Experimental $P-T-\rho$ and Enthalpy-Increment Measurements of an Equimolar Mixture of Trichlorofluoromethane (R-11) + Dichlorodifluoromethane (R-12)

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We have measured experimental liquid densities and enthalpy increments for an equimolar mixture of trichlorofluoromethane (R-11) + dichlorodifluoromethane (R-12). We have used a continuously weighed pycnometer for measuring the liquid densities and a thermoelectric flow calorimeter for measuring the enthalpy increments. The temperature range for all measurements is from (230 to 425) K. The experimental measurements range up to 69 MPa with the pycnometer and 6.8 MPa with the calorimeter, respectively.

Introduction

Accurate pressure−temperature−density and enthalpy measurements are essential for the development of equations of state. Also, these measurements are useful for design, production, and efficiency in industrial plants. Although the production of chlorofluoromethanes is limited because of ozone depletion concerns, experimental measurements on their mixtures are valuable for understanding polar contributions to equations of state. Mixtures of chlorofluoromethanes also appear as contaminants in water sources. Jacobsen et al.[1] and Penoncello et al.[2] have reported thermodynamic measurements for the pure substances of the mixture trichlorofluoromethane (R-11) + dichlorodifluoromethane (R-12). Loi[3] has reported the only known measurements in the two-phase region, as reported by Morrison and McLinden,[4] and in the single phase, Ström[5] has measured densities from 288.5 K to 333 K at three different pressures (0.575, 1.06, and 1.555) MPa. Unfortunately, they do not report measurements for an equimolar mixture.

In this work, we have used a pycnometer to measure liquid densities and a calorimeter to measure enthalpy increments for an equimolar mixture of R-11 + R-12 from (230 to 425) K. The maximum measured pressure in the pycnometer is 69 MPa while for the calorimeter it is 6.8 MPa.

Experimental Section

Continuously Weighed Pycnometer. A detailed description of the apparatus appears in ref 6. The pycnometer consists of a sample cell of known volume suspended from an electronic balance. The internal volume of the cell is approximately 10 cm^3. Paroscientific Inc. and Rosemount Inc. transducers that were calibrated using a dead weight gauge standard were used to measure pressure. The accuracy of the pressure transducers after calibration is ±0.008 MPa. A four-lead platinum resistance thermometer manufactured by MINCO Products Inc. was used to measure temperature. The thermometer calibration is closer than ±0.005 K to the IPTS-68. Temperature control was better than ±0.002 K. The reported temperatures are on the ITS-90. The uncertainties in the density measurements arise from the error in the measurements and from the cell volume calibration. A calibration with water gives an uncertainty in the cell volume calibration of about ±0.04%. The estimated accuracy within 95% confidence limits[6] is

$$\Delta\rho = \{(0.15)^2 + (0.0004\rho)^2\}^{1/2}$$

or

$$\Delta\rho/\rho = \{(0.15/\rho)^2 + (1.6 \times 10^{-7})^2\}^{1/2}$$

where the units of ρ are kilograms per cubic meter.

Flow Calorimeter. Castro-Gomez et al.[7] have reported the design and operation of this apparatus. The apparatus measures the enthalpy increments of a flowing fluid at an inlet temperature, T_{inlet}, and an outlet temperature, T_{outlet}, at constant pressure. The fluid flows at a constant mass flow rate, so the enthalpy increment is

$$H(T_{inlet},P) - H(T_{outlet},P) = \Delta\dot{W}/\dot{m}$$

where H is the enthalpy, P is the pressure, $\Delta\dot{W}$ is the power difference for flow and nonflow conditions, and $\dot{m}$ is the mass flow rate. Calibrated thermistors measure inlet and outlet temperatures. The thermistor calibrations are precise to ±0.005 K and are traceable to NIST. Möller et al.[8] have shown that long-term instabilities cause uncertainties in the calibrations up to ±0.1 and ±0.02 K for the outlet and inlet temperatures, respectively. Two pressure transducers (Stratham) measure pressures up to (3.5 and 35) MPa. Both transducers show a linear response with a hysteresis of less than ±0.2% of full scale at their low-pressure limits. During runs, pressure fluctuations are less than 0.005 MPa. The mass of the discharged fluid and elapsed time provides the flow rate. Measurements are

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Table 1. Experimental Measurements for R-11 (x = 0.4998) + R-12 (1 − x)

T	P	ρ,		T	P	ρ,		T	P	ρ,		T	P	ρ,	
K	MPa	$kg \cdot m^{-3}$	Z	K	MPa	$kg \cdot m^{-3}$	Z	K	MPa	$kg \cdot m^{-3}$	Z	K	MPa	$kg \cdot m^{-3}$	Z
230.007	63.788	1677.26	2.568 09	298.143	50.266	1527.35	1.714 47	319.991	1.077	1338.31	0.039 06	374.972	2.486	1147.25	0.089 76
230.013	50.366	1660.98	2.047 56	298.142	42.543	1512.90	1.464 92	349.980	67.876	1472.90	2.045 08	374.972	2.088	1141.80	0.075 73
229.988	36.407	1642.58	1.147 53	298.149	36.116	1499.98	1.254 27	349.983	63.152	1463.40	1.915 10	399.975	68.677	1390.42	1.917 99
230.006	22.197	1621.64	0.924 29	298.151	28.151	1482.31	0.989 32	349.988	56.839	1449.70	1.739 92	399.975	62.903	1376.29	1.774 78
230.012	10.736	1602.83	0.452 30	298.140	20.993	1465.01	0.746 49	349.979	49.699	1433.10	1.539 02	399.970	56.478	1359.31	1.613 42
230.003	3.560	1589.87	0.151 21	298.145	14.368	1447.12	0.517 21	349.980	42.725	1415.50	1.339 52	399.967	49.196	1338.37	1.427 39
230.008	3.080	1589.00	0.130 90	298.141	6.905	1424.28	0.252 57	349.979	35.848	1396.40	1.139 27	399.967	42.176	1315.43	1.245 05
230.006	2.764	1588.35	0.117 51	298.151	3.454	1412.44	0.127 39	349.980	27.731	1370.90	0.897 70	399.975	35.409	1290.45	1.065 51
230.015	2.415	1587.69	0.102 71	298.147	3.086	1411.10	0.113 91	349.979	21.180	1347.20	0.697 68	399.974	27.495	1255.89	0.850 12
229.997	2.061	1587.07	0.087 68	298.142	2.749	1409.89	0.101 57	349.980	14.242	1317.80	0.479 60	399.963	21.341	1223.13	0.677 54
230.011	1.769	1586.39	0.075 30	298.144	2.429	1408.71	0.089 84	349.978	7.128	1280.11	0.247 13	399.968	14.445	1176.05	0.476 97
230.013	1.362	1585.49	0.058 00	298.145	2.067	1407.39	0.076 50	349.983	3.564	1256.93	0.125 85	399.973	7.297	1101.78	0.257 16
230.004	1.073	1584.87	0.045 71	298.147	1.714	1406.06	0.063 50	349.981	3.057	1253.22	0.108 24	399.968	6.171	1085.57	0.220 74
270.004	63.322	1601.09	2.275 02	298.150	1.398	1404.87	0.051 85	349.979	2.793	1251.27	0.099 07	399.971	5.593	1075.12	0.202 00
270.003	56.182	1590.70	2.031 67	298.142	1.019	1403.48	0.037 81	349.979	2.476	1248.87	0.087 99	399.969	4.902	1062.22	0.179 21
269.998	45.944	1574.79	1.678 25	319.988	69.080	1521.10	2.204 32	349.979	2.137	1246.23	0.076 11	399.964	4.220	1047.59	0.156 41
270.003	35.970	1557.73	1.328 30	319.987	62.748	1510.07	2.016 89	349.985	1.706	1242.74	0.060 91	399.967	3.545	1030.57	0.133 56
270.003	25.381	1538.00	0.949 28	319.991	56.704	1498.94	1.836 13	349.975	1.415	1240.40	0.050 63	399.965	3.164	1019.46	0.120 51
269.997	15.483	1517.06	0.587 10	319.991	49.802	1485.45	1.627 29	374.976	69.602	1432.06	2.013 13	424.966	68.657	1352.82	1.854 84
270.007	8.526	1500.56	0.326 82	319.990	43.292	1471.79	1.427 71	374.975	61.365	1413.75	1.797 89	424.967	62.391	1335.91	1.706 87
270.005	3.627	1487.88	0.140 22	319.989	36.829	1456.94	1.226 96	374.980	55.869	1400.52	1.652 30	424.967	56.094	1317.32	1.556 27
270.006	3.077	1486.41	0.119 09	319.992	27.780	1434.19	0.940 14	374.977	49.122	1383.05	1.471 10	424.969	49.019	1294.18	1.384 30
270.004	2.768	1485.54	0.107 20	319.994	20.555	1413.23	0.705 96	374.975	42.480	1364.11	1.289 89	424.966	41.997	1268.18	1.210 30
270.004	2.400	1484.58	0.092 99	319.992	14.192	1392.66	0.494 62	374.974	35.276	1341.17	1.089 46	424.969	35.181	1238.98	1.037 76
269.996	2.040	1483.59	0.079 09	319.991	7.540	1367.61	0.267 59	374.976	27.477	1312.44	0.867 15	424.963	27.401	1198.64	0.835 49
270.005	1.716	1482.68	0.066 56	319.990	3.382	1349.54	0.121 65	374.970	21.029	1284.30	0.678 22	424.966	21.076	1156.90	0.665 80
270.008	1.412	1481.79	0.054 83	319.990	3.154	1348.46	0.113 53	374.971	13.814	1245.37	0.459 44	424.960	13.955	1091.53	0.467 24
270.005	1.039	1480.78	0.040 38	319.990	2.807	1346.81	0.101 14	374.972	7.191	1197.39	0.248 75	424.963	7.091	972.83	0.266 39
269.999	0.755	1479.99	0.029 35	319.991	2.468	1345.14	0.089 06	374.971	3.513	1160.16	0.125 41	424.958	6.222	944.04	0.240 87
298.139	69.807	1559.74	2.331 56	319.990	2.102	1343.35	0.075 94	374.973	3.125	1156.09	0.111 96	424.960	5.555	914.74	0.221 95
298.139	63.755	1550.31	2.142 35	319.992	1.769	1341.72	0.064 00	374.975	2.825	1151.69	0.101 59	424.961	4.905	873.33	0.205 27
298.140	57.226	1539.49	1.936 46	319.990	1.422	1340.05	0.051 49								

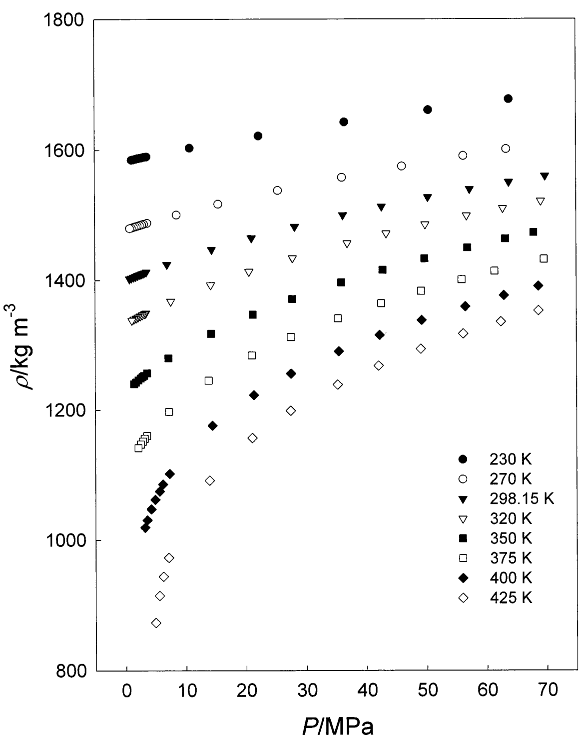

Figure 1. Experimental liquid density measurements.

accurate to ±0.01 g with a reproducibility of the mass flow rate of 0.3%. The overall accuracy of the enthalpy differences is 0.6 $J \cdot g^{-1}$.

Chemicals. Scientific Gas Products Inc. supplied the purified trichlorofluoromethane (R-11) and dichlorodifluoromethane (R-12). The stated purity for R-11 and R-12 was 99.9% and 99.0%, respectively. We removed dissolved air from the samples by freezing them and reducing the pressure to 1 Pa. Analysis of the sample using gas chromatography indicated purities better than 99.95% and 99.5% for R-11 and R-12, respectively. Two mixtures prepared gravimetrically had an overall uncertainty of 0.1%. The final compositions of the different mixtures were as follows:

Table 2. Experimental Enthalpy Increments for R-11 (x = 0.5024) + R-12 (1 − x)

T_{inlet}	T_{outlet}	P	ΔH	T_{inlet}	T_{outlet}	P	ΔH
K	K	MPa	$J \cdot g^{-1}$	K	K	MPa	$J \cdot g^{-1}$
230.119	298.155	6.589	−58.01	464.390	298.203	6.853	184.25
266.353	298.150	6.624	−27.05	264.478	298.148	4.366	−29.15
348.356	298.184	6.716	44.98	369.167	298.184	4.324	66.96
367.331	298.181	6.652	62.74	397.353	298.189	4.397	93.26
394.248	298.186	6.702	86.42	410.841	298.145	2.370	207.91[a]
411.282	298.198	6.675	102.36				

[a] Vapor phase.

Mixture 1 (liquid density measurements):

R-11 = 50.02, R-12 = 49.98

Mixture 2 (enthalpy measurements):

R-11 = 50.24, R-12 = 49.76

Results and Conclusions

Experimental pressures (P), temperatures (T), mass densities (ρ), and compression factors ($Z = MP/RT\rho$) for mixture 1 from (230 to 425) K at pressures up 69 MPa appear in Table 1. Figure 1 presents the experimental results. The value for the gas constant is R = 8.314 51 $J \cdot mol^{-1} \cdot K^{-1}$, and the molar masses ($M$) of R-11 and R-12 are (137.369 and 120.913) $g \cdot mol^{-1}$, respectively. Table 2 shows the experimental enthalpy increments together with the inlet and outlet temperatures. We believe these measurements are suitable for testing and developing new equations of state as well as for designing processes for removing chlorofluoromethanes.

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