Experimental $P-T-\rho$ and Enthalpy-Increment Measurements of an Equimolar Mixture of Trichlorofluoromethane (R-11) + Chlorotrifluoromethane (R-13)

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In this paper, we present experimental liquid densities and enthalpy-increment measurements for an equimolar mixture of trichlorofluoromethane (R-11) + chlorotrifluoromethane (R-13). We use a continuously weighed pycnometer to measure the liquid densities from 230 K to 425 K at pressures up to 69 MPa and a thermoelectric flow calorimeter to measure enthalpy increments from 232 K to 460 K at 4.4 MPa and 6.6 MPa.

Introduction

Experimental thermodynamic properties are essential for the development of equations of state as well as for the design, production, and efficiency in industrial plants. Although the production of chlorofluoromethanes has been forbidden because of ozone depletion concerns, experimental measurements covering mixtures of chlorofluoromethanes are important for understanding the polar contributions to equations of state and molecular theories. Jacobsen et al.[1] and Platzer et al.[2] have developed equations of state for trichlorofluoromethane and chlorotrifluoromethane, and they include experimental data compilations. Kriebel and Löffler[3] have measured saturated liquid densities for the mixture trichlorofluoromethane (R-11) + chlorotrifluoromethane (R-13) from (203 K to 293) K over the entire composition range. They also measure the phase boundary pressures and temperatures. In this work, we have measured the liquid densities and enthalpy increments of an equimolar mixture of R-11 + R-13 from (230 to 425) K with the liquid density measurements at pressures up to 69 MPa while enthalpy measurements are at (4.4 and 6.6) MPa.

Experimental Section

Continuously Weighed Pycnometer. A detailed description of the apparatus appears in ref 4. The pycnometer consists of a sample cell of known volume suspended from an electronic balance. Paroscientific Inc. and Rosemount Inc. transducers calibrated using a dead weight gauge standard were used to measure pressures. The accuracy of the pressure transducers after calibration is ±0.008 MPa. A four-lead platinum resistance thermometer manufactured by MINCO Products Inc. measures temperatures. The thermometer calibration is better than ±0.005 K on the IPTS-68. Temperature control is 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[4] is given by

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

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.[5] 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 at outlet temperature, T_{outlet}, at constant pressure. The fluid flows at a constant mass flow rate, so the enthalpy increment is

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

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.[6] 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 Model) measure pressures up to (3.5 and 35) MPa. Both transducers show a linear response with hysteresis 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 provides the flow rate. Measurements are 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 purified trichlorofluoromethane (R-11) and chlorotrifluoromethane (R-13). The stated purity for R-11 and R-13 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 resultant sample using

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Table 1. Experimental Temperatures, Pressures, Densities, and Compression Factors for R-11 (x = 0.4998) + R-13 (1 − x)

T	P	ρ		T	P	ρ		T	P	ρ		T	P	ρ	
K	MPa	kg·m^{-3}	Z	K	MPa	kg·m^{-3}	Z	K	MPa	kg·m^{-3}	Z	K	MPa	kg·m^{-3}	Z
230.010	65.713	1646.78	2.522 74	298.145	13.586	1373.19	0.482 53	319.987	3.104	1241.42	0.113 63	374.977	6.229	1002.85	0.240 85
230.010	56.454	1634.26	2.183 87	298.144	7.446	1344.93	0.270 02	319.985	2.766	1238.35	0.101 50	374.975	5.508	978.01	0.218 39
230.009	44.014	1615.50	1.722 44	298.145	6.211	1338.49	0.226 30	319.986	2.754	1234.20	0.101 40	374.974	4.814	875.16	0.213 31
230.009	28.639	1589.11	1.139 36	298.144	5.516	1334.74	0.201 55	349.986	64.884	1415.65	1.904 28	399.967	69.092	1339.90	1.874 72
230.008	15.789	1563.93	0.638 26	298.141	4.872	1331.18	0.178 51	349.982	61.425	1407.04	1.813 82	399.965	62.308	1320.05	1.716 07
230.009	8.318	1547.23	0.339 89	298.142	4.132	1326.95	0.151 88	349.981	55.114	1390.72	1.646 56	399.967	55.491	1298.22	1.553 99
230.010	3.674	1536.02	0.151 22	298.142	3.449	1322.91	0.127 15	349.983	48.408	1371.52	1.466 47	399.967	48.446	1272.44	1.384 21
230.014	3.188	1534.86	0.131 33	298.143	3.104	1320.81	0.114 62	349.983	41.906	1350.76	1.289 01	399.969	41.281	1242.15	1.208 23
230.018	2.573	1533.30	0.106 08	298.147	2.778	1318.79	0.102 74	349.982	34.580	1324.58	1.084 68	399.971	34.348	1207.68	1.034 02
269.998	65.145	1564.96	2.241 90	298.141	2.407	1316.46	0.089 17	349.979	27.411	1294.63	0.879 70	399.970	27.341	1164.91	0.853 28
270.002	56.409	1549.99	1.960 00	298.145	2.069	1314.31	0.076 77	349.979	21.094	1262.99	0.693 95	399.969	20.693	1111.34	0.676 95
270.005	46.015	1530.41	1.619 28	298.143	1.998	1313.82	0.074 15	349.981	13.898	1217.04	0.474 48	399.968	14.186	1033.46	0.499 06
270.003	35.631	1508.68	1.271 94	298.145	1.816	1312.12	0.067 52	349.979	7.031	1152.33	0.253 53	399.967	10.139	951.31	0.387 50
269.997	25.912	1485.54	0.939 42	319.986	69.846	1482.48	2.141 03	349.979	6.332	1143.41	0.230 08	399.970	7.340	834.92	0.319 60
270.004	16.889	1460.69	0.622 69	319.992	62.362	1466.93	1.931 85	349.980	5.545	1132.59	0.203 41	399.972	6.401	747.38	0.311 38
269.997	8.340	1433.25	0.313 40	319.993	55.504	1451.81	1.737 30	349.977	4.871	1122.27	0.180 33	424.964	69.519	1300.26	1.829 46
270.001	4.011	1417.01	0.152 45	319.992	48.470	1434.61	1.535 32	349.981	4.147	1109.87	0.155 23	424.962	62.269	1276.87	1.668 69
270.002	3.431	1414.69	0.130 60	319.992	41.353	1415.60	1.327 49	374.975	67.597	1378.93	1.901 01	424.962	55.546	1252.47	1.517 52
270.000	2.973	1412.68	0.113 34	319.991	34.435	1395.04	1.121 69	374.975	61.916	1363.67	1.760 73	424.959	48.489	1223.50	1.356 11
269.999	2.501	1410.75	0.095 48	319.993	27.565	1371.78	0.913 13	374.972	55.245	1344.15	1.593 84	424.959	41.522	1190.20	1.193 74
298.143	68.788	1519.84	2.207 46	319.990	20.780	1345.44	0.701 87	374.971	48.370	1321.88	1.419 03	424.965	34.546	1150.21	1.027 71
298.145	62.801	1508.47	2.030 51	319.987	13.920	1313.37	0.481 62	374.971	41.104	1295.20	1.230 70	424.964	27.408	1098.36	0.853 86
298.143	56.117	1495.00	1.830 76	319.989	7.562	1275.80	0.269 36	374.971	34.445	1266.81	1.054 45	424.963	20.813	1032.51	0.689 76
298.142	49.512	1480.56	1.631 03	319.988	6.166	1266.03	0.221 34	374.974	27.568	1232.43	0.867 45	424.968	14.133	923.74	0.523 51
298.143	42.035	1462.99	1.401 36	319.986	5.572	1261.65	0.200 71	374.975	20.821	1189.97	0.678 53	424.966	10.657	816.56	0.446 57
298.146	34.987	1444.72	1.181 12	319.987	4.847	1256.00	0.175 38	374.974	13.897	1130.11	0.476 88	424.965	7.204	553.31	0.445 51
298.142	27.332	1422.41	0.937 19	319.985	4.162	1250.48	0.151 25	374.974	7.507	1035.79	0.281 07	424.963	5.213	299.90	0.594 80
298.146	21.044	1401.76	0.732 20	319.987	3.451	1244.44	0.126 04								

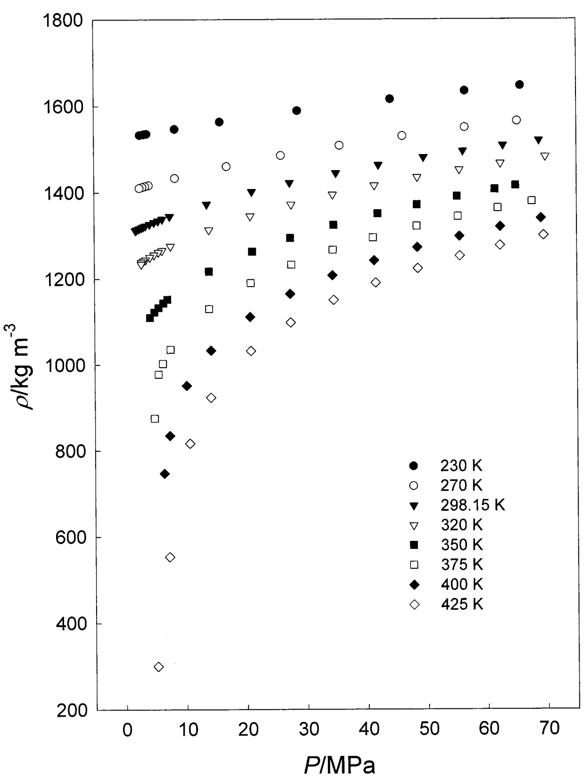

Figure 1. Experimental liquid density measurements.

gas chromatography indicated purities better than 99.95% and 99.5% for R-11 and R-13, respectively. Two mixtures prepared gravimetrically had an overall uncertainty of 0.1% with the final compositions being x_{R11} = 49.98% (mixture 1) and x_{R11} = 49.46% (mixture 2).

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 liquid densities. The value for the gas constant is R = 8.314 51 J·mol^{-1}·K^{-1}, and the molar masses (M) of R-11 and R-13 are (137.369 and 104.459) g·mol^{-1}, respectively. Table 2 contains the experimental enthalpy increments together with the inlet and outlet temperatures. Although no high-pressure data exist for this mixture, we believe the measurements are valuable for testing and developing new equations and correlations that involve these components.

Table 2. Experimental Enthalpy Increments for R-11 (x = 0.4946) + R-13 (1 − x)

T_{inlet}	T_{outlet}	P	ΔH	T_{inlet}	T_{outlet}	P	ΔH
K	K	MPa	J·g^{-1}	K	K	MPa	J·g^{-1}
231.991	298.151	6.628	−59.91	448.729	298.224	6.641	185.28
265.032	298.148	6.693	−29.25	455.881	298.234	6.621	197.06
351.336	298.189	6.571	52.46	460.769	298.246	6.612	203.61
372.504	298.196	6.613	76.13	265.461	298.148	4.594	−29.45
407.245	298.234	6.621	124.61	357.608	298.195	4.414	62.06
417.712	298.232	6.652	142.68				

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