

Registry No. N<sub>2</sub>, 7727-37-9; CH<sub>4</sub>, 74-82-8; C<sub>2</sub>H<sub>6</sub>, 74-84-0.

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Received for review April 6, 1990. Accepted September 7, 1990.

# Density, Isothermal Compressibility, and the Volume Expansion Coefficient of Liquid Chlorodifluoromethane for Temperatures of 310-400 K and Pressures up to 10 MPa

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The density measurements at given temperatures and pressures for liquid chlorodifluoromethane were carried out with the variable-volume method using a metal bellows. The results cover the high-density region from 510 to 1197 kg/m<sup>3</sup> along ten isotherms between 310 and 400 K for fourteen pressures from 1.5 to 10.0 MPa. The experimental uncertainty in the density measurements was estimated to be no greater than 0.2%. On the basis of the present results the density derivatives were calculated, and numerical values of the volume expansion coefficient and the isothermal compressibility are tabulated as a function of temperature and pressure.

### Introduction

As a part of volumetric property measurements for the mixtures of the R 22 + R 114 system, we have measured density of liquid chlorodifluoromethane, one of the pure components of the R 22 + R 114 system, at given temperatures and pressures. The *PVTX* properties of this system in the supercritical region (1) and the composition dependence of critical parameters (2) were reported in our previous publications. In this paper, we report the experimental results of density for chlorodifluoromethane in the liquid region along ten isotherms between 310 and 400 K for fourteen pressures from 1.5 to 10.0 MPa. The values of the volume expansion coefficient and isothermal compressibility are also reported. The purity of the sample used was 99.99 wt % chlorodifluoromethane (CHClF<sub>2</sub>, R 22).

### Experimental Section

The density measurements of this work have been made with the variable-volume method using a metal bellows. The apparatus and experimental procedures used here were described in detail in a previous publication (3). A metal bellows made of stainless steel (AM 350) was chosen as a vessel in which the sample of known mass was filled and whose volume could be varied. Dimensions of the bellows were 75 mm in length, 0.15 mm in thickness, 30 mm in outer diameter, and 4.3 cm<sup>2</sup> in effective area. The bellows hung vertically downward in a pressure vessel made of 304 stainless steel and traveled

longitudinally upward to a maximum distance of 16 mm. The volume of the bellows at the reference position was about 27 cm<sup>3</sup>. The volume change of the bellows was detected by measuring the bellows displacement with the aid of a linear variable differential transformer with a resolution of less than 1 μm. The inner volume of the bellows and its variation with the bellows displacement were calibrated with an uncertainty of ±0.2%.

Nitrogen gas was supplied into the pressure vessel, and it surrounded the bellows. When the pressure of the nitrogen gas was increased or reduced, the bellows was compressed or expanded. The pressure of the nitrogen gas was measured with two different air-piston pressure gauges (Ruska, Models 2465 and 2470), depending on the pressure range. The precision of the two air-piston pressure gauges used was guaranteed by the supplier to be 0.015% for high pressures above 5 MPa and 0.010% for low pressures below 5 MPa, respectively. These pressure gauges were used also as the device for generating a constant pressure. Even if the bellows is held in balance, the pressure of the sample confined in the bellows is different from that of the nitrogen gas exerted on the bellows, mainly because of the reaction of the bellows against the compression. Prior to the experiments, the difference of the internal and external pressure of the bellows was calibrated in the experimental range of temperatures and pressures to be studied with an uncertainty of ±0.5 kPa. The pressure of the sample was set at the values desired within ±2 kPa.

In the body of the pressure vessel, a well was drilled for inserting a 25-Ω platinum resistance thermometer (Chino, Model R 800-2) calibrated with a precision of 2 mK on IPTS-68. The temperature was measured with the aid of this thermometer by a thermometer bridge (Tinsley, Type 5840). The resistance of the thermometer at the triple point of water was measured periodically. The pressure vessel was immersed in a circulating silicone oil bath (425 × 285 × 470 mm in inner dimensions). The temperature detected at the well drilled in the pressure vessel was set at the values desired within ±3 mK, and it was kept constant within a fluctuation of ±3 mK during the measurements of a given isotherm.

The mass of the sample prepared in a supply vessel was weighed with a precision chemical balance (Chyo, Model C<sub>2</sub>-3000) with an uncertainty of 2 mg, and then the sample was supplied to the bellows, being evacuated up to around 0.5 mPa, from the supply vessel. After thermodynamic equilibrium of the sample was confirmed, temperature, pressure, and bellows position were measured. The uncertainty in the density mea-

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Table I. Experimental Density Data at Various Temperatures

P, MPa	density, kg/m <sup>3</sup>									
	310 K	320 K	330 K	340 K	350 K	360 K	370 K	380 K	390 K	400 K
1.5	1143.3									
2.0	1147.4	1099.4								
2.5	1151.3	1104.5	1050.6							
3.0	1154.9	1109.2	1057.3	994.5						
3.5	1158.5	1113.9	1063.6	1004.1	921.6					
4.0	1161.9	1118.2	1069.5	1013.0	938.0					
4.5	1165.6	1122.5	1075.1	1020.9	951.8	848.3				
5.0	1168.5	1126.7	1080.4	1028.5	963.5	875.1				
5.5	1171.7	1130.6	1085.4	1035.4	974.0	895.1	759.6			
6.0	1174.9	1134.4	1090.5	1041.8	983.2	911.0	805.4	510.4		
7.0	1180.8	1141.7	1099.6	1053.8	999.8	936.9	856.3	734.3	519.9	
8.0	1186.6	1148.6	1108.2	1064.6	1014.2	957.4	889.4	801.6	676.6	521.2
9.0	1192.1	1155.2	1116.1	1074.6	1027.0	974.7	914.6	842.5	750.8	636.6
10.0	1197.4	1161.4	1123.5	1083.7	1038.5	989.9	935.1	872.4	797.4	707.8

Table II. Volume Expansion Coefficient at Various Temperatures

P, MPa	volume expansion coefficient, (1000 K) <sup>-1</sup>								
	320 K	330 K	340 K	350 K	360 K	370 K	380 K	390 K	
2.5	4.56								
3.0	4.40	5.43							
3.5	4.26	5.16	7.07						
4.0	4.14	4.92	6.49						
4.5	4.03	4.72	6.04	9.07					
5.0	3.91	4.55	5.69	7.96					
5.5	3.82	4.39	5.38	7.20	11.98				
6.0	3.72	4.25	5.15	6.65	9.76	24.88			
7.0	3.56	4.00	4.74	5.85	7.66	11.83	22.90		
8.0	3.42	3.79	4.41	5.28	6.52	8.76	13.28	20.72	
9.0	3.29	3.61	4.15	4.86	5.76	7.22	9.72	13.72	
10.0	3.18	3.46	3.92	4.51	5.22	6.28	7.89	10.29	

Table III. Isothermal Compressibility at Various Temperatures

P, MPa	isothermal compressibility, GPa <sup>-1</sup>									
	310 K	320 K	330 K	340 K	350 K	360 K	370 K	380 K	390 K	400 K
2.0	6.93									
2.5	6.45	8.87								
3.0	6.23	8.47	12.36							
3.5	6.13	8.09	11.48	18.39						
4.0	6.10	7.71	10.68	16.56	32.1					
4.5	5.63	7.52	10.17	15.19	26.70					
5.0	5.26	7.20	9.59	14.07	23.05	53.4				
5.5	5.45	6.87	9.30	12.88	20.28	40.2				
6.0	5.25	6.63	8.79	12.17	18.47	33.9				
7.0	4.98	6.22	8.02	10.80	15.51	24.74	49.0	198.2		
8.0	4.75	5.89	7.44	9.75	13.40	19.75	32.8	67.5	170.7	
9.0	4.51	5.53	6.88	8.88	11.84	16.66	25.00	42.0	80.5	147.1

measurements was estimated to be no greater than  $\pm 0.2\%$ .

## Results and Discussion

We carried out four different experimental runs along ten isotherms between 310 and 400 K for fourteen pressures from 1.5 to 10.0 MPa. The results given in Table I cover the high-density region from 510 to 1197 kg/m<sup>3</sup>. The uncertainties in temperatures and pressures given in Table I were estimated to be less than 8 mK and 5 kPa, respectively. The reproducibility in density measurements among different experimental runs was not greater than 0.1%. The present results were compared with the literature data by depicting deviation plots of both density and pressure from the equation of state proposed by Kagawa et al. (4). As typical illustrations of comparison, Figures 1 and 2 show the deviation plots of density along the 310 and 340 K isotherms, respectively. Our results are in good agreement with most of the data by Oguchi et al. (5), those by Takaiishi et al. (6), and those by Kohlen et al. (7) within  $\pm 0.1\%$  in density deviation between 310 and 370 K. The data by Kumagai et al. (8) deviate from our results by about 0.3% in density. For high temperatures of 380 and 400 K, our

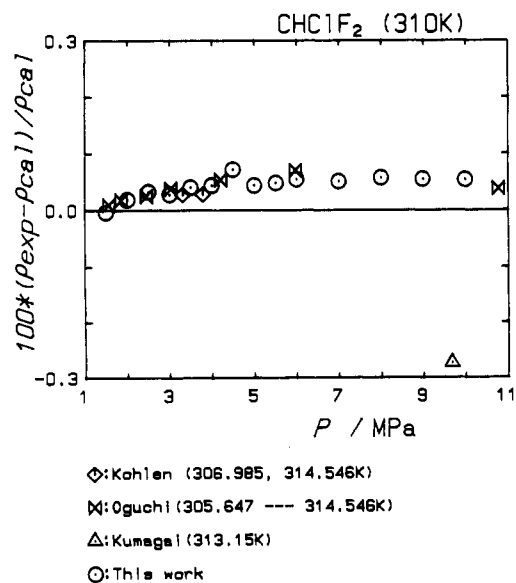


Figure 1. Deviation plots of the density data from the equation of state proposed by Kagawa et al. along the 310 K isotherm.

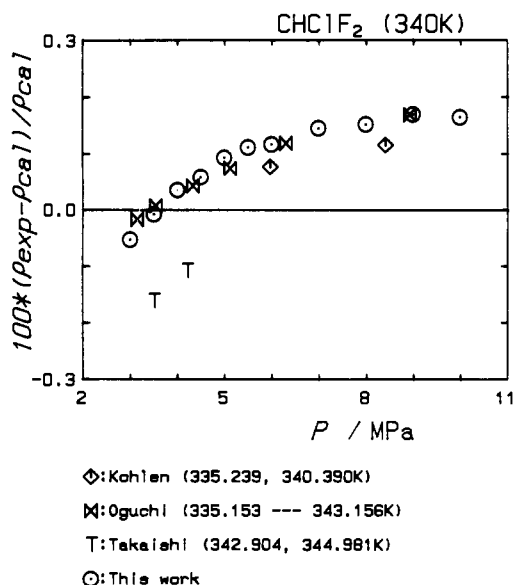


Figure 2. Deviation plots of the density data from the equation of state proposed by Kagawa et al. along the 340 K isotherm.

results agree well with the data by Michels (9) and those by Zander (10) within  $\pm 0.2\%$  in pressure deviation.

We calculated the derivatives of density with respect to temperature at constant pressure and those of density with respect to pressure at constant temperature from the data given in Table I by approximation as differences of these

quantities. The values of the volume expansion coefficient and the isothermal compressibility thus obtained are given in Tables II and III, respectively.

#### Acknowledgment

M. Yamamoto, Y. Takiguchi, and K. Nakagima have provided valuable assistance in the present work. The National Research Laboratory of Metrology, Tsukuba, Japan, kindly calibrated the platinum resistance thermometer. We are greatly indebted to Professor K. Watanabe, Keio University, for his kind support to use the research-grade pure sample.

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Received for review May 2, 1990. Accepted July 26, 1990.

## Solubility Products of the Trivalent Rare-Earth Phosphates

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The solubility and solubility products of 14 rare-earth phosphates in aqueous solution have been determined at  $25 \pm 1$  °C. The most soluble compound is yttrium phosphate ( $pK = 24.76$ ). The least soluble ones are lanthanum phosphate ( $pK = 26.15$ ) and ytterbium phosphate ( $pK = 26.17$ ). The rare-earth phosphates were prepared by precipitation from homogeneous solution. Saturated solutions were analyzed for pH, the concentrations of some rare-earth cations, and the total concentration of phosphate. Activity products were calculated from the experimental data. The solubilities of the rare-earth phosphates are so low that the solubility products and the activity products are essentially the same value. The rare-earth phosphates are more insoluble at higher temperatures. Lanthanum phosphate has a  $pK$  of 26.49 at 70 °C. Twelve values for the activity product of rare-earth phosphates at elevated temperatures were determined.

#### Introduction

Previous work by Jonasson, Bancroft, and Nesbitt (1) reported on the solubilities of only the lanthanum, praseodymium, neodymium, and erbium phosphates. Limited experimental in-

formation was presented. The study reported here involved the entire trivalent rare-earth series, excluding scandium and cerium. Solubilities at 25 °C and at higher temperatures are reported.

#### Experimental Section

Commercial rare-earth phosphates were unsatisfactory for use in this study. Colloidal suspensions formed that did not settle out of solution even after months of standing.

Satisfactory crystals of rare-earth phosphates were prepared by precipitation from homogeneous solution using the hydrolysis of urea.

Equimolar amounts (0.005 mol) of rare-earth cation and phosphoric acid were added to a 1-L beaker with 5 mL of 70% HClO<sub>4</sub> to prevent the rare-earth phosphate from precipitating. Deionized water was added to bring the volume to about 900 mL. A 3–5-g amount of urea was slowly added with constant stirring. The solution was heated to hydrolyze the urea, increase the pH, and bring about the precipitation of the rare-earth phosphate. The solution was heated for an additional hour after precipitation began. The resulting crystals were washed 10–15 times with deionized water. The last two washings were made with a 0.10 M perchloric acid solution to eliminate the possibility of rare-earth carbonate being present. No fizzing