine correlations obtained in this work agree fairly well with the experimental data from the literature. So for R 32 the mean deviations vary from 0.5 %, compared to [SATT1941], to 4 %, compared to [BOUC1970], for R 125 the deviations are less than 2 % in all cases, for R 134a the mean deviation, estimated in the working temperature range indicated in Table 1, is less than 3 %, and lastly for R 227ea the mean deviation from the values measured by [WEBL0980] is close to 3 %.

The correlated vapor pressure values were used to calculate two characteristic quantities for the present refrigerants [REIR0870]. The acentric factors  $\omega$  were obtained from a linear regression of  $\ln P_r$  vs.  $1/T_r$ . The values shown in Table 2 are similar to those calculated using the Lee-Kesler vapor-pressure relations.

The same relations were used to estimate the molar enthalpies of vaporization,  $\Delta H_{\rm vap}$ , as:

$$\Delta H_{\rm vap} = \Theta R T_c \Delta Z_{\rm vap} \tag{4}$$

where  $\Delta Z_{\rm vap}$  is the difference in compressibility factors of saturated vapor and saturated liquid, taken from generalized compressibility tables [HOU00590].  $\Theta$  was calculated from the slope of the straight line given by:

$$\Theta = -d \left( \ln P_r \right) / d(1/T_r) \tag{5}$$

The  $\Delta H_{\rm vap}$  values (Table 2) of R 32, R 125 and R 134a agree well with those obtained from saturation property tables. The largest discrepancy was found for R 32 whose value (Table 2) is 5 % higher than found in saturation tables [MCLM1900; TILR0940]. To our knowledge, no literature  $\Delta H_{\rm vap}$  value is available for R 227ea.

TABLE 2

Acentric factors  $\omega$  and molar enthalpies of vaporization  $\Delta H_{\rm vap}$  at 298.15 K

Refrigerant	ω	$\Delta H_{\mathrm{vap}}/10^{3}\mathrm{J}\;\mathrm{mol}^{-1}$
R 32	0.313	14.9
R 125	0.312	13.4
R 134a	0.337	18.4
R 227ea	0.359	18.8

The present results prove the suitability of the new apparatus for precise measurements of the vapor pressures of pure liquids and liquid mixtures at high pressures.

#### Acknowledgment

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Copyright © 1998 ELDATA SARL France. All rights reserved Property Code: [VPTG1020] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES RAUJ0980.001 Single-component gaseous system [P1]  $\rho$ /kg m<sup>-3</sup>, Mass density [X1] T/K, Temperature State: Parameters: Variables: [Y1] P/Pa, Pressure Direct measurement of P at variable T and constant  $\rho$ Method: 1. CH<sub>2</sub>F<sub>2</sub>, Difluoromethane Components:

Components.	1. CH2F2, Dillu	oi oinemane		
[P1] = .82	6000E+02	[P1] = .88	5000E+02	
[X1]	[Y1]	[X1]	[Y1]	
[X1]  .280100E+03 .283300E+03 .289700E+03 .299700E+03 .304100E+03 .311800E+03 .326000E+03 .331100E+03 .344200E+03 .349900E+03 .353800E+03	[Y1] .890000E+06 .90000E+06 .940000E+06 .990000E+07 .105000E+07 .115000E+07 .115000E+07 .112000E+07 .121000E+07 .123000E+07 .125000E+07	[X1]  .287800E+03 .288600E+03 .290400E+03 .291700E+03 .291700E+03 .295500E+03 .305700E+03 .310600E+03 .317700E+03 .325300E+03 .325300E+03 .331700E+03 .331700E+03 .331700E+03 .33100E+03 .33100E+03 .334300E+03 .334300E+03	[Y1] .122000E+07 .123000E+07 .124000E+07 .125000E+07 .125000E+07 .128000E+07 .13000E+07 .13000E+07 .136000E+07 .14000E+07 .14000E+07 .15000E+07 .153000E+07 .153000E+07 .157000E+07 .157000E+07 .157000E+07 .157000E+07 .157000E+07	[Y1] .258E+07  • [P1] = .826000E+02 • [P1] = .885000E+02  .169E+07  .125E+07  .800E+06  .280E+03 .300E+03 .320E+03 .340E+03 .360E+03
				[X1]

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Components:

RAUJ0980.001 Property Code: [VPTG1020] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES

Single-component gaseous system [P1]  $\rho$ /kg m<sup>-3</sup>, Mass density [X1] T/K, Temperature [Y1] P/Pa, Pressure State: Parameters: Variables:

1. CH<sub>2</sub>F<sub>2</sub>, Difluoromethane

Direct measurement of P at variable T and constant  $\rho$ Method:

	2 2								
[P1] = .10	7600E+03	[P1] = .141800E+03 [P1] = .184500E+03		[P1] = .141800E+03 [P1] = .184500E+03		[P1] = .141800E+03		[P1] = .28	2500E+03
[X1]	[Y1]	[X1]	[Y1]	[X1]	[Y1]	[X1]	[Y1]		
.305300E+03	.198000E+07	.323500E+03	.308000E+07	.335500E+03	.409000E+07	.350200E+03	.557000E		

.305300E+03 .306300E+03 .307300E+03 .308300E+03 .310300E+03 .311600E+03 .315000E+03 .315000E+03 .316300E+03 .322900E+03 .322900E+03 .325900E+03 .325900E+03 .331900E+03 .334700E+03 .334700E+03 .345900E+03 .345900E+03 .345900E+03 .345900E+03	.198000E+07 .199000E+07 .200000E+07 .201000E+07 .201000E+07 .204000E+07 .206000E+07 .208000E+07 .212000E+07 .212000E+07 .214000E+07 .223000E+07 .224000E+07 .231000E+07 .234000E+07 .239000E+07 .242000E+07 .242000E+07 .242000E+07 .245000E+07 .245000E+07 .245000E+07 .245000E+07 .245000E+07 .255000E+07	.323500E+03 .324500E+03 .325500E+03 .328900E+03 .335300E+03 .341300E+03 .341300E+03 .347300E+03 .353500E+03	.308000E+07 .312000E+07 .315000E+07 .325000E+07 .333000E+07 .341000E+07 .354000E+07 .361000E+07 .368000E+07 .375000E+07 .382000E+07	.335500E+03 .336500E+03 .337500E+03 .340500E+03 .347300E+03 .350600E+03 .352800E+03	.409000E+07 .415000E+07 .419000E+07 .431000E+07 .458000E+07 .471000E+07 .481000E+07 .485000E+07	.350200E+03 .351200E+03 .352400E+03 .353400E+03	.557000E+07 .565000E+07 .574000E+07 .581000E+07
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Property Code: [VPTG1020] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES RAUJ0980.002 Single-component gaseous system [P1]  $\rho$ /kg m<sup>-3</sup>, Mass density [X1] T/K, Temperature State: Parameters:

Variables: Temperature [Y1] P/Pa, Pressure

Method: Direct measurement of P at variable T and constant  $\rho$ 

#### Components: 1. C<sub>2</sub>HF<sub>5</sub>, Pentafluoroethane

[P1] = .62	1000E+02	[P1] = .12	3300E+03	
[X1]	[Y1]	[X1]	[Y1]	
.277300E+03 .278200E+03 .280000E+03 .283600E+03 .289200E+03 .295200E+03 .306600E+03 .314200E+03 .324200E+03 .338600E+03 .338600E+03 .344700E+03 .353200E+03	.740000E+06 .750000E+06 .750000E+06 .760000E+06 .800000E+06 .820000E+06 .850000E+06 .870000E+06 .970000E+06 .970000E+06 .100000E+07 .102000E+07	[X1] .304500E+03 .305100E+03 .309900E+03 .313800E+03 .318200E+03 .326200E+03 .331500E+03 .341000E+03 .345200E+03 .349200E+03 .353200E+03	156000E+07 .157000E+07 .157000E+07 .162000E+07 .170000E+07 .174000E+07 .179000E+07 .183000E+07 .189000E+07 .193000E+07 .201000E+07	.175E+07 .140E+07
				• [P1] = .123300E+03
				.700E+06
				[Ai]

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RAUJ0980.002 Property Code: [VPTG1020] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES

Single-component gaseous system [P1]  $\rho/kg \text{ m}^{-3}$ , Mass density State: Parameters: Variables: [X1] *T*/K, Temperature [Y1] P/Pa, Pressure

Direct measurement of P at variable T and constant  $\rho$ Method:

Components: 1. C<sub>2</sub>HF<sub>5</sub>, Pentafluoroethane

Components.	1. 02111 5 , 1 011			
[P1] = .	191600E+03	[P1] = .22	2200E+03	
[X1]	[Y1]	[X1]	[Y1]	
.321500E+03 .328900E+03 .335100E+03 .338500E+03 .345400E+03 .353700E+03	.237000E+07 .253000E+07 .266000E+07 .272000E+07 .286000E+07 .294000E+07 .302000E+07	.326200E+03 .327000E+03 .328200E+03 .339200E+03 .332200E+03 .338200E+03 .341200E+03 .350200E+03 .350200E+03	.265000E+07 .268000E+07 .272000E+07 .275000E+07 .277000E+07 .282000E+07 .305000E+07 .317000E+07 .326000E+07 .336000E+07	[Y1] .340E+07  O [P1] = .191600E+03 O [P1] = .222200E+03  .285E+07  .258E+07  .320E+03 .330E+03 .340E+03 .350E+03 .360E+03 [X1]

Property Code: [VPTG1020] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES RAUJ0980.003

Single-component gaseous system parameters: [P1]  $\rho$ /kg m<sup>-3</sup>, Mass density Variables: [X1] T/K, Temperature [Y1] P/Pa, Pressure

Method: Direct measurement of P at variable T and constant  $\rho$ 

# Components: 1. C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>, 1,1,1,2-Tetrafluoroethane

[P1] = .420	0000E+02	[P1] = .61	7000E+02	
[X1]	[Y1]	[X1]	[Y1]	
283200E+03 285200E+03 287200E+03 292200E+03 297200E+03 307200E+03 324100E+03 335900E+03 340400E+03 353200E+03	.380000E+06 .380000E+06 .400000E+06 .400000E+06 .410000E+06 .420000E+06 .460000E+06 .500000E+06	.310200E+03 .316600E+03 .319800E+03 .326600E+03 .331000E+03 .334700E+03 .342200E+03 .346700E+03 .353500E+03	.890000E+06 .920000E+06 .950000E+06 .980000E+07 .101000E+07 .103000E+07 .104000E+07 .106000E+07	[Y1] .130E+07
				.800E+06 _
				○ [P1] = .420000E+02 • [P1] = .617000E+02
				.300E+06

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Property Code: [VPTG1020] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES

RAUJ0980.003

State: Single-component gaseous system Parameters: [P1]  $\rho$ /kg m<sup>-3</sup>, Mass density Variables: [X1] T/K, Temperature [Y1] P/Pa, Pressure

Method: Direct measurement of P at variable T and constant  $\rho$ 

# Components: 1. C<sub>2</sub>H<sub>2</sub>F<sub>4</sub>, 1,1,1,2-Tetrafluoroethane

[P1] = .877000E+02	components.		1,2 1 001 001 001					
STI	[P1] = .87	7000E+02	[P1] = .11	1300E+03	0E+03 [P1] = .161800E+03			
327300E+03       .143000E+07       .339700E+03       .188000E+07       .355200E+03       .273000E+07         .328600E+03       .144000E+07       .340700E+03       .190000E+07       .355700E+03       .274000E+07         .331800E+03       .149000E+07       .341700E+03       .192000E+07       .356200E+03       .276000E+07         .336500E+03       .154000E+07       .342700E+03       .194000E+07       .356700E+03       .277000E+07         .341200E+03       .157000E+07       .344100E+03       .196000E+07       .357700E+03       .278000E+07         .347200E+03       .162000E+07       .351900E+03       .207000E+07       .358200E+03       .280000E+07         .351200E+03       .166000E+07       .353500E+03       .208000E+07       .358200E+03       .280000E+07         .351200E+03       .168000E+07       .168000E+07       .36800E+07       .208000E+07       .208000E+07	[X1]	[Y1]	' [X1]	[Y1]	[X1]	[Y1]		
	.326100E+03 .327300E+03 .328600E+03 .331800E+03 .3316500E+03 .341200E+03 .344600E+03 .347200E+03 .350200E+03 .351200E+03 .352700E+03	.141000E+07 .143000E+07 .144000E+07 .144000E+07 .154000E+07 .157000E+07 .160000E+07 .162000E+07 .165000E+07 .166000E+07 .168000E+07	.338700E+03 .339700E+03 .340700E+03 .341700E+03 .342700E+03 .344100E+03 .347600E+03	.186000E+07 .188000E+07 .190000E+07 .192000E+07 .194000E+07 .196000E+07 .200000E+07	.354700E+03 .355200E+03 .355700E+03 .356200E+03 .356700E+03 .357200E+03	.272000E+07 .273000E+07 .274000E+07 .276000E+07 .277000E+07 .278000E+07 .279000E+07		

Copyright@1998 ELDATA SARL France. All rights reserved Property Code: [VPTG1020] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES RAUJ0980.004 Single-component gaseous system [P1]  $\rho$ /kg m<sup>-3</sup>, Mass density [X1] T/K, Temperature State: Parameters: Variables: [Y1] P/Pa, Pressure Method: Direct measurement of P at variable T and constant  $\rho$ Components: 1. C<sub>3</sub>HF<sub>7</sub>, 1,1,1,2,3,3,3-Heptafluoropropane [P1] = .800000E + 02[P1] = .893000E+02[X1] [Y1] [X1] [Y1] [Y1] .287700E+03 .310000E+06 .305700E+03 .540000E+06 .320000E+06 .292700E+03 .307700E+03 .550000E+06 .700E+06 .302700E+03 .330000E+06 .312700E+03 .560000E+06 .312700E+03 .330000E+06 .317700E+03 .570000E+06 .322700E+03 .340000E+06 .322700E+03 .580000E+06 .332700E+03 .332700E+03 .350000E+06 .610000E+06 .342700E+03 .360000E+06 .342700E+03 .620000E+06 .575E+06 .352700E+03 .370000E+06 .352700E+03 .630000E+06 .450E+06

> $\circ$  [P1] = .800000E+02

o.o....o....o....o....o

.280E+03 .300E+03 .320E+03 .340E+03 .360E+03

[X1]

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<b>Property Code:</b>	[VPTG1010] VOLUMETRIC PROPERTIES OF PURE GASES AND MIXTURES	RAUJ0980.004
State:	Single-component gaseous system	

.325E+06

.200E+06

Parameters: [P1] T/K, Temperature Variables: [X1] P/Pa, Pressure [Y1]  $\rho$ /kg m<sup>-3</sup>, Mass density

Method: Direct measurement of  $\rho$  at variable P and constant T

