

# PVT<sub>x</sub> Property Measurements for Difluoromethane + Pentafluoroethane (R32 + R125) in the Gaseous Phase

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*PVT<sub>x</sub>* property measurements in the gaseous phase for difluoromethane (1) + pentafluoroethane (2) (R32 + R125) at  $x_1 = 0.25$  ( $w_1 = 12.62\%$ ),  $x_1 = 0.5$  ( $w_1 = 30.24\%$ ), and  $x_1 = 0.75$  ( $w_1 = 56.53\%$ ) are reported. The measurements were performed by means of a magnetic suspension densimeter. 298 *PVT<sub>x</sub>* values for R32 + R125 mixtures were obtained over the range of temperatures (283 to 313) K and at pressures up to 2.4 MPa including the region near saturation. The experimental uncertainties are estimated to be 10 mK for temperature, 0.76 kPa for pressure, ( $0.03\% + 0.005 \text{ kg}\cdot\text{m}^{-3}$ ) for density, and 0.18 % for mole fraction. The purities of R32 and R125 were both 99.99 %. The measurements are compared with the available data including existing equations of state.

## Introduction

For the development of energy conversion systems, accurate thermodynamic properties of the working fluids are required. These properties are calculated from thermodynamic equations of state. To develop the equations of state which accurately represent the whole thermodynamic surfaces, reliable measurements of the thermodynamic properties must be available.

For hydrofluorocarbons, many measurements of the thermodynamic properties have been reported, especially for mixtures of hydrofluorocarbons that have already been used as working fluids. However, the *PVT<sub>x</sub>* properties have not been reported in the region near saturation in the gaseous phase where it is important to calculate reliable saturation properties and virial coefficients.<sup>1</sup>

*PVT<sub>x</sub>* properties of R32 + R125 in the gaseous phase including the region near saturation were measured with a magnetic suspension densimeter. The magnetic suspension densimeter can measure in the region near saturation with high accuracy.

## Experimental Apparatus

An experimental apparatus which has two densimeters with a magnetic suspension balance was used for density measurements. The apparatus and procedure used here were reported in detail in our previous publication.<sup>2</sup>

Pressure is measured by a quartz digital pressure gauge. The quartz digital pressure gauge was calibrated by using a dead-weight pressure gauge (model 5201, DH Instruments). The temperature is measured by a standard platinum resistance thermometer. The temperature values were processed in accordance with the ITS-90. The thermometer was installed in the middle, between the two cells of the A and B densimeters in the thermostatic bath. A density measurement system is a set of two magnetic suspension densimeters.

The expanded uncertainty of temperature measurements with a coverage factor of 2, having a level of confidence of 95 %, is estimated to be not greater than 10 mK. The expanded uncertainty of the pressure measurements is estimated to be not greater than 0.76 kPa. The expanded uncertainty of the density measurement is estimated to be not greater than ( $0.03\% + 0.005 \text{ kg}\cdot\text{m}^{-3}$ ) in density with the uncertainty of composition being 0.18 % for mole fraction. The sample purities of R32 and R125 were better than 99.99 % according to the calibration by the manufacturer.

## Experimental Results

*PVT<sub>x</sub>* properties for R32 + R125 at  $x_1 = 0.25$  (118 points),  $x_1 = 0.5$  (60 points), and  $x_1 = 0.75$  (120 points) were measured on four different isotherms in the temperature range of (283 to 313) K at pressures up to 2.4 MPa. The composition of the mixture was precisely prepared by using a chemical balance. The measured data for R32 + R125 are listed in Table 1. As an example, the experimental data distribution at  $x_1 = 0.5$  is shown on a pressure–temperature plane in Figure 1, together with those by Kleemiss.<sup>8</sup> As shown in Figure 1, our measurements contain many data points in the region near saturation.

## Discussion

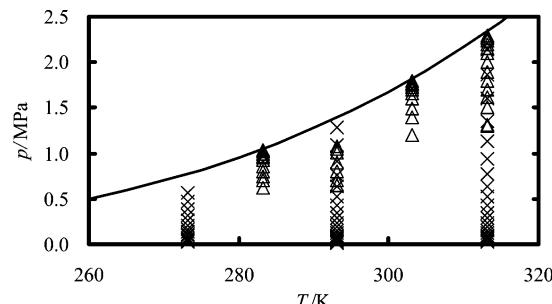
An equation of state has been developed by Tillner-Roth and Yokozeki<sup>3</sup> for R32 and by Lemmon and Jacobsen<sup>4</sup> for R125. The generalized model for the properties of the mixture developed by Lemmon and Jacobsen<sup>5</sup> is applied as the reference equation of Figure 2. We have compared our density measurements with the R32 + R125 equation developed by Adachi et al.<sup>6</sup> in Figure 3, who developed it based on the equations of state for R32 and R125 developed by Astina.<sup>7</sup>

Figure 2 shows the deviations of the existing *PVT<sub>x</sub>* properties,<sup>8–12</sup> along with the present work from the mixture equation of state developed by Lemmon and Jacobsen.<sup>5</sup> In the same manner, Figure 3 shows the deviations of existing *PVT<sub>x</sub>* properties<sup>8–12</sup> with the present work from the mixture equation of state developed by Adachi.<sup>6</sup>

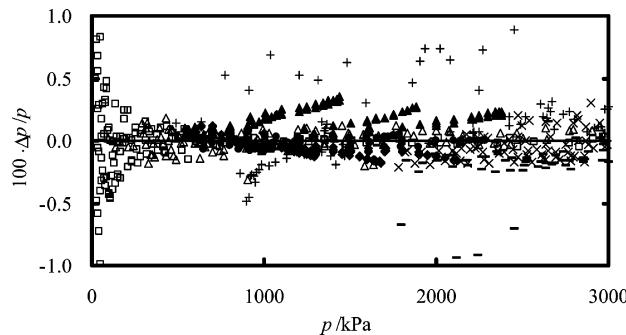
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**Table 1.** Experimental PVTx Properties of R32 + R125 at  $x_1 = 0.25, 0.5$ , and  $0.75$ 

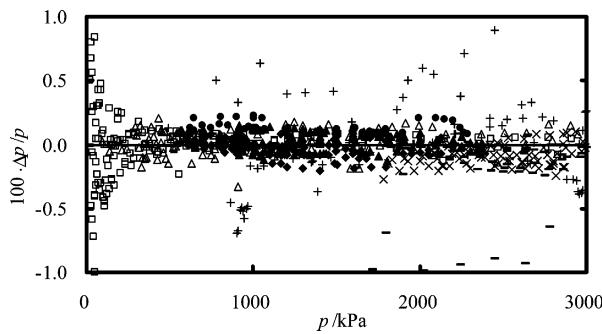
$x_1$	T/K	$p/\text{MPa}$	$\rho/\text{kg}\cdot\text{m}^{-3}$												
0.25	283.15	0.6063	29.862	0.25	293.15	1.0032	51.231	0.25	303.15	1.2008	60.203	0.25	313.15	1.3020	62.509
0.25	283.15	0.6063	29.870	0.25	293.15	1.0033	51.241	0.25	303.15	1.2008	60.228	0.25	313.15	1.3020	62.498
0.25	283.15	0.7029	35.450	0.25	293.15	1.0046	51.360	0.25	303.15	1.2017	60.266	0.25	313.15	1.4035	68.758
0.25	283.15	0.7029	35.438	0.25	293.15	1.0046	51.385	0.25	303.15	1.2017	60.278	0.25	313.15	1.4035	68.778
0.25	283.15	0.7502	38.291	0.25	293.15	1.0534	54.572	0.25	303.15	1.3017	66.863	0.25	313.15	1.4871	74.174
0.25	283.15	0.7502	38.307	0.25	293.15	1.0535	54.558	0.25	303.15	1.3017	66.878	0.25	313.15	1.4871	74.155
0.25	283.15	0.8045	41.673	0.25	293.15	1.1031	57.913	0.25	303.15	1.3040	67.023	0.25	313.15	1.5023	75.185
0.25	283.15	0.8045	41.662	0.25	293.15	1.1031	57.897	0.25	303.15	1.3043	67.056	0.25	313.15	1.5023	75.166
0.25	283.15	0.8387	43.867	0.25	293.15	1.1416	60.559	0.25	303.15	1.4040	74.046	0.25	313.15	1.5027	75.213
0.25	283.15	0.8387	43.855	0.25	293.15	1.1416	60.587	0.25	303.15	1.4040	74.064	0.25	313.15	1.5028	75.229
0.25	283.15	0.8709	45.974	0.25	293.15	1.1723	62.770	0.25	303.15	1.4516	77.585	0.25	313.15	1.6026	82.026
0.25	283.15	0.8709	45.961	0.25	293.15	1.1723	62.748	0.25	303.15	1.4516	77.567	0.25	313.15	1.6026	82.056
0.25	283.15	0.9012	47.992	0.25	293.15	1.2018	64.917	0.25	303.15	1.5000	81.288	0.25	313.15	1.6040	82.138
0.25	283.15	0.9012	48.005	0.25	293.15	1.2018	64.899	0.25	303.15	1.5000	81.277	0.25	313.15	1.6040	82.117
0.25	283.15	0.9306	50.003	0.25	293.15	1.2325	67.170	0.25	303.15	1.5528	85.505	0.25	313.15	1.6997	89.082
0.25	283.15	0.9306	50.014	0.25	293.15	1.2326	67.209	0.25	303.15	1.5528	85.496	0.25	313.15	1.6997	89.102
0.25	283.15	0.9499	51.343	0.25	293.15	1.2499	68.527	0.25	303.15	1.6014	89.547	0.25	313.15	1.7055	89.500
0.25	283.15	0.9499	51.360	0.25	293.15	1.2500	68.498	0.25	303.15	1.6014	89.557	0.25	313.15	1.7056	89.521
0.25	283.15	0.9705	52.800	0.25	293.15	1.2726	70.284	0.25	303.15	1.6324	92.233	0.25	313.15	1.7996	96.813
0.25	283.15	0.9705	52.815	0.25	293.15	1.2726	70.249	0.25	303.15	1.6324	92.224	0.25	313.15	1.7996	96.837
0.25	293.15	0.6348	29.858	0.25	293.15	1.2905	71.688	0.25	303.15	1.6502	93.810	0.25	313.15	1.9010	105.295
0.25	293.15	0.6349	29.855	0.25	293.15	1.2905	71.653	0.25	303.15	1.6502	93.797	0.25	313.15	1.9010	105.323
0.25	293.15	0.7014	33.435	0.25	303.15	0.8704	40.758	0.25	303.15	1.6708	95.666	0.25	313.15	1.9520	109.850
0.25	293.15	0.7015	33.431	0.25	303.15	0.8704	40.738	0.25	303.15	1.6708	95.652	0.25	313.15	1.9521	109.872
0.25	293.15	0.8044	39.200	0.25	303.15	0.9036	42.563	0.25	303.15	1.6817	96.655	0.25	313.15	2.0015	114.475
0.25	293.15	0.8045	39.201	0.25	303.15	0.9036	42.583	0.25	303.15	1.6818	96.676	0.25	313.15	2.0015	114.493
0.25	293.15	0.8312	40.790	0.25	303.15	1.0022	48.138	0.25	313.15	1.1683	54.696	0.25	313.15	2.0537	119.615
0.25	293.15	0.8312	40.779	0.25	303.15	1.0022	48.159	0.25	313.15	1.1683	54.685	0.25	313.15	2.0538	119.633
0.25	293.15	0.9035	45.066	0.25	303.15	1.1004	53.948	0.25	313.15	1.1685	54.697	0.25	313.15	2.1019	124.620
0.25	293.15	0.9035	45.083	0.25	303.15	1.1004	53.972	0.25	313.15	1.1685	54.681	0.25	313.15	2.1019	124.636
0.25	293.15	0.9049	45.110	0.25	303.15	1.1144	54.815	0.25	313.15	1.2026	56.659	0.25	313.15	2.1252	127.154
0.25	293.15	0.9049	45.111	0.25	303.15	1.1144	54.805	0.25	313.15	1.2026	56.644	0.25	313.15	2.1254	127.180
0.5	283.15	0.6268	25.748	0.5	293.15	0.9013	37.121	0.5	303.15	1.6019	72.527	0.5	313.15	1.3053	51.651
0.5	283.15	0.7005	29.258	0.5	293.15	1.0056	42.366	0.5	303.15	1.6019	72.522	0.5	313.15	1.5049	61.721
0.5	283.15	0.7514	31.767	0.5	293.15	1.0058	42.366	0.5	303.15	1.6595	76.354	0.5	313.15	1.6095	67.369
0.5	283.15	0.8027	34.375	0.5	293.15	1.0062	42.433	0.5	303.15	1.6595	76.358	0.5	313.15	1.6114	67.482
0.5	283.15	0.8510	6.905	0.5	293.15	1.0067	42.442	0.5	303.15	1.7002	79.161	0.5	313.15	1.7031	72.745
0.5	283.15	0.9213	40.710	0.5	293.15	1.0541	44.947	0.5	303.15	1.7002	79.156	0.5	313.15	1.7979	78.443
0.5	283.15	0.9502	42.325	0.5	293.15	1.0733	45.942	0.5	303.15	1.7208	80.609	0.5	313.15	1.8004	78.547
0.5	283.15	0.9721	43.563	0.5	303.15	1.1963	49.260	0.5	303.15	1.7208	80.615	0.5	313.15	1.8978	84.807
0.5	283.15	1.0005	45.223	0.5	303.15	1.1963	49.254	0.5	303.15	1.7516	82.822	0.5	313.15	1.9967	91.461
0.5	283.15	1.0185	46.273	0.5	303.15	1.2070	49.815	0.5	303.15	1.7516	82.829	0.5	313.15	2.1014	99.132
0.5	283.15	1.0301	46.960	0.5	303.15	1.2070	49.810	0.5	303.15	1.7719	84.320	0.5	313.15	2.1496	102.888
0.5	293.15	0.6470	25.341	0.5	303.15	1.4004	60.269	0.5	303.15	1.7720	84.338	0.5	313.15	2.2004	107.036
0.5	293.15	0.6475	25.378	0.5	303.15	1.4005	60.280	0.5	303.15	1.7915	85.787	0.5	313.15	2.2423	110.627
0.5	293.15	0.6985	27.627	0.5	303.15	1.4984	66.037	0.5	303.15	1.7916	85.795	0.5	313.15	2.2684	112.939
0.5	293.15	0.8040	32.457	0.5	303.15	1.4984	66.040	0.5	313.15	1.2989	51.317	0.5	313.15	2.2860	114.527
0.75	283.15	0.6493	21.366	0.75	293.15	0.9031	29.568	0.75	303.15	0.7083	21.306	0.75	313.15	1.2910	40.393
0.75	283.15	0.6493	21.371	0.75	293.15	0.9032	29.572	0.75	303.15	0.7084	21.318	0.75	313.15	1.2910	40.396
0.75	283.15	0.6993	23.254	0.75	293.15	0.9180	30.119	0.75	303.15	0.8043	24.543	0.75	313.15	1.4031	44.709
0.75	283.15	0.6993	23.259	0.75	293.15	0.9180	30.130	0.75	303.15	0.8043	24.562	0.75	313.15	1.4031	44.699
0.75	283.15	0.7976	27.102	0.75	293.15	1.0063	33.623	0.75	303.15	0.9050	28.081	0.75	313.15	1.6001	52.749
0.75	283.15	0.7976	27.111	0.75	293.15	1.0063	33.606	0.75	303.15	0.9051	28.074	0.75	313.15	1.6002	52.749
0.75	283.15	0.9057	31.570	0.75	293.15	1.1020	37.556	0.75	303.15	1.2332	40.537	0.75	313.15	1.6157	53.397
0.75	283.15	0.9057	31.574	0.75	293.15	1.1020	37.576	0.75	303.15	1.2332	40.537	0.75	313.15	1.6157	53.422
0.75	283.15	0.9391	33.005	0.75	293.15	1.2028	41.945	0.75	303.15	1.4023	47.660	0.75	313.15	1.8064	61.941
0.75	283.15	0.9391	33.005	0.75	293.15	1.2029	41.966	0.75	303.15	1.4023	47.663	0.75	313.15	1.8064	61.944
0.75	283.15	0.9703	34.371	0.75	293.15	1.2501	44.089	0.75	303.15	1.5037	52.229	0.75	313.15	1.9056	66.714
0.75	283.15	0.9703	34.372	0.75	293.15	1.2501	44.105	0.75	303.15	1.5038	52.230	0.75	313.15	1.9056	66.711
0.75	283.15	1.0006	35.722	0.75	293.15	1.2995	46.395	0.75	303.15	1.5993	56.771	0.75	313.15	2.0008	71.523
0.75	283.15	1.0006	35.723	0.75	293.15	1.2996	46.415	0.75	303.15	1.5994	56.779	0.75	313.15	2.0011	71.553
0.75	283.15	1.0216	36.673	0.75	293.15	1.3400	48.354	0.75	303.15	1.6512	59.343	0.75	3		



**Figure 1.** Experimental data distribution for R32 + R125 mixtures at  $x_1 = 0.5$ .  $\Delta$ , this work;  $\times$ , ref 8. The line is the saturation curve calculated from ref 5.



**Figure 2.** Fractional deviation,  $\Delta p = \{p(\text{exptl}) - p(\text{calcd})\}$ , of the experimental pressure,  $p(\text{exptl})$ , of R32 + R125 mixtures from values,  $p(\text{calcd})$ , calculated from the equation of state developed by Lemmon and Jacobsen.<sup>5</sup>  $\blacklozenge$ , this work ( $x_1 = 0.25$ );  $\bullet$ , this work ( $x_1 = 0.5$ );  $\blacktriangle$ , this work ( $x_1 = 0.75$ );  $\square$ , ref 8;  $\times$ , ref 9;  $\Delta$ , ref 10;  $-$ , ref 11;  $+$ , ref 12.



**Figure 3.** Fractional deviation,  $\Delta p = \{p(\text{exptl}) - p(\text{calcd})\}$ , of the experimental pressure,  $p(\text{exptl})$ , of R32 + R125 mixtures from values,  $p(\text{calcd})$ , calculated from the equation of state developed by Adachi.<sup>6</sup>  $\blacklozenge$ , this work ( $x_1 = 0.25$ );  $\bullet$ , this work ( $x_1 = 0.5$ );  $\blacktriangle$ , this work ( $x_1 = 0.75$ );  $\square$ , ref 8;  $\times$ , ref 9;  $\Delta$ , ref 10;  $-$ , ref 11;  $+$ , ref 12.

As shown in Figure 2, the saturation state of each temperature for a certain composition is located near the right-hand limit of all series of our data (this work, shown by filled symbols). All series have systematic deviations, (0 to  $-0.1$ ) % or (0 to  $-0.2$ ) % at  $x_1 = 0.25$  and (0 to  $+0.3$ ) % or (0 to  $+0.2$ ) % at  $x_1 = 0.75$ , and no systematic errors are observed at  $x_1 = 0.5$ . There is a possibility that the equations of state for R32 and R125 do

not well represent the thermal properties in the region near saturation.<sup>2</sup> On the other hand, as shown in Figure 3, most of the data including our data are represented within  $\pm 0.2$  % by the equation of state developed by Adachi. In particular, the deviations of the data near saturation are represented without any systematic deviation from the mixture equation of state developed by Adachi.

## Conclusions

*PVT<sub>x</sub>* properties of R32 (1) + R125 (2) mixtures in the gaseous phase including near saturation have been measured with a magnetic suspension densimeter. 298 *PVT<sub>x</sub>* values at  $x_1 = 0.25$ , 0.5, and 0.75 with an uncertainty of (0.03 % + 0.005 kg·m<sup>-3</sup>) were obtained. The measured data are compared with the existing equations of state for R32 + R125 mixtures.

## Literature Cited

- Ichikura, K.; Kano, Y.; Sato, H. Importance of Third Virial Coefficients for Representing the Gaseous Phase Based on Measuring PVT-Properties of 1,1,1-Trifluoroethane (R143a). *Int. J. Thermophys.* **2006**, 27, 23–38.
- Mukoubayashi, M.; Ichikura, K.; Kano, Y.; Sato, H. *PVT*-Property Measurements for R143a, R125, and R32 in the Gaseous Phase. *J. Chem. Eng. Data*, to be published.
- Tillner-Roth, R.; Yokozeki, A. An International Standard Equation of State for Difluoromethane (R-32) for Temperatures from the Triple Point at 136.34 K to 435 K and Pressures up to 70 MPa. *J. Phys. Chem. Ref. Data* **1997**, 26, 1273–1328.
- Lemmon, E. W.; Jacobsen, R. T. A New Functional Form and New Fitting Techniques for Equations of State with Application to Pentane (HFC-125). *J. Phys. Chem. Ref. Data* **2005**, 34, 69–108.
- Lemmon, E. W.; Jacobsen, R. T. Equations of State for Mixtures of R-32, R-125, R-134a, R-143a, and R-152a. *J. Phys. Chem. Ref. Data* **2004**, 33, 593–620.
- Adachi, T. A Study on Development of Thermodynamic Equations of State for HFC Refrigerant R143a, HFC Mixture Refrigerant and Natural Refrigerants. Master's dissertation, Keio University, Yokohama, Japan, 2004.
- Astina, I. M. Development of Fundamental Equations of State for Thermodynamic Properties of HFC Refrigerants. Ph.D. dissertation, Keio University, Yokohama, Japan, 2003.
- Kleemann, M. Thermodynamic Properties of Binary and Ternary Refrigerant Mixtures of R32, R125, R143a and R134a – Measurements and Equation of State. Ph.D. Dissertation, University of Hannover, Hannover, Germany, 1997.
- Sato, T.; Kiyoura, H.; Sato, H.; Watanabe, K. Measurements of *PVT<sub>x</sub>* Properties of Refrigerant Mixture HFC-32+HFC-125 in the Gaseous Phase. *Int. J. Thermophys.* **1996**, 17, 43–54.
- Zhang, H.; Sato, H.; Watanabe, K. In *Measurement of PVT<sub>x</sub> Property of R-32/125 System Mixed Refrigerants by Burnet Method*, Proceedings of the 31st Japanese Joint conference on Air-Conditioning and Refrigeration, 1996; pp 113–116.
- Kiyoura, H.; Takebe, J.; Sato, H.; Watanabe, K. Proceedings of the 16th Japan Symposium Thermophys. Prop. Conference, 1995; pp 177–180.
- Bivens, D. B.; Yokozeki, A.; Geller, V. Z. Proceedings of the 4th Asian Thermophys. Prop. Conference, 1995.

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