ACKNOWLEDGMENT

The author acknowledges the assistance of Eli Rosenthal in the calculations and Ronald Dixon in collecting the data.

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RECEIVED for review June 5, 1969. Accepted October 17, 1969.

Pressure-Volume-Temperature Relationship for a Mixture of Monochlorotrifluoromethane and Trifluoromethane

The pressure-volume-temperature properties of a 50-50 mole % mixture of monochlorotrifluoromethane and trifluoromethane in the ranges of 14.7 to 74.8 atm., 1.6 to 19.1 cc. per gram, and 298° to 492° K. were correlated, using the Martin-Hou equation of state. Vapor pressures and saturated liquid densities were determined to near the critical temperature (292.6° K.) from 203° and 229.8° K., respectively.

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IN A PROGRAM to supply accurate and reliable data on refrigerants, the authors measured the pressure-volume-temperature properties, vapor pressure, and liquid densities of Refrigerant 503. This refrigerant (*1*), which has a composition of 50-50 mole % trifluoromethane and monochlorotrifluoromethane, forms a minimum-boiling azeotrope at −87.85° C., 1 atm. No published equations correlating the above properties are presently available.

EXPERIMENTAL

Sample Preparation. Each component of the mixture was purified to 99.9 mole % or better, as indicated by gas chromatographic analysis. The bulk mixture being above the critical temperature at 23° C., no segregation problems were encountered upon sampling.

Due to the low freezing point of the mixture, special precautions were taken in degassing the sample to avoid pumping off any refrigerant. During the vapor pressure measurements, the degassing cycles were repeated until reproducible pressure readings were observed.

Temperature Measurements. All temperature measurements were made by a calibrated platinum resistance thermometer (degrees Centigrade, Int. 1948) whose resistance was measured by a Leeds and Northrup Speedomax high-precision resistance recording bridge. Periodically, the accuracy of the recorder was checked with the ice point resistance of the thermometer. The absolute temperature scale is defined as 0° C. = 273.15° K.

Pressure Measurements. All pressure measurements were taken with the *PVT* apparatus described in an earlier paper (*5*).

Vapor Pressure. The term vapor pressure is used here in the general sense, since the composition of the azeotrope does not remain invariant with changes in temperature (*5*). However, accurate vapor pressure data of this mixture can be obtained by taking measurements at the bubble point.

For the vapor pressure measurements, the sample cell was filled to a point which enabled measurement of several data points at close to the bubble point pressure. The data covered the temperature range from 203° to 283° K. (Table I) and is represented by the following equation.

$$\mathrm{Log}_{10}P_{(\mathrm{atm})} = A + B/T + CT + DT^2 \qquad (1)$$

where T is ° K. = 273.15 + t° C.

The constants for Equation 1 are shown in Table I.

This equation has a standard per cent deviation of 0.10 for the experimental data. Extra significant figures have been kept for consistency in computation.

Liquid Density. The saturated liquid densities were determined by a float technique which has been described in detail in an earlier paper (*5*). The data covered the temperature range from 229.8° to 284.2° K.

The equation used to correlate the saturated liquid densities was that of Martin and Hou (*3*).

$$d = d_0 + \sum_{i=1}^{4} A_i\left[\left(1 - \frac{T}{T_c}\right)^{1/3}\right]^i \qquad (2)$$

The constants for Equation 2 and the experimental data are shown in Table II.

***PVT* Measurements.** The range which was covered by the *PVT* data (Table III) is from 298° to 492° K., 1.6 to 19.1 cc. per gram, 14.7 to 75.0 atm. The data, consisting of eight isochors, were fitted with a Martin-Hou equation

Table I. Vapor Pressure

$A = 8.48908$ $\quad C = -1.66749 \times 10^{-2}$
$B = -1.143932 \times 10^3$ $\quad D = 2.25561 \times 10^{-5}$

Temp., °K.	Pressure, Atm. Obsd.	Calcd.	Dev. %[a]
203.15	2.518	2.5205	0.00
223.15	5.818	5.8209	0.00
233.15	8.335	8.3375	0.00
243.15	11.57	11.575	0.00
252.82	15.51	15.502	0.06
258.65	18.32	18.300	0.11
264.19	21.27	21.287	−0.09
273.15	26.84	26.875	−0.11
279.85	31.73	31.729	0.00
283.15	34.38	34.354	0.08

[a] $(P_{obsd.} - P_{calcd.})\, P_{obsd.} \times 100$. The calculated normal boiling point of the mixture, using Equation 1, is −87.85° C.

Table II. Liquid Density

$A_1 = 1.2802$ $\quad A_4 = -2.9158$
$A_2 = -1.6817$ $\quad T_c = 292.65°$ K.
$A_3 = 4.4210$ $\quad d_0 = 0.5640$ gram per cc.

Temp., °K.	Density, Gram per Cc. Obsd.	Calcd.
229.78	1.302	1.3021
248.46	1.201	1.2019
263.73	1.101	1.1001
275.41	1.001	1.0011
284.21	0.900	0.9001

Table III. Pressure-Volume-Temperautre Relationship

Vol., Cc. per Gram	Temp., °K.	Pressure, Atm. Obsd.	Calcd.	% Deviation
1.6438	299.75	51.08	51.174	−0.18
1.6444	307.01	59.48	59.541	−0.10
1.6450	313.39	66.95	66.912	0.08
1.7948	297.78	48.29	48.317	−0.05
1.7953	302.40	53.20	53.080	0.24
1.7957	307.24	58.04	58.060	−0.04
1.7963	313.12	64.09	64.090	0.00
2.1928	297.60	47.03	47.000	0.13
2.1932	300.47	49.35	49.311	0.09
2.1941	308.24	55.59	55.600	−0.01
2.1955	319.97	64.94	64.918	0.04
2.1970	332.43	74.67	74.671	0.00
2.9729	302.55	47.01	47.070	−0.13
2.9754	318.29	55.63	55.663	−0.05
2.9778	333.48	63.65	63.709	−0.09
4.8271	298.20	36.64	36.677	−0.10
4.8336	322.97	43.86	43.917	−0.12
4.8387	342.46	49.30	49.370	−0.14
4.8494	383.62	60.39	60.453	−0.10
4.8598	423.37	70.77	70.826	−0.08
5.9763	310.55	35.42	35.230	0.53
5.9962	372.20	48.47	48.295	0.35
6.0102	415.48	57.19	57.021	0.30
6.0258	464.03	66.66	66.611	0.07
9.2075	301.22	34.37	24.433	−0.27
9.2280	342.55	29.68	29.722	−0.14
9.2532	393.12	35.90	35.897	0.01
9.2776	442.30	41.75	41.750	0.00
9.3024	492.25	47.43	47.614	−0.38
18.9500	323.01	14.69	14.618	0.50
19.0006	372.60	17.41	17.320	0.49
19.0547	425.48	20.26	20.138	0.59
19.1101	479.75	23.07	22.994	0.32

Table IV. Constants for the Martin-Hou Equation of State

$$P_{Atm.} = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2e^{-kT/Tc}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT/Tc}}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{A_5 + B_5T + C^5e^{-kT/Tc}}{(V-b)^5}$$

$R = 0.94056886$ [cc./° K.]/[atm./g.]
$b = 0.3440809$
$K = 5.475$
$T_c = 292.65°$ K.
$A_2 = -9.8902899 \times 10^2$
$B_2 = 1.2327089$
$C_2 = -1.8509064 \times 10^4$
$A_3 = 1.0968311 \times 10^3$
$B_3 = -1.0625844$
$C_3 = 2.9079090 \times 10^4$
$A_4 = -5.8622059 \times 10^2$
$A_5 = -5.8740372 \times 10^1$
$B_5 = 0.8136030$
$C_5 = -6.4500245 \times 10^3$

Table V. Critical Properties

Critical temperature, ° K.	292.6	± 0.1
Critical pressure, atm.	43.00	± 0.07
Critical density, g./cc.	0.564	± 0.001

of state (*2, 4*). The constants for the equation are given in Table IV. The equation fits over the entire temperature-volume range with a standard per cent deviation of 0.27 and an average per cent deviation of 0.17.

Critical Properties. The critical temperature was determined by observation of the meniscus in a sealed glass tube filled approximately one third with liquid at atmospheric pressure. The average value of several observations was 19.5° ± 0.1° C. Extrapolation of the near-critical isochor to the critical temperature determined the critical pressure as 43.00 ± 0.07 atm.

A standard rectilinear diameter plot was used to determine the critical density. Liquid densities were calculated from Equation 2 and saturated vapor densities were calculated from the equation of state. The value obtained was 0.564 gram per cc.

Errors. The uncertainties in the measured variables are estimated to be 0.1% for pressure, 0.01% for temperature, 0.1% for volume, and 0.1% for liquid density.

ACKNOWLEDGMENT

The authors acknowledge the contribution of K. P. Murphy in determining the critical temperature.

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RECEIVED for review July 8, 1969. Accepted November 6, 1969.