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Experimental Densities of Trichlorofluoromethane (R-11) and Chlorodifluoromethane (R-22) at 270 K and up to 67 MPa

Gustavo A. Iglesias-Silva

Departamento de Ingeniería Química, Instituto Tecnológico de Celaya, Celaya, Guanajuato, CP 38010, Mexico

Kenneth R. Hall* and James C. Holste

Chemical Engineering Department, Texas A&M University, College Station, Texas 77843

We have used a continuously weighed pycnometer to measure compressed liquid densities of trichlorofluoromethane (R-11) and chlorodifluoromethane (R-22) at 270 K and pressures to 67 MPa. The precision of the liquid density measurements is better than ±0.1 kg·m^{-3}, and the accuracy is ±0.08% at the 95% confidence limit. The new results agree within the combined uncertainties with published measurements in regions of overlap, and they show that existing equations of state extrapolate well to higher pressures.

Introduction

Accurate density measurements are essential for developing equations of state. Although production of trichlorofluoromethane (R-11) has been limited by international agreement, chlorodifluoromethane (R-22) retains technical importance because it causes less ozone depletion. Experimental measurements on substances such as R-11 and R-22 are important for understanding the polar contributions to generalized correlations and equations of state. Simple molecules of a polar nature are attractive substances for such studies.

Few *pVT* measurements at high pressures and low temperatures have appeared for R-11. DeZwaan and Jonas (1975) reported experimental measurements at high pressures and temperatures above 340 K. Recently, Blanke and Weiss (1992) measured densities between 253 and 453 K at pressures to 32 MPa, and Ström (1990) measured liquid densities at pressures below 1.6 MPa and temperatures between 267 and 322 K. For R-22, only Kumagai and Iwasaki (1978) have measured densities at low temperatures and high pressures; Wagner *et al.* (1993) summarize other investigations.

Several equations of state have been developed for R-11. Stewart *et al.* (1986), Platzer *et al.* (1990), and Jacobsen *et al.* (1992) have published equations of state that cover the vapor and liquid states. Since 1968, equations of state have appeared for R-22. Kamei *et al.* (1992) have published an equation of state for R-22 based upon heat capacities and *pVT* data. This equation is valid at pressures up to 60 MPa. Wagner *et al.* (1993) have proposed an expression to extend the pressure range up to 200 MPa. This latter formulation uses the *pVT* data and heat capacities, enthalpies, and Maxwell criteria pseudoexperimental values to obtain an equation valid from 116 to 550 K.

Experimental Apparatus

Lau (1986) has provided a detailed description of the apparatus, so we mention only the most important aspects of the experimental device. The apparatus is a pycnometer that uses a continuous weighing technique for fluid density measurements. It consists of a weighing device, a sample cell, an isothermal bath, a pressurizing system, and a high vacuum system.

The singular features of this apparatus are suspension of the sample cell from an electronic balance by a wire, and use of a 200 mm straight length of 0.8 mm diameter capillary tubing contained within the isothermal bath as the feed line. The length of the feed line results from consideration of forces transmitted to the cell resulting from the mechanical elasticity of the tubing under changing pressures. With this length, the vertical displacement of the cell is less than 1 μm during the weighing procedure which is within the accuracy of the balance and equivalent to 0.05 mg. The straight length also minimizes spurious forces from bending caused by internal pressures. With this arrangement, the spurious forces are less than the resolution of the balance. Both the balance and the sample cell are immersed in helium to reduce buoyancy effects and promote heat transfer. The balance readings show a short-term precision of ±0.3 mg, and the tare readings reproduce to better than ±1 mg from the beginning to the end of an isotherm.

The internal volume of the cell is approximately 10 cm^3. The effective internal volume of the cell is calibrated by measuring known fluids. An extensive calibration with water at temperatures between 275 and 400 K provided a correlation which describes all the measured cell volumes with random scatter and a standard deviation of 0.04%. This calibration is the limiting factor for the accuracies of the measurements reported here. The estimated accuracy in the pycnometric density measurements (95% confidence limits) is

$$\Delta\varrho = \{(0.15\ \mathrm{kg{\cdot}m^{-3}})^2 + (0.0008\varrho)^2\}^{1/2}$$

or

$$\frac{\Delta\varrho}{\varrho} = \left\{\left(\frac{0.15}{\varrho}\right)^2 + 6.4\times10^{-7}\right\}^{1/2}$$

where ϱ has units of kg·m^{-3}. The first term is a random error because it arises from the scatter in the mass measurements, and the second term is a systematic error (bias) because it arises from the cell volume calibration.

The Paroscientific Inc. and Rosemount Inc. transducers used for the pressure measurements are calibrated using a dead weight gauge specified by the manufacturer to be accurate to ±0.005%. The overall accuracy of the transducers after calibration is ±0.008 MPa.

A platinum resistance thermometer (PRT) manufactured by MINCO Products, Inc., is adjacent to the sample cell

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Table 1. Experimental Temperatures, Pressures, Densities, and Compression Factors for R-11

T_{90}/K	p/MPa	ϱ/(kg·m^{-3})	Z
270.006	67.189	1643.95	2.494 13
270.001	62.102	1637.88	2.313 89
269.999	55.374	1629.56	2.073 76
269.999	48.503	1620.60	1.826 48
270.004	41.627	1611.15	1.576 72
270.001	34.884	1601.44	1.329 33
270.004	20.459	1578.78	0.790 82
270.001	13.720	1567.04	0.534 32
269.999	6.322	1553.21	0.248 40
270.006	5.564	1551.70	0.218 82
270.006	4.922	1550.40	0.193 74
270.006	4.257	1549.11	0.167 70
270.006	3.461	1547.53	0.136 48
270.004	2.827	1546.24	0.111 57
270.001	2.084	1544.76	0.082 33
270.004	1.442	1543.43	0.057 02
270.006	0.706	1541.92	0.027 94

Table 2. Experimental Temperatures, Pressures, Densities, and Compression Factors for R-22

T_{90}/K	p/MPa	ϱ/(kg·m^{-3})	Z
269.999	66.090	1439.48	1.758 85
270.004	62.345	1433.78	1.665 75
270.001	56.152	1423.88	1.510 73
269.999	49.131	1411.93	1.333 04
270.001	42.258	1399.48	1.156 75
270.001	35.316	1385.90	0.976 19
269.999	28.384	1352.44	0.804 00
270.001	14.048	1335.85	0.402 86
270.001	7.067	1315.13	0.205 86
269.999	6.267	1312.49	0.182 92
270.001	5.578	1310.22	0.163 09
269.999	4.903	1307.96	0.143 60
269.999	4.138	1305.38	0.121 44
270.001	3.476	1303.04	0.102 19
269.996	2.794	1300.71	0.082 29
269.999	2.058	1298.08	0.060 74
269.996	1.418	1295.75	0.041 92
270.001	0.987	1294.19	0.029 22

for temperature measurements. This thermometer is calibrated to better than ±0.005 K compared to IPTS-68. The overall precision of the temperature measurement is ±0.002 K. The temperatures have been converted to ITS-90 for reporting.

Samples

The research grade trichlorofluoromethane (R-11) and chlorodifluoromethane (R-22) are products of Scientific Gas Products Inc., which stated the purity as 99.9% for both refrigerants. Dissolved air is removed from the R-11 sample by freezing it and reducing the pressure above the solid to less than 10^{-6} MPa. Analysis of the samples using gas chromatography indicated purities of better than 99.95% for R-11 and 99.9% for R-22.

Results

Experimental pressures (p), temperatures (T), mass densities (ϱ), and compression factors ($Z = Mp/RT\varrho$) for R-11 and R-22 at 270 K and pressures to 67 MPa appear in Tables 1 and 2. The value for the gas constant is R = 8.314 51 J·mol^{-1}·K^{-1}; the molar mass (M) of R-11 is 137.368, and that of R-22 is 86.468. We have used the equation of state proposed by Jacobsen *et al.* (1992) for R-11 to compare our measurements with those of Rivkin and Kremnevskaya (1975). Figure 1 shows that the agreement is better than ±0.1%. The equation of state describes our results within ±0.05% at low pressures. At higher pressures, the deviations increase systematically to 0.15%, primarily because

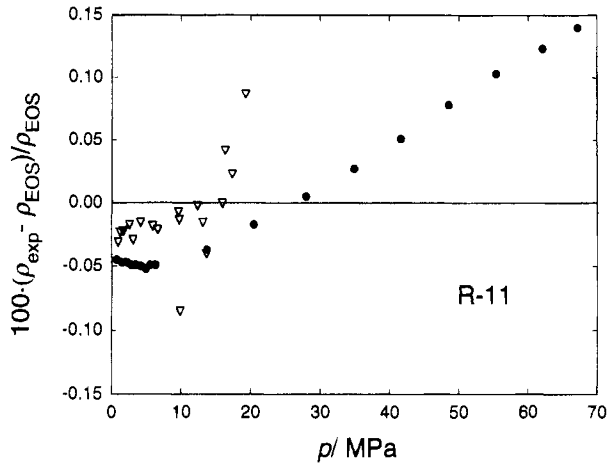

Figure 1. Relative deviations of R-11 experimental densities from the equation of state of Jacobsen *et al.* (1992): (▽) Rivkin and Kremnevskaya (1975); (●) this work.

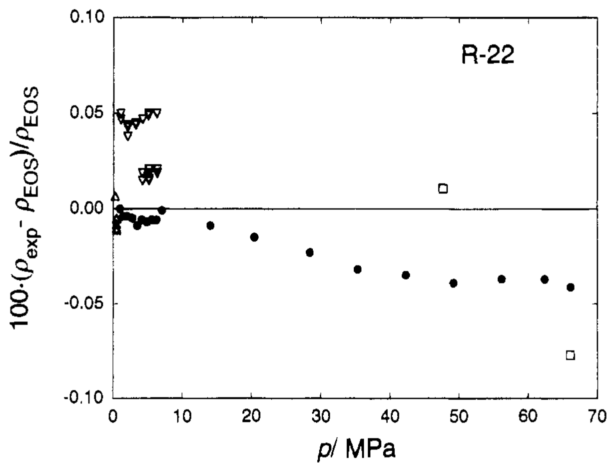

Figure 2. Relative deviations of R-22 experimental densities from the equation of state of Wagner *et al.* (1993): (△) Händel *et al.* (1992); (▽) Defibaugh and Morrison (1992); (□) Kumagai and Iwasaki (1975); (●) this work.

the equation of state has been developed utilizing only measurements at less than 30 MPa.

Figure 2 shows the deviations of the experimental densities for R-22 from the equation of state of Wagner *et al.* (1993). Our results agree within ±0.01% with those of Händel *et al.* (1992) and within 0.05% with those of Defibaugh and Morrison (1992). At pressures up to 70 MPa, the agreement between Kumagai and Iwasaki (1978) and the present values is ±0.05%, but at higher pressures the Kumagai and Iwasaki results deviate up to 0.4% from the equation of state.

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