# Experimental $P-T-\rho$ and Enthalpy-Increment Measurements of Trichlorofluoromethane, R-11 ($x$ = 0.83), + Chlorodifluoromethane, R-22 (1 − $x$)

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We have measured experimental liquid densities for R-11 ($x$ = 0.83 nominal) + R-22 (1 − $x$) using a continuously weighed pycnometer (for liquid densities) and a semi automated, isochoric apparatus (for measurements in the vapor and liquid regions). We calculate phase boundaries from the isochoric measurements. A thermoelectric flow calorimeter was used to measure enthalpy differences in the vapor and liquid regions. The temperature range for all measurements is (230 to 425) K. The experimental pressures range up to 69 MPa for the pycnometer, 9 MPa for the isochoric apparatus, and 6.5 MPa for the calorimeter.

## Introduction

Accurate density, isochoric, and enthalpy measurements for fluids are essential for developing equations of state, and they are important for the design, operation, and efficiency of industrial plants. Although production of trichlorofluoromethane (R-11) and chlorodifluoromethane (R-22) is not generally permitted because they may cause ozone depletion, experimental measurements for mixtures of R-11 and R-22 are important for understanding polar contributions to equations of state. Jacobsen et al.[1] and Wagner et al.[2] have reported measurements using the chlorofluoromethanes considered in this work. Meskel-Lesavre et al.[3] have measured equilibrium properties in the liquid region for R-11 + R-22 mixtures.

In this work, we have used a pycnometer, an isochoric apparatus, a fast Burnett apparatus, and a calorimeter to measure the densities, phase boundaries, and enthalpy increments for the mixture R-11 ($x$ = 0.83 nominal) + R-22 (1 − $x$) from 230 to 425 K. The maximum measured pressures in the pycnometer, the isochoric apparatus, and the calorimeter are (69, 9, and 6.5) MPa, respectively.

## Experimental Section

***Continuously Weighed Pycnometer.*** The pycnometer consists of a sample cell with a known volume suspended from an electronic balance. The internal volume of the cell is approximately 10 $cm^3$. Lau et al.[4] provide a detailed description of the apparatus. Paroscientific Inc. and Rosemount Inc. transducers calibrated using a dead weight gauge measure the pressures. The accuracy of the pressure transducers after calibration is ±0.008 MPa. A MINCO Products Inc. four-lead platinum resistance thermometer located adjacent to the sample cell measures temperatures. Temperature control is within ±0.002, and the thermometer calibration is better than ±0.005 on the IPTS-68. We report temperatures on the ITS-90. The uncertainties in the density measurements arise from errors in observables and from the cell volume calibration. An extensive calibration with water indicates an error in the cell volume calibration of about ±0.04%. The estimated accuracy within 95% confidence limits is[4]

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

or

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

where the units of $\rho$ are kilograms per cubic meter.

***Isochoric Apparatus.*** Yurttas et al.[5] provide a detailed description of the apparatus. The apparatus consists of an isochoric cell made of high strength beryllium−copper alloy (Be−Cu 175). A diaphragm differential pressure transducer is in the upper part of the cell, enabling pressure measurements using a dead weight gauge. Nitrogen is the medium between the dead weight gauge and the diaphragm. The accuracy of the gauge is better than 0.01%. An Ideal-Aerosmith Inc. (model 11-11-60) mercury barometer measures atmospheric pressures better than ±0.003 kPa. A Leeds and Northrup 25 Ω platinum resistance thermometer mounted in the isochoric cell was used to measure temperature. The thermometer (calibrated for the manufacturer) has an accuracy better than ±0.003 K with respect to the IPTS-68. We report temperatures on the ITS-90. Because one characteristic of this apparatus is rapid temperature stabilization, Yurttas et al.[5] use digital control for temperature acquisition. The temperature and pressure dependence of the cell volume using $CO_2$ as a calibrating fluid is

$$V/V_0 = 1 + (5.264 \times 10^{-5})(T - T_0) + (2.727 \times 10^{-11})(P - P_0)$$

where $T$ is in kelvin and $P$ is in bar. The pressure coefficient is the elastic modulus of Be−Cu 175 while the temperature

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**Table 1. Experimental Temperatures, Pressures, Densities, and $Z$-Factors for R-11 ($x$ = 0.8336) + R-22 (1 − $x$)**

| $T$ | $P$ | $\rho$ | | $T$ | $P$ | $\rho$ | | $T$ | $P$ | $\rho$ | | $T$ | $P$ | $\rho$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| K | MPa | $kg \cdot m^{-3}$ | $Z$ | K | MPa | $kg \cdot m^{-3}$ | $Z$ | K | MPa | $kg \cdot m^{-3}$ | $Z$ | K | MPa | $kg \cdot m^{-3}$ | $Z$ |
| 230.009 | 65.2520 | 1686.03 | 2.608 47 | 298.144 | 49.0691 | 1542.62 | 1.653 97 | 319.987 | 1.0876 | 1380.16 | 0.038 18 | 374.977 | 1.8020 | 1206.68 | 0.061 74 |
| 230.018 | 51.6290 | 1672.95 | 2.079 94 | 298.148 | 42.2238 | 1531.13 | 1.433 89 | 319.987 | 0.6907 | 1378.66 | 0.024 27 | 374.981 | 1.5927 | 1204.96 | 0.054 65 |
| 230.019 | 38.5126 | 1657.76 | 1.565 74 | 298.147 | 35.2949 | 1518.86 | 1.208 28 | 349.987 | 68.2312 | 1479.10 | 2.043 32 | 399.967 | 63.2135 | 1383.07 | 1.771 51 |
| 230.003 | 25.8603 | 1641.63 | 1.061 76 | 298.147 | 27.6336 | 1504.00 | 0.955 35 | 349.979 | 62.6770 | 1469.23 | 1.889 64 | 399.971 | 56.2812 | 1366.92 | 1.595 86 |
| 230.012 | 12.7068 | 1623.40 | 0.527 55 | 298.145 | 21.1800 | 1490.62 | 0.738 81 | 349.981 | 56.5656 | 1457.80 | 1.718 75 | 399.965 | 49.1523 | 1348.85 | 1.412 41 |
| 230.014 | 3.6373 | 1609.58 | 0.152 31 | 298.146 | 14.2555 | 1474.84 | 0.502 59 | 349.983 | 49.5713 | 1443.89 | 1.520 73 | 399.975 | 41.8879 | 1328.37 | 1.222 19 |
| 230.007 | 3.0670 | 1608.63 | 0.128 50 | 298.147 | 7.0604 | 1456.68 | 0.252 02 | 349.983 | 42.5321 | 1428.61 | 1.318 74 | 399.968 | 35.3542 | 1307.71 | 1.047 87 |
| 230.009 | 2.6899 | 1608.01 | 0.112 75 | 298.146 | 3.5411 | 1447.03 | 0.127 24 | 349.984 | 35.5961 | 1412.26 | 1.116 46 | 399.971 | 28.4907 | 1283.14 | 0.860 60 |
| 230.007 | 2.3744 | 1607.47 | 0.099 56 | 298.141 | 3.0324 | 1445.59 | 0.109 07 | 349.985 | 27.7030 | 1391.72 | 0.881 72 | 399.969 | 21.5232 | 1253.75 | 0.665 38 |
| 230.011 | 2.0333 | 1606.97 | 0.085 28 | 298.142 | 2.7282 | 1444.75 | 0.098 19 | 349.981 | 20.9068 | 1371.66 | 0.675 15 | 399.971 | 14.5262 | 1217.33 | 0.462 51 |
| 230.016 | 1.6913 | 1606.39 | 0.070 96 | 298.149 | 2.4094 | 1443.80 | 0.086 77 | 349.984 | 14.2871 | 1349.36 | 0.469 00 | 399.962 | 7.5365 | 1168.49 | 0.249 99 |
| 230.013 | 1.0040 | 1605.02 | 0.042 16 | 298.148 | 2.3813 | 1443.01 | 0.085 81 | 349.980 | 7.4573 | 1322.34 | 0.249 80 | 399.968 | 5.3339 | 1148.20 | 0.180 06 |
| 230.013 | 0.6685 | 1604.47 | 0.028 08 | 298.145 | 2.1131 | 1442.22 | 0.076 18 | 349.988 | 3.5776 | 1304.32 | 0.121 49 | 399.970 | 3.8385 | 1132.14 | 0.131 41 |
| 269.997 | 62.2106 | 1601.52 | 2.230 37 | 298.143 | 1.7724 | 1441.18 | 0.063 95 | 349.977 | 3.0919 | 1301.88 | 0.105 20 | 399.970 | 3.4599 | 1127.62 | 0.118 93 |
| 270.003 | 55.5347 | 1592.86 | 2.001 81 | 298.149 | 1.3835 | 1440.04 | 0.049 95 | 349.984 | 2.7474 | 1300.08 | 0.093 61 | 399.969 | 3.1010 | 1123.20 | 0.107 01 |
| 269.999 | 48.8942 | 1583.80 | 1.772 55 | 298.143 | 1.0691 | 1439.09 | 0.038 63 | 349.976 | 2.4089 | 1298.31 | 0.082 19 | 399.975 | 2.7912 | 1119.29 | 0.096 65 |
| 269.993 | 41.9329 | 1573.88 | 1.529 80 | 298.147 | 0.7177 | 1438.05 | 0.025 95 | 349.975 | 2.0813 | 1296.63 | 0.071 10 | 399.976 | 2.4389 | 1114.58 | 0.084 81 |
| 269.995 | 35.2708 | 1563.81 | 1.295 03 | 298.147 | 0.3902 | 1436.97 | 0.014 12 | 349.981 | 1.7691 | 1294.97 | 0.060 51 | 399.976 | 2.3790 | 1111.44 | 0.082 96 |
| 270.004 | 27.4671 | 1551.32 | 1.016 59 | 319.985 | 66.5139 | 1534.42 | 2.100 11 | 349.980 | 1.4184 | 1293.05 | 0.048 59 | 424.962 | 65.3445 | 1352.80 | 1.762 09 |
| 269.994 | 21.5612 | 1541.21 | 0.803 27 | 319.990 | 62.5951 | 1523.41 | 1.990 63 | 349.975 | 1.0873 | 1291.23 | 0.037 30 | 424.972 | 61.9799 | 1344.58 | 1.681 54 |
| 270.002 | 14.7265 | 1528.68 | 0.553 12 | 319.988 | 56.5488 | 1513.51 | 1.810 12 | 374.972 | 67.4383 | 1430.60 | 1.948 92 | 424.969 | 56.2825 | 1329.70 | 1.544 07 |
| 269.997 | 7.6253 | 1514.59 | 0.289 07 | 319.985 | 49.6034 | 1501.44 | 1.600 58 | 374.974 | 63.2011 | 1422.20 | 1.837 24 | 424.965 | 49.6616 | 1310.90 | 1.381 98 |
| 269.996 | 3.8545 | 1506.62 | 0.146 90 | 319.987 | 42.2178 | 1486.74 | 1.375 72 | 374.974 | 56.1183 | 1407.35 | 1.648 56 | 424.967 | 42.7384 | 1289.02 | 1.209 50 |
| 270.001 | 3.1300 | 1505.05 | 0.119 41 | 319.987 | 35.1801 | 1473.50 | 1.156 69 | 374.972 | 48.9359 | 1391.15 | 1.454 31 | 424.967 | 35.7003 | 1263.74 | 1.030 53 |
| 269.999 | 2.7081 | 1504.16 | 0.103 37 | 319.985 | 27.6303 | 1456.91 | 0.918 81 | 374.974 | 42.2120 | 1374.59 | 1.269 60 | 424.967 | 27.9003 | 1230.65 | 0.827 03 |
| 269.995 | 2.4100 | 1503.54 | 0.092 03 | 319.986 | 20.9363 | 1440.83 | 0.703 98 | 374.967 | 35.1882 | 1355.43 | 1.073 32 | 424.964 | 20.7444 | 1193.05 | 0.634 30 |
| 269.993 | 2.0968 | 1502.82 | 0.080 11 | 319.989 | 13.9928 | 1422.16 | 0.476 68 | 374.970 | 27.8440 | 1332.88 | 0.863 67 | 424.967 | 14.2028 | 1148.26 | 0.451 21 |
| 270.004 | 1.7420 | 1502.02 | 0.066 59 | 319.987 | 7.3684 | 1402.12 | 0.254 60 | 374.972 | 21.5665 | 1310.86 | 0.680 19 | 424.965 | 7.3315 | 1077.17 | 0.248 29 |
| 269.997 | 1.3838 | 1501.23 | 0.052 93 | 319.987 | 3.8052 | 1390.08 | 0.132 62 | 374.970 | 14.0510 | 1279.66 | 0.453 96 | 424.967 | 6.1694 | 1059.78 | 0.212 36 |
| 269.999 | 1.0810 | 1500.54 | 0.041 36 | 319.989 | 3.1658 | 1387.81 | 0.110 52 | 374.975 | 7.5193 | 1245.72 | 0.249 55 | 424.967 | 5.4574 | 1047.58 | 0.190 04 |
| 269.999 | 0.6960 | 1499.67 | 0.026 65 | 319.987 | 2.7260 | 1386.19 | 0.095 27 | 374.978 | 3.5008 | 1219.67 | 0.118 67 | 424.968 | 4.8530 | 1035.91 | 0.170 90 |
| 270.000 | 0.3780 | 1498.95 | 0.014 48 | 319.984 | 2.4199 | 1385.12 | 0.084 64 | 374.971 | 3.1169 | 1216.83 | 0.105 90 | 424.963 | 4.5179 | 1028.76 | 0.160 20 |
| 298.148 | 67.8697 | 1570.81 | 2.246 59 | 319.987 | 2.0544 | 1383.74 | 0.071 93 | 374.973 | 2.7811 | 1214.30 | 0.094 69 | 424.966 | 4.1902 | 1021.29 | 0.149 67 |
| 298.144 | 63.1350 | 1564.13 | 2.098 82 | 319.987 | 1.7211 | 1382.53 | 0.060 31 | 374.973 | 2.4545 | 1211.80 | 0.083 74 | 424.963 | 3.8543 | 1012.94 | 0.138 81 |
| 298.148 | 56.4754 | 1554.44 | 1.889 11 | 319.984 | 1.4194 | 1381.39 | 0.049 78 | 374.974 | 2.1404 | 1209.34 | 0.073 17 | 424.971 | 3.5927 | 1005.84 | 0.130 30 |

coefficient differs by 10% from the thermal expansion of Be−Cu 175. Nevertheless, this value agrees with the value reported by Lau.[6]

***Flow Calorimeter.*** Castro-Gomez et al.[7] provide the detailed design and operating characteristics for this apparatus. The apparatus measures the enthalpy increments of a fluid flowing with constant mass flow rate at an inlet temperature, $T_{inlet}$, and at outlet temperature, $T_{outlet}$, at constant pressure. The enthalpy increment is a function of the difference in power provided by an electric heater under flow and nonflow conditions,

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

where $H$ is the enthalpy, $P$ is the pressure, $\Delta \dot{W}$ is the power difference, and $\dot{m}$ is the mass flow rate. Thermistors calibrated within ±0.005 K using a platinum resistance thermometer traceable to NIST measure the inlet and outlet temperatures. 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, respectively. Both transducers have a linear response to hysteresis of less than ±0.2% of full scale at their low-pressure limits. During runs, pressure fluctuations are less than ±0.005 MPa. We calculate flow rate by measuring the mass of the discharged fluid as a function of time. Measurements are accurate to 0.01 g with reproducibility for the mass flow rate of 0.3%. The overall accuracy of the enthalpy differences is 0.6 $J \cdot g^{-1}$.

***Fast Burnett Apparatus.*** Leonard[9] provides a detailed design description of this apparatus. Its main characteristic is that it can function as a gasometer to determine high-pressure compressibility factors and as a Burnett apparatus capable of rapid measurements. This apparatus includes three cells: 10 $cm^3$ (high-pressure cell), 1200 $cm^3$ (low-pressure cell), and 600 $cm^3$ (Burnett cell). The first cell is Hastelloy C-276, a corrosion-resistant nickel alloy, and the other two are aluminum 6063. The high-pressure cell uses a Transducer Technologies quartz capacitance pressured transducer calibrated with a precision of 10 kPa for pressure measurement. A differential pressure indicator (DPI) connected to a Ruska quartz bourdon tube gauge measures pressures in the Burnett cells. After calibration, the accuracy of the pressure measurements is within 0.07%. A MINCO Products Inc. four-lead platinum resistance thermometer was used to measure temperature. The thermometer calibration is better than ±0.010 K compared to the IPTS-68.

***Chemicals.*** We purchased purified trichlorofluoromethane (R-11) and chlorodifluoromethane (R-22) from Scientific Gas Products Inc. The stated purity for both refrigerants was 99.9%. We removed dissolved air from the samples by freezing them and reducing the pressure to 1 Pa. Analyses of the samples using gas chromatography indicated purities better than 99.95% and 99.9% for R-11 and R-22, respectively. We prepared four mixtures gravimetrically with an overall uncertainty in mole fraction of 0.1%. The final compositions of the different mixtures were as follows:

Mixture 1 (liquid density measurements):
R-11 = 0.8336, R-22 = 0.1664

Mixture 2 (isochoric measurements):
R-11 = 0.8320, R-22 = 0.1680

Mixture 3 (enthalpy measurements):
R-11 = 0.8294, R-22 = 0.1706

Mixture 4 (enthalpy measurements):
R-11 = 0.8310, R-22 = 0.1690

**Table 2. Fast Burnett Expansions for R-11 ($x$ = 0.832) + R-22 (1 − $x$)**

| | $T$ | $P$ | $P^{calc}$ | $\rho$ | |
|---|---|---|---|---|---|
| isotherm | K | MPa | MPa | kg·m$^{-3}$ | $Z$ |
| I-a | 374.971 | 0.712 23 | 0.712 16 | 33.1519 | 0.887 58 |
| | 374.976 | 0.523 72 | 0.523 72 | 23.5280 | 0.919 71 |
| | 374.979 | 0.381 00 | 0.380 93 | 16.6977 | 0.942 59 |
| | 374.980 | 0.275 03 | 0.275 03 | 11.8505 | 0.958 90 |
| | 374.977 | 0.197 47 | 0.197 60 | 8.4097 | 0.970 83 |
| | 374.976 | 0.141 34 | 0.141 41 | 5.9685 | 0.978 93 |
| | 379.977 | 0.100 73 | 0.100 94 | 4.2353 | 0.984 71 |
| I-b | 374.972 | 0.705 75 | 0.705 82 | 32.8139 | 0.888 73 |
| | 374.977 | 0.518 62 | 0.518 83 | 23.2877 | 0.920 51 |
| | 374.978 | 0.377 56 | 0.377 28 | 16.5279 | 0.943 14 |
| | 374.975 | 0.272 55 | 0.272 34 | 11.7304 | 0.959 26 |
| | 374.975 | 0.195 81 | 0.195 60 | 8.3248 | 0.970 82 |
| | 374.974 | 0.140 10 | 0.140 03 | 5.9076 | 0.979 38 |
| | 374.975 | 0.099 90 | 0.099 97 | 4.1920 | 0.985 36 |
| I-c | 374.967 | 0.775 25 | 0.775 11 | 36.5414 | 0.876 44 |
| | 374.972 | 0.572 06 | 0.572 19 | 25.9340 | 0.911 62 |
| | 374.981 | 0.417 41 | 0.417 34 | 18.4053 | 0.936 86 |
| | 374.976 | 0.301 92 | 0.301 85 | 13.0615 | 0.954 85 |
| | 374.975 | 0.216 98 | 0.217 12 | 9.2699 | 0.967 72 |
| | 374.974 | 0.155 55 | 0.155 55 | 6.5788 | 0.976 89 |
| II-a | 424.969 | 1.317 45 | 1.317 45 | 55.8677 | 0.859 71 |
| | 424.966 | 0.977 19 | 0.977 26 | 39.6298 | 0.899 02 |
| | 424.959 | 0.715 19 | 0.715 26 | 28.1109 | 0.927 64 |
| | 424.968 | 0.518 76 | 0.518 62 | 19.9414 | 0.948 15 |
| | 424.964 | 0.373 90 | 0.373 56 | 14.1459 | 0.962 74 |
| | 424.963 | 0.268 07 | 0.267 93 | 10.0340 | 0.973 49 |
| | 424.963 | 0.191 33 | 0.191 47 | 7.1170 | 0.980 80 |
| | 424.965 | 0.136 17 | 0.136 58 | 5.0490 | 0.986 23 |
| II-b | 424.965 | 1.085 99 | 1.085 72 | 44.6324 | 0.886 85 |
| | 424.965 | 0.797 38 | 0.797 86 | 31.6606 | 0.918 74 |
| | 424.973 | 0.580 12 | 0.580 12 | 22.4579 | 0.941 73 |
| | 424.961 | 0.418 92 | 0.418 79 | 15.9304 | 0.958 41 |
| | 424.967 | 0.300 89 | 0.300 68 | 11.3011 | 0.969 99 |
| | 424.969 | 0.215 05 | 0.215 18 | 8.0157 | 0.978 70 |
| | 424.969 | 0.153 48 | 0.153 55 | 5.6866 | 0.984 39 |
| II-c | 424.964 | 0.567 37 | 0.567 37 | 21.9341 | 0.943 04 |
| | 424.969 | 0.409 41 | 0.409 41 | 15.5588 | 0.959 32 |
| | 424.963 | 0.293 85 | 0.293 92 | 11.0367 | 0.970 91 |
| | 424.963 | 0.210 50 | 0.210 22 | 7.8282 | 0.979 03 |
| | 424.972 | 0.150 03 | 0.150 03 | 5.5536 | 0.984 87 |
| | 424.962 | 0.106 80 | 0.106 87 | 3.9390 | 0.989 14 |
| | 424.962 | 0.076 05 | 0.076 05 | 2.7936 | 0.992 46 |
| III-a | 474.997 | 12.412 88 | 12.431 43 | 958.8677 | 0.422 87 |
| | 474.998 | 5.875 08 | 5.857 15 | 503.9422 | 0.379 10 |
| | 474.992 | 4.708 08 | 4.705 53 | 264.7859 | 0.579 65 |
| | 474.994 | 3.211 71 | 3.207 71 | 139.0887 | 0.752 23 |
| | 474.992 | 1.933 08 | 1.931 63 | 73.0924 | 0.861 99 |
| | 474.988 | 1.081 51 | 1.089 30 | 38.4124 | 0.924 98 |
| | 474.987 | 0.590 67 | 0.593 84 | 20.1833 | 0.959 70 |
| III-b | 475.012 | 13.484 40 | 13.452 89 | 988.8223 | 0.443 74 |
| | 475.000 | 5.905 76 | 5.913 55 | 518.0384 | 0.372 33 |
| | 474.951 | 4.750 00 | 4.758 75 | 271.5137 | 0.571 73 |
| | 474.977 | 3.255 77 | 3.257 77 | 142.1802 | 0.747 38 |
| | 474.977 | 1.965 55 | 1.962 93 | 74.5021 | 0.859 41 |
| | 474.974 | 1.107 99 | 1.105 43 | 39.0371 | 0.923 68 |
| | 474.978 | 0.601 70 | 0.601 29 | 20.4396 | 0.959 56 |
| | 474.980 | 0.322 47 | 0.321 23 | 10.7116 | 0.978 18 |
| III-c | 474.981 | 13.635 05 | 13.633 94 | 993.7880 | 0.447 49 |
| | 474.981 | 5.920 10 | 5.932 03 | 522.5236 | 0.370 30 |
| | 474.977 | 4.786 81 | 4.784 75 | 274.8775 | 0.567 78 |
| | 474.975 | 3.296 58 | 3.294 24 | 144.5029 | 0.743 61 |
| | 474.975 | 1.995 20 | 1.995 48 | 75.9597 | 0.856 90 |
| | 474.985 | 1.126 12 | 1.129 15 | 39.9341 | 0.922 28 |

**Table 3. Virial Coefficients for R-11 ($x$ = 0.832) + R-22 (1 − $x$)**

| $T$ | $B_m$ | $C_m$ | $D_m$ |
|---|---|---|---|
| K | cm$^3$·mol$^{-1}$ | cm$^6$·mol$^{-2}$ | cm$^9$·mol$^{-3}$ |
| 375 | −441.2 ± 3.1 | 25 585[a] | |
| 425 | −336.2 ± 1.7 | 31 860[a] | |
| 475 | −257.2 ± 2.5 | 26 425 ± 10% | −301 109 |

[a] Estimated using the Orbey and Vera[12] correlation.

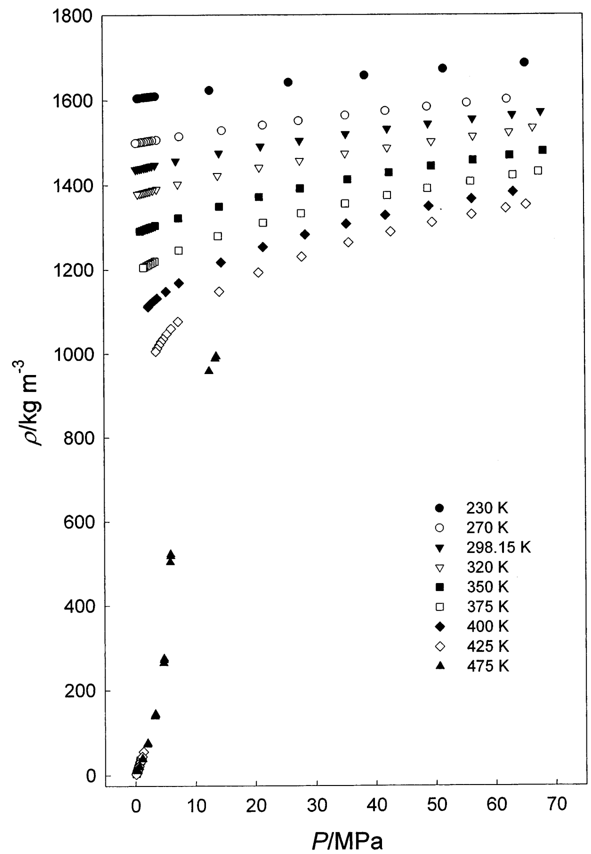


**Figure 1.** Isothermal density measurements using a pycnometer and a Burnett apparatus.

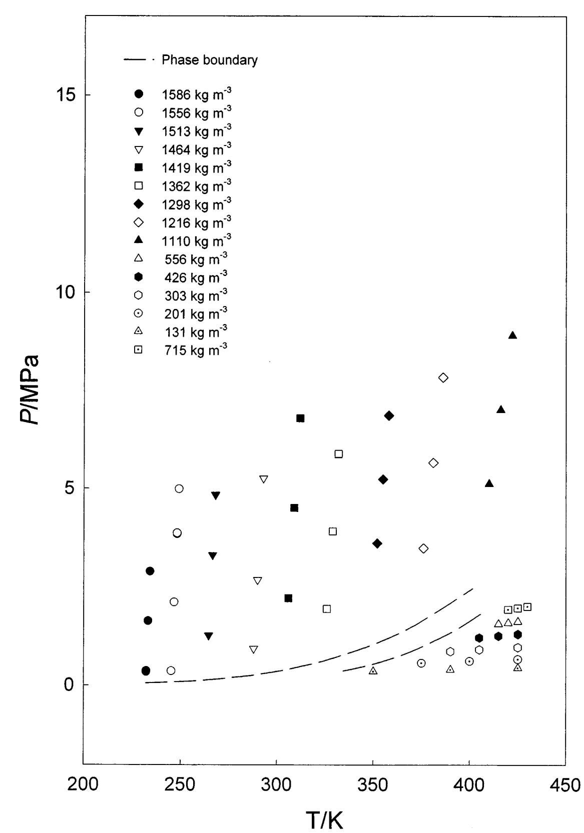


**Figure 2.** Experimental isochoric measurements.

## Results and Conclusions

Experimental pressures ($P$), temperatures ($T$), mass densities ($\rho$), and compression factors ($Z = MP/RT\rho$) for mixture 1 from (230 to 425) K at pressures up 69 MPa are presented in Table 1. The value for the gas constant is $R$

**Table 4. Experimental Isochoric Measurements for R-11 ($x$ = 0.832) + R-22 (1 − $x$)**

| isochore | $T$ / K | $P$ / MPa | $\rho$ / kg·m$^{-3}$ |
|---|---|---|---|
| I | 234.009 | 2.8899 | 1585.673 |
| | 233.007 | 1.6301 | 1585.802 |
| | 232.008 | 0.3679 | 1585.931 |
| | 232.009 | 0.3445 | 1585.932 |
| II | 249.004 | 4.9908 | 1555.677 |
| | 248.005 | 3.8435 | 1555.799 |
| | 246.505 | 2.1066 | 1555.981 |
| | 245.007 | 0.3637 | 1556.164 |
| | 248.007 | 3.8703 | 1555.797 |
| | 248.004 | 3.8655 | 1555.798 |
| III | 268.001 | 4.8301 | 1512.983 |
| | 266.504 | 3.3025 | 1513.151 |
| | 264.503 | 1.2621 | 1513.377 |
| | 268.003 | 4.8464 | 1512.982 |
| IV | 292.996 | 5.2583 | 1463.777 |
| | 289.995 | 2.6700 | 1464.085 |
| | 287.997 | 0.9325 | 1464.291 |
| | 292.996 | 5.2595 | 1463.777 |
| V | 311.989 | 6.7984 | 1419.386 |
| | 308.993 | 4.5086 | 1419.673 |
| | 305.994 | 2.2094 | 1419.961 |
| | 305.992 | 2.2097 | 1419.961 |
| | 311.990 | 6.8001 | 1419.386 |
| VI | 331.985 | 5.8798 | 1362.326 |
| | 328.987 | 3.9119 | 1362.590 |
| | 325.989 | 1.9393 | 1362.854 |
| | 331.986 | 5.8905 | 1362.325 |
| VII | 357.978 | 6.8680 | 1298.305 |
| | 357.979 | 6.8685 | 1298.305 |
| | 354.979 | 5.2393 | 1298.544 |
| | 351.980 | 3.6071 | 1298.784 |
| | 357.979 | 6.8725 | 1298.305 |
| | 357.981 | 6.8765 | 1298.305 |
| VIII | 385.972 | 7.8436 | 1215.660 |
| | 380.974 | 5.6622 | 1216.016 |
| | 375.975 | 3.4811 | 1216.372 |
| | 375.976 | 3.4813 | 1216.372 |
| | 385.974 | 7.8459 | 1215.660 |
| IX | 421.966 | 8.9158 | 1110.383 |
| | 415.966 | 7.0159 | 1110.751 |
| | 409.966 | 5.1217 | 1111.120 |
| X | 424.965 | 1.6172 | 556.221 |
| | 419.964 | 1.5879 | 556.352 |
| | 414.966 | 1.5582 | 556.482 |
| | 424.964 | 1.6192 | 556.221 |
| XI | 424.964 | 1.2984 | 426.053 |
| | 414.966 | 1.2546 | 426.252 |
| | 404.967 | 1.2097 | 426.452 |
| | 424.965 | 1.2994 | 426.053 |
| XII | 424.965 | 0.9672 | 303.998 |
| | 404.968 | 0.9097 | 304.283 |
| | 389.970 | 0.8643 | 304.496 |
| | 424.964 | 0.9690 | 303.998 |
| XIII | 424.965 | 0.6621 | 200.808 |
| | 399.968 | 0.6170 | 201.042 |
| | 374.975 | 0.5690 | 201.277 |
| | 424.964 | 0.6637 | 200.808 |
| XIV | 424.966 | 0.4448 | 131.354 |
| | 389.971 | 0.3997 | 131.569 |
| | 349.982 | 0.3537 | 131.816 |
| | 424.963 | 0.4453 | 131.354 |
| XV | 429.962 | 2.0008 | 715.595 |
| | 429.961 | 2.0006 | 715.595 |
| | 424.963 | 1.9604 | 715.763 |
| | 419.964 | 1.9240 | 715.930 |
| | 429.964 | 2.0024 | 715.595 |

= 8.314 51 J·mol$^{-1}$·K$^{-1}$, and the molar masses ($M$) of R-11 and R-22 are (137.369 and 86.468) g·mol$^{-1}$, respectively. Table 2 contains Burnett data for three isotherms: (375, 425, and 475) K. The first two isotherms come from the fast Burnett apparatus described here while the last isotherm comes from a conventional Burnett apparatus described by Liu et al.[10] Hwang et al.[11] have described the measurement and calculation techniques. Figure 1 presents isothermal density measurements using the pycnometer and Burnett apparatuses. Table 3 contains the second virial coefficients extracted from the data and the third virial coefficients obtained from Orbey and Vera.[12] Table 4 and Figure 2 present the isochoric measurements including the corresponding densities. We assign densities to each isochore using the pycnometer density measurements in the

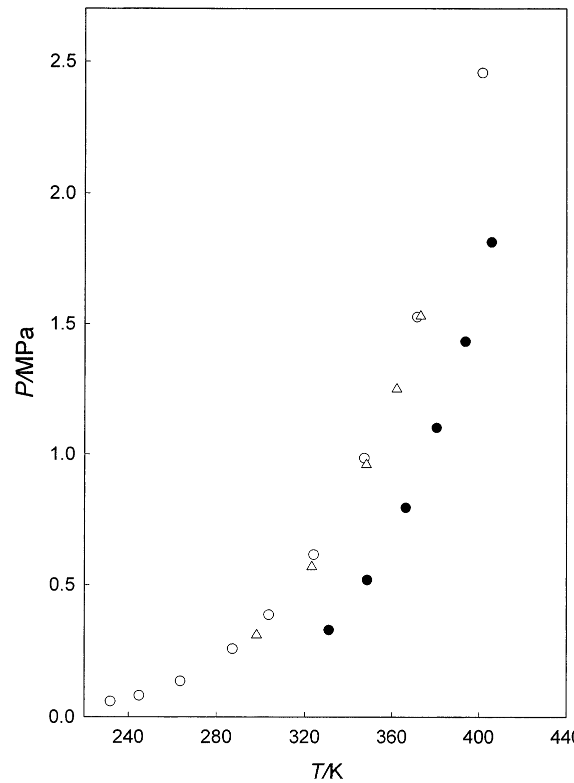


**Figure 3.** Experimental $P-T$ measurements: ○, this work—bubble point measurements; ●, this work—dew point measurements; △, Meskel-Lesavre et al.[3]

**Table 5. Phase Boundary Conditions for R-11 ($x$ = 0.832) + R-22 (1 − $x$)**

| $T$ / K | $P$ / MPa | $\rho$ / kg·m$^{-3}$ | $T$ / K | $P$ / MPa | $\rho$ / kg·m$^{-3}$ |
|---|---|---|---|---|---|
| 231.763 | 0.0595 | 1585.962 | 401.542 | 2.4568 | 1111.637 |
| 244.749 | 0.0814 | 1556.195 | 405.696[a] | 1.8134 | 716.4095 |
| 263.398 | 0.1361 | 1513.501 | 393.749[a] | 1.4330 | 557.0352 |
| 287.214 | 0.2583 | 1464.372 | 380.520[a] | 1.1016 | 426.9404 |
| 303.611 | 0.3876 | 1420.189 | 366.279[a] | 0.7952 | 304.8341 |
| 323.973 | 0.6162 | 1363.031 | 348.513[a] | 0.5202 | 201.5268 |
| 347.156 | 0.9855 | 1299.169 | 330.940[a] | 0.3297 | 131.9332 |
| 371.497 | 1.5271 | 1216.691 | | | |

[a] Vapor phase.

**Table 6. Experimental Enthalpy Increments for R-11 + R-22**

| $T_{inlet}$ / K | $T_{outlet}$ / K | $P$ / MPa | $\Delta H$ / J·g$^{-1}$ | $T_{inlet}$ / K | $T_{outlet}$ / K | $P$ / MPa | $\Delta H$ / J·g$^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | $x_{R11}$ = 0.8294 | | | | |
| 230.291 | 298.155 | 6.408 | −58.99 | 390.656 | 298.186 | 6.528 | 84.18 |
| 231.342 | 298.157 | 6.412 | −57.17 | 393.650 | 298.200 | 6.514 | 88.00 |
| 239.418 | 298.154 | 6.473 | −50.33 | 416.865 | 298.199 | 6.490 | 110.50 |
| 271.589 | 298.150 | 6.512 | −23.07 | 229.692 | 298.153 | 4.423 | −58.16 |
| 341.008 | 298.163 | 6.708 | 38.77 | 269.756 | 298.149 | 4.423 | −23.68 |
| 361.614 | 298.164 | 6.518 | 57.56 | 228.576 | 298.145 | 3.030 | −59.61 |
| 365.572 | 298.174 | 6.498 | 62.38 | 271.854 | 298.148 | 3.458 | −22.78 |
| | | | $x_{R11}$ = 0.8310 | | | | |
| 390.987 | 298.215 | 2.667 | 93.64 | 389.703 | 298.247 | 0.751 | 225.24[a] |
| 392.502 | 298.207 | 3.354 | 94.11 | 390.399 | 298.241 | 1.270 | 216.70[a] |
| 465.649 | 298.238 | 4.721 | 224.21 | 404.861 | 298.237 | 0.737 | 237.09[a] |
| 471.080 | 298.245 | 5.498 | 209.40 | 405.894 | 298.237 | 1.251 | 232.59[a] |
| 472.788 | 298.250 | 6.399 | 188.20 | 456.531 | 298.233 | 3.200 | 245.73[a] |

[a] Vapor phase.

liquid phase and using a virial equation of state in the vapor phase at 425 K. We determine phase boundaries by finding the discontinuities in the slopes of the isochores. Table 5 has the $P-T$ values at the phase boundaries, and Figure 3 shows the phase envelope from this work along with the results for a similar mixture ($x_{R11} = 0.8432$) from Meskel-Lesevre et al.[3] The latter saturated densities agree with our values within 1%, which is within the uncertainty claimed by those authors. Table 6 contains the experimental enthalpy increments together with the inlet and outlet temperatures for mixtures 3 and 4. These measurements are suitable for testing and developing new equations of state.

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