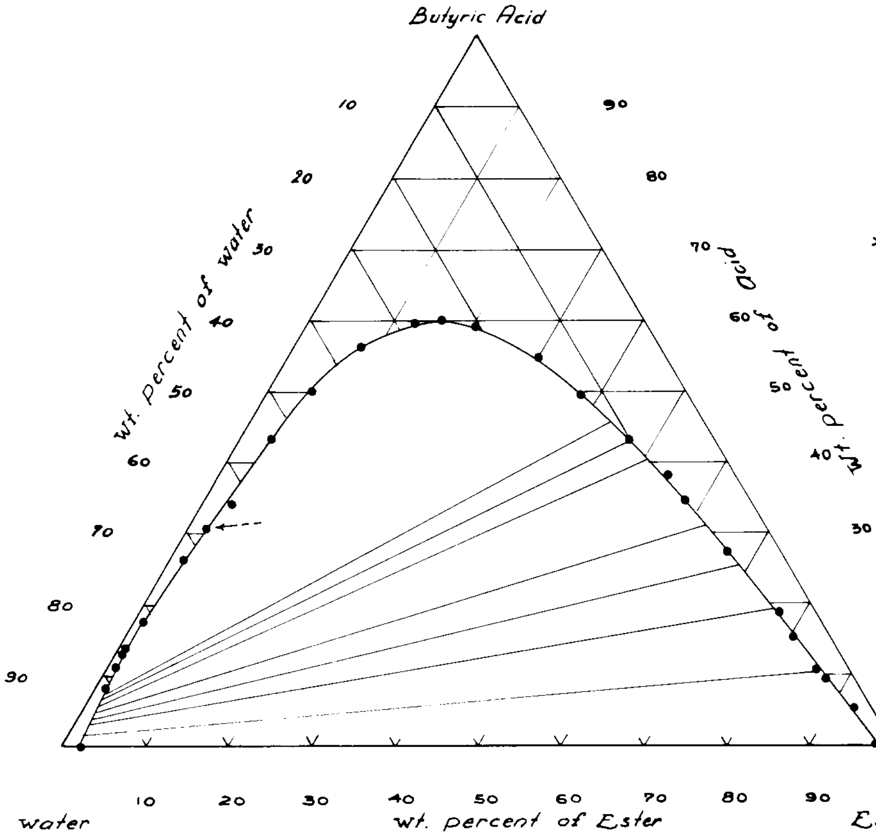

Figure 3. Ternary phase equilibrium diagram for system water–butyric acid–methyl butyrate

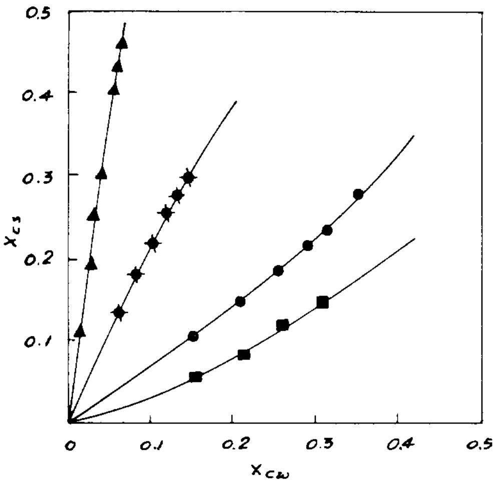

Figure 4. Distribution curves

■ Formic acid (5)

● Acetic acid

✦ Propionic acid

▲ Butyric acid

Figures 1, 2, and 3 show that the region of heterogeneity increases as the solute is changed from acetic to butyric acid. The distribution curves (Figure 4) show that the solute prefers the solvent phase rather than the water phase, when the solute is changed in a homologous series in the increasing order of molecular weight, thus confirming earlier results (*4, 5*).

NOMENCLATURE

C = solute
W = water
S = solvent
X_{cw} = weight fraction of solute in water layer
X_{cs} = weight fraction of solute in ester layer
X_{ww} = weight fraction of water in water layer
X_{ss} = Weight fraction of solvent in solvent layer

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Pressure-Volume-Temperature Behavior of Pentafluoromonochloroethane

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FOR a number of years, this laboratory has investigated the physical and chemical properties of molecules containing fluorine. As a part of this continuing study, both a Benedict-Webb-Rubin and a Martin-Hou equation of state have been obtained for pentafluoromonochloroethane. Vapor pressure and liquid density data have been determined over a wide temperature range. Finally, the rectilinear diameter line has been computed.

MATERIAL

The sample of CF_3CF_2Cl originated from commercially available Genetron 115 (Allied Chemical) with a minimum purity of 98 mole %. Impurities detected by gas chromatography were removed from the sample by distillation in a 5 foot × ½ inch vacuum-jacketed column packed with Helipak. The distillate was collected until the concentra-

The pressure-volume-temperature properties of pentafluoromonochloroethane, in the ranges of 12 to 69 atm., 1.1 to 10.1 cc. per gram, and 313° to 450° K., were correlated using both the Benedict-Webb-Rubin and the Martin-Hou equations of state. Vapor pressure has been determined from 205° to 345.5° K., the measured critical temperature. Densities of liquid have been obtained from 197° K. to near the critical temperature. From this information, the rectilinear diameter line has been computed.

tion of impurities in the vapor began to increase. The sample was then purged of noncondensable gases by freezing it in liquid nitrogen, pumping off any residual gas, closing off the cylinder, and allowing it to reach room temperature. This process was repeated until no pressure was observed on a manometer when the sample was cooled in liquid nitrogen. Final analysis by the gas chromatograph indicates less than 0.05 mole % impurity. Accordingly, the purity was better than 99.9 mole %.

APPARATUS AND EXPERIMENTAL PROCEDURE

The experimental techniques employed for obtaining vapor pressure and vapor density data were similar to those of earlier work (*3*, *8*), except for certain refinements described here.

The equipment was constructed with high pressure fittings throughout and equipped with a 1000-p.s.i. temperature-compensated Heise gage having 1-pound subdivisions. This gage was calibrated, under experimental conditions, against a Harwood dead weight tester, Model 50. This calibration was repeated before and after each run. The average deviation was applied to the pressure reading. For vapor pressures below 300 p.s.i.g., 300- or 50-p.s.i. Heise gages were employed, using the same calibration procedure as above. The accuracy was ±0.5, ±0.3, and ±0.1 p.s.i. for the 1000-, 300-, and 50-p.s.i. gages, respectively. For pressures below 1 atm., the unit was connected to a mercury manometer which had a precision of ±0.2 mm. at 26° C. Measurement of the bomb volume of the equipment from the weight of water contained, plus 2.56 cc. for the included volume of the high pressure fittings, resulted in a total volume of 1055.84 ± 0.10 cc. at 26° C. for the equipment. A cubical coefficient of thermal expansion for stainless steel 304 of $54 \times 10^{-6}\,^\circ C.^{-1}$ served to correct the equipment for temperature changes. Expansion due to pressure is negligible. The resulting accuracy for this volume is ±0.1% or better. An oil thermostat maintained this unit at a temperature constant to ±0.03° C. for measurements at 25° C. and above, while below 25° C. an ethylene glycol–water thermostat held the equipment to the same temperature constancy. A platinum resistance thermometer, calibrated by the National Bureau of Standards, determined the experimental temperatures.

To initiate a vapor pressure or isochor determination, a weighed quantity of CF_3CF_2Cl (100 to 900 grams) was distilled from a tared sample bomb into the apparatus. After the run, the material was distilled back into the tared container and reweighed. The initial and final sample weights agreed within 0.05 gram. In the sample bomb and again in the equipment, the degassing technique, mentioned above, removed noncondensables. Vapor pressure points required a 2-hour equilibrium time, but for vapor density measurements a half hour was adequate. When plotting the isochor data at constant specific volume, we corrected the pressure-temperature points of the actual data by the equation:

$$P_{\text{calcd.}} = P_{\text{obsd.}} \frac{V_{\text{obsd.}}}{V_{\text{isochor}}}$$

where V_{isochor} is the specific volume of the desired plotted isochor and $V_{\text{obsd.}}$ is the specific volume of the data point.

The liquid densities were measured in a high pressure steel pycnometer developed by this laboratory. It consisted of a 200-cc. bomb equipped with a small valve at the bottom for discarding sample and a 6-inch Saran sight tube at the top. A Hoke needle valve above the Saran tube served to fill the equipment. The volume of the bomb, 221.6 cc., was determined from the weight of water it contained. The Saran tube was calibrated from the weight of mercury it held and the level of the meniscus was read with a cathetometer.

To carry out a series of determinations, the pycnometer was thermostated at 0° C. and a quantity of CF_3CF_2Cl sufficient to show a meniscus in the sight tube was distilled into the equipment. Enough time was allowed to attain thermal equilibrium and the volume of the sample was determined. The liquid density points, above room temperature, were determined by direct weighing of the pycnometer. Below room temperature, the sample was transferred into a tared bomb and weighed. Subsequent data were procured by thermostating at successively higher temperatures and removing excess CF_3CF_2Cl through the bleed valve at the bottom, until the liquid meniscus again fell within the marked section of the Saran tubing.

Corrections for the weight of the vapor in the vapor phase in the pyconometer were calculated from the equation of state and the vapor pressure. Calculation from the cubical coefficient of expansion of the steel used, and also experimental measurement, yielded a value of 0.0154 cc. per °C. for the volume increase of the pycnometer with temperature over the experimental temperature range. Because of the small internal volume of the Saran sight tube (1.05 cc.), changes in this volume with temperature and pressure were negligible.

The critical temperature was found by the usual sealed tube technique (*9*).

RESULTS AND DISCUSSION

Both the Benedict-Webb-Rubin (*2*) and the Martin-Hou (*6*) equations of state were used to correlate the *PVT* data. The various constants were evaluated from the data by the least squares technique. The constants and derived equations are given in Table I. The molecular weight used for CF_3CF_2Cl was 154.48. For the molar gas constant, the value used was 82.057 cc. atm./° K. gram mole. The equation defining Kelvin temperatures was: $T\,^\circ K. = T\,^\circ C. + 273.16$. The calculations were carried out on a digital computer. Extra significant figures have been kept for consistency in computation. The underlined digits may be discarded in rounding off the numbers for hand calculation. From the information given above, it can be said that the uncertainty of the input variables for the equations of state is ±0.2% or better for pressure, ±0.05% for the absolute temperature, and ±0.1% or better for the specific volume. The Benedict-Webb-Rubin equation fits the data within a ±0.26% average error, with a 1.1% maximum error. The Martin-Hou equation agrees with the data within an average error of ±0.34% and has a maximum error of 1.2%.

Table I. Equations of State for Pentafluoromonochloroethane

Benedict-Webb-Rubin Equation

$$P_{\text{atm.}} = \frac{RT}{V} + \frac{B_0RT\text{-}A_0\text{-}C_0/T^2}{V^2} + \frac{bRT\text{-}a}{V^3} + \frac{a\alpha}{V^6} + \frac{C}{T^2}\left(\frac{1}{V^3} + \frac{\gamma}{V^5}\right)e^{-\gamma/V^2} \qquad (1)$$

where $R = 0.5311\underline{79}\ \frac{\text{ml. atm.}}{{}^\circ\text{K.} - \text{g.}}$

$A_0 = 8.169\underline{31} \times 10^1$

$B_0 = 0.1124\underline{173}$

$C_0 = 4.06201\underline{8} \times 10^7$

$\alpha = 0.2005247\underline{5}$

$\gamma = 1.22$

$a = 9.21694\underline{3} \times 10^2$

$b = 3.080691\underline{4}$

$c = 7.67597\underline{2} \times 10^7$

Martin-Hou Equation

$$P_{\text{atm}} = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2e^{-kT/Tc}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT/Tc}}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{A_5 + B_5T + C_5e^{-kT/Tc}}{(V-b)^5} \qquad (2)$$

where $R = 0.5311\underline{79}\ \frac{\text{ml. atm.}}{{}^\circ\text{K.} - \text{g.}}$

$T_c = 353.1^\circ$ K.

$b = 0.381351\underline{6}$

$k = 5.475$

$A_2 = -6.72022\underline{8} \times 10^2$

$B_2 = 7.20449\underline{7} \times 10^{-1}$

$C_2 = -8.1281\underline{7} \times 10^3$

$A_3 = 6.76432\underline{6} - 10^2$

$B_3 = -0.512382\underline{9}$

$C_3 = 1.17947\underline{2} \times 10^4$

$A_4 = -3.29904\underline{5} \times 10^2$

$A_5 = 1.3794\underline{99} \times 10^1$

$B_5 = 0.209169\underline{8}$

$C_5 = -1.7427\underline{45} \times 10^3$

Table II. *PVT* Experimental Points, Calculated Points, and Percentage Deviation from Derived Equations for Pentafluoromonochloroethane

			Benedict-Webb-Rubin		Martin-Hou	
Volume, Cc./Gram	Temp., °K.	Obsd. Pres., Atm.	Calcd. pres., atm.	% dev.	Calcd. pres., atm.	% dev.
1.1304	352.69	34.18	34.20	−0.1	34.23	−0.2
1.1307	357.79	40.71	40.73	−0.0	40.69	0.1
1.1310	362.84	47.26	47.26	−0.0	47.23	0.1
1.1313	367.72	53.76	53.64	0.2	53.66	0.2
1.1316	373.15	60.88	60.80	0.1	60.94	−0.1
1.1319	378.07	67.58	67.34	0.4	67.65	−0.1
1.6586	353.06	31.24	31.10	0.4	31.14	0.3
1.6590	358.12	34.53	34.46	0.2	34.49	0.1
1.6595	363.16	37.81	37.81	0.0	37.83	−0.0
1.6598	367.23	40.52	40.52	0.0	40.53	−0.0
1.6604	373.16	44.48	44.47	0.0	44.46	0.0
1.6608	378.16	47.81	47.81	0.0	47.78	0.1
1.6613	383.16	51.12	51.15	−0.0	51.09	0.1
1.6617	388.16	54.47	54.49	−0.0	54.41	0.1
1.6622	393.13	57.79	57.81	−0.0	57.71	0.1
1.6631	403.17	64.58	64.54	0.1	64.37	0.3
1.7338	353.11	31.27	31.13	0.5	31.17	0.3
1.7342	358.13	34.32	34.27	0.1	34.33	−0.0
1.7347	363.16	37.52	37.43	0.2	37.49	0.1
1.7352	368.15	40.63	40.56	0.2	40.62	0.0
1.7357	373.17	43.79	43.71	0.2	43.77	0.0
1.7366	383.13	50.03	49.96	0.2	50.01	0.1
1.7370	393.11	56.33	56.22	0.2	56.25	0.1
1.7378	403.11	62.61	62.49	0.2	62.49	0.2
1.7393	413.16	68.97	68.78	0.3	68.73	0.3
1.9032	353.16	31.03	31.15	−0.4	31.19	−0.5
1.9038	358.19	33.89	33.96	−0.2	34.22	−0.4
1.9044	363.16	36.69	36.73	−0.1	36.81	−0.3
1.9054	373.16	42.27	42.28	−0.0	42.40	−0.3
1.9064	383.17	47.84	47.81	0.1	47.95	−0.2
1.9073	393.16	53.31	53.31	0.0	53.46	−0.3
1.9084	403.16	58.77	58.78	−0.0	58.95	−0.3
1.9094	413.21	64.22	64.26	−0.1	64.44	−0.3
1.9104	420.21	68.12	68.06	0.1	68.24	−0.2

(*Continued*)

Table II. *PVT* Experimental Points, Calculated Points, and Percentage Deviation from Derived Equations for Pentafluoromonochloroethane (*Continued*)

			Benedict-Webb-Rubin		Martin-Hou	
Volume, Cc./Gram	Temp., °K.	Obsd. Pres., Atm.	Calcd. pres., atm.	% dev.	Calcd. pres., atm.	% dev.
2.3513	353.16	30.73	30.90	−0.6	30.92	−0.6
2.3527	363.17	35.22	35.20	0.0	35.24	−0.1
2.3539	373.16	39.49	39.44	0.1	39.49	0.0
2.3552	383.18	43.67	43.64	0.1	43.70	−0.1
2.3563	393.17	47.80	47.78	0.0	47.86	−0.1
2.3576	403.19	51.88	51.88	0.0	51.99	−0.2
2.3589	413.19	55.86	55.93	−0.1	56.07	−0.4
2.3601	423.16	59.83	59.93	−0.2	60.12	−0.5
3.0753	350.03	28.47	28.57	−0.3	28.61	−0.5
3.0758	353.15	29.48	29.54	−0.2	29.56	−0.3
3.0776	363.30	32.68	32.66	0.1	32.64	0.1
3.0793	373.16	35.62	35.63	−0.0	35.57	0.1
3.0809	383.10	38.61	38.57	0.1	38.49	0.3
3.0824	393.12	41.44	41.48	−0.1	41.39	0.1
3.0841	403.10	44.31	44.34	0.1	44.25	0.1
3.0857	413.17	47.16	47.18	−0.0	47.11	0.1
3.0874	423.12	49.89	49.94	−0.1	49.90	−0.0
3.0890	433.18	52.71	52.70	0.0	52.71	0.0
3.0899	438.21	54.07	54.07	0.0	54.10	−0.0
3.0907	443.21	55.39	55.42	−0.1	55.48	−0.2
4.3958	343.24	23.92	23.90	0.1	24.02	−0.4
4.3982	353.16	25.88	25.88	0.0	25.92	−0.1
4.4008	363.16	27.85	27.82	0.1	27.80	0.2
4.4032	373.26	29.80	29.74	0.2	29.66	0.4
4.4055	383.22	31.52	31.60	−0.3	31.48	0.1
4.4076	393.08	33.35	33.40	−0.2	33.25	0.3
4.4101	403.12	35.11	35.20	−0.2	35.04	0.2
4.4124	413.19	36.86	36.97	−0.3	36.81	0.1
4.4148	423.16	38.65	38.70	−0.1	38.55	0.2
4.4171	433.17	40.39	40.42	−0.1	40.28	0.3
4.4195	443.17	42.12	42.10	0.1	42.00	0.3
6.6981	333.34	18.13	17.95	1.0	18.12	0.1
6.7046	353.09	20.47	20.28	0.9	20.32	0.8
6.7129	373.13	22.70	22.52	0.8	22.47	1.0
6.7197	393.11	24.86	24.68	0.7	24.58	1.1
6.7234	403.15	25.88	25.73	0.6	25.62	1.0
6.7234	403.10	25.87	25.73	0.6	25.61	1.0
6.7269	415.09	27.07	26.97	0.4	26.85	0.8
6.7342	433.16	29.02	28.80	0.8	26.68	1.2
6.7400	449.26	30.65	30.39	0.8	30.30	1.1
6.7004	326.45	17.18	17.11	0.4	17.32	−0.8
6.7012	328.54	17.52	17.36	0.9	17.56	−0.3
6.7047	338.44	18.67	18.56	0.6	18.68	−0.1
6.7086	349.06	19.88	19.80	0.4	19.86	0.1
6.7158	369.54	22.13	22.13	0.1	22.08	0.2
6.7239	391.67	24.54	24.51	0.1	24.41	0.5
6.7307	410.34	26.48	26.77	0.1	26.34	0.5
6.7382	430.71	28.59	28.54	0.2	28.42	0.6
10.0307	313.39	12.36	12.22	1.1	12.42	−0.5
10.0415	332.17	13.77	13.62	1.1	13.72	0.4
10.0513	352.59	15.18	15.06	0.7	15.09	0.6
10.0637	374.09	16.58	16.52	0.3	16.50	0.5
10.0739	394.06	17.88	17.84	0.3	17.78	0.6
10.0848	413.86	19.21	19.10	0.6	19.03	0.9
10.0956	433.08	20.43	20.30	0.6	20.23	1.0
10.1043	447.83	21.35	21.20	0.7	21.14	1.0
			Av.	0.26		0.34

While both equations represent the data well, the Benedict-Webb-Rubin equation is recommended and published refrigeration tables will be based on this equation.

The data were also checked against an equation found in the literature (*5*). The values calculated from this equation agreed with the data to within 2%, with an average deviation of about 1% except on the high density isochor, where the values deviated by as much as 15%.

A technique, similar to that described earlier (*4*), was employed to determine the critical volume, critical pressure, and slope of the critical isochor. These critical constants

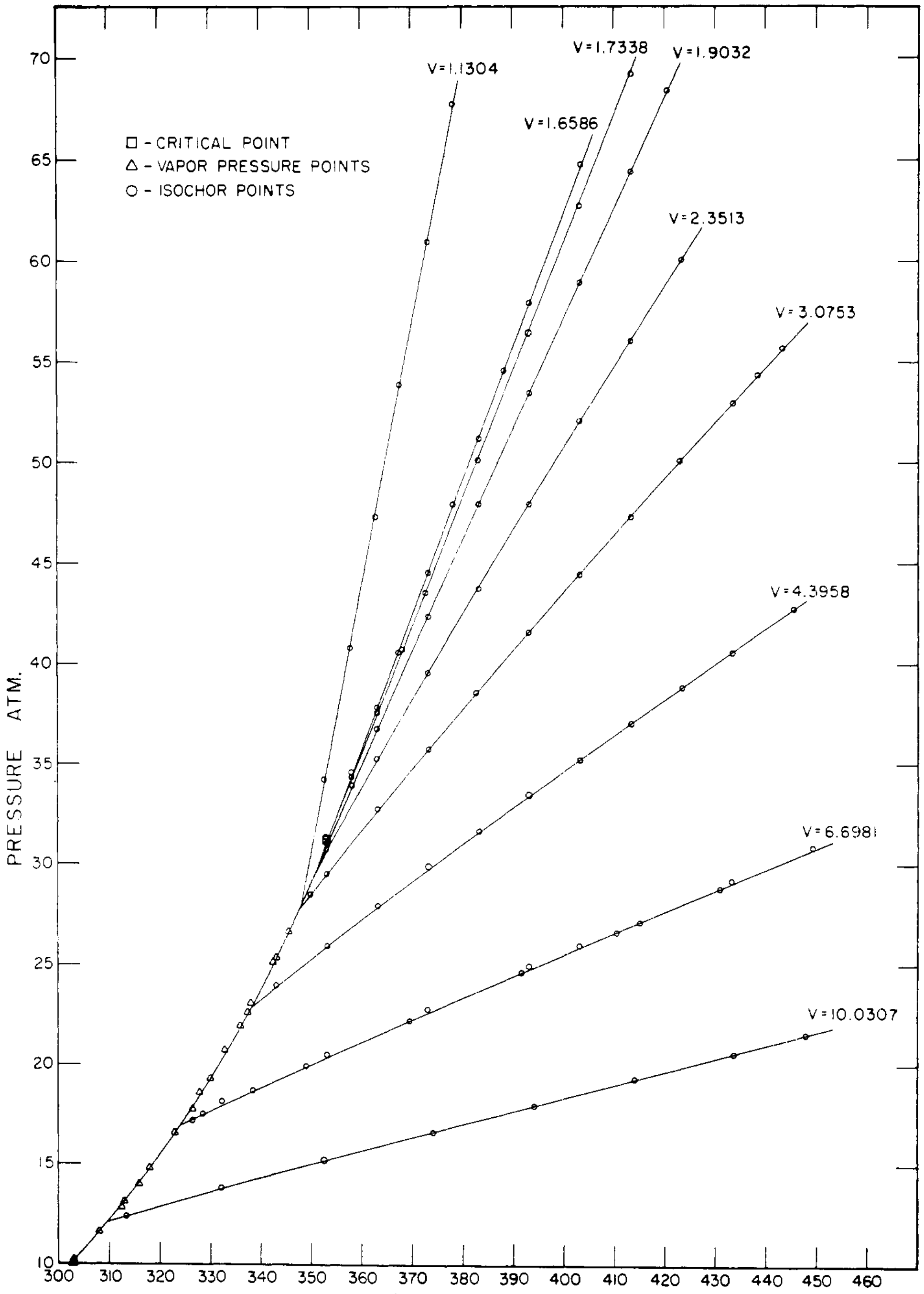

Figure 1. Vapor pressure and equation of state for pentafluoromonochloroethane

were used in deriving the Martin-Hou equation. The equation of state data are shown in Table II and Figure I.

The vapor pressure experimental data are presented in Table III. A four-constant equation, derived to fit these data, is:

$$\text{Log}\, P_{\text{atm.}} = A + B/T + CT + D \log T \qquad (3)$$

where

$A = 3.89497\underline{64} \times 10^1$
$B = -1.93213\underline{47} \times 10^3$
$C = 1.00647\underline{05} \times 10^{-2}$
$D = -1.39491\underline{79} \times 10^1$

As stated above, the uncertainties of the input variables in the vapor pressure equation, pressure and absolute temperature, are ±0.2 and ±0.05%, respectively. The vapor pressure equation agrees with both the data of this paper and the Aston (*1*) data within ±0.33% average error, including a maximum error of 1.34%.

The calculated and experimental values for liquid densities together with per cent deviation are presented in Table IV. The liquid densities obtained from the experimental data and correlated using the following equation (7):

$$\rho = \rho_c + A\,(1 - T_R)^{1/3} + B(1 - T_R)^{2/3} + C(1 - T_R) + D(1 - T_R)^{4/3} \quad (4)$$

where

$\rho_c = 0.61310$ gram/cc.
$T_c = 353.1\,^\circ$K.
$T_R = T/T_c$

$A = 1.5024$
$B = -2.0583$
$C = 4.0351$
$D = -2.0214$

Figure 2 is a plot of the saturated liquid and vapor densities for pentafluoromonochloroethane over the range 300° to 350° K. The uncertainties in the input variables for the liquid density equations are ±0.1% or better for the volume of the pycnometer, ±0.05% for the sample weight, and ±0.05% for the absolute temperature. The density equation agrees with the experimental data within an aver-

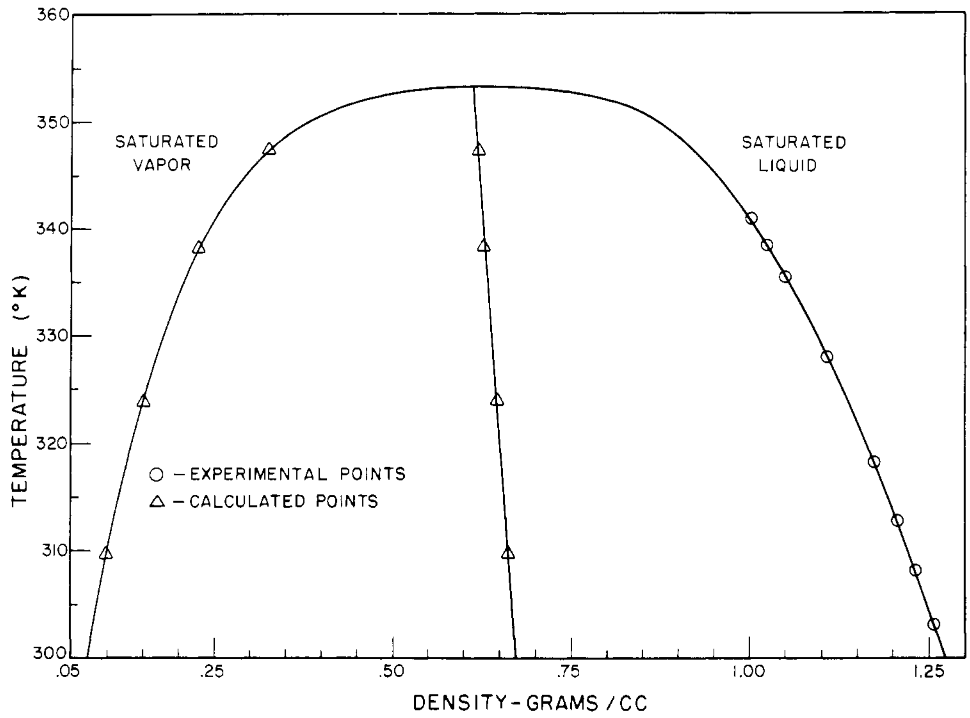

Figure 2. Saturated liquid and vapor densities of pentafluoromonochloroethane and the rectilinear diameter

Table III. Vapor Pressure of Pentafluoromonochloroethane

	Pressure, Atm.		
Temp., ° K.	Obsd.	Calcd.	% Dev.
177.838[a]	0.03085	0.03084	0.05
182.830[a]	0.04659	0.04659	0.00
190.728[a]	0.08483	0.08495	–0.15
205.89	0.2312	0.2314	–0.10
208.066[a]	0.26350	0.26346	0.01
217.131[a]	0.43781	0.43782	–0.00
222.34	0.5757	0.5736	0.36
225.342[a]	0.66590	0.66576	0.02
233.303[a]	0.96753	0.96759	–0.01
233.43	0.9779	0.9731	0.48
233.925[a]	0.99500	0.99504	–0.00
243.38	1.48	1.49	–0.55
253.18	2.20	2.19	0.63
263.16	3.17	3.13	1.13
272.46	4.29	4.27	0.47
273.07	4.41	4.35	1.34
282.97	5.93	5.89	0.77
292.71	7.89	7.76	0.50
302.65	10.08	10.11	–0.24
303.11	10.24	10.23	0.18
308.13	11.62	11.60	0.14
312.41	12.83	12.88	–0.41
313.08	13.10	13.09	0.08
316.07	14.00	14.06	–0.40
318.12	14.80	14.75	0.32
323.01	16.56	16.50	0.39
326.51	17.73	17.85	–0.67
328.14	18.59	18.50	0.49
330.17	19.28	19.34	–0.32
333.14	20.69	20.62	0.36
336.14	21.90	21.97	–0.32
337.52	22.60	22.62	–0.09
338.16	23.02	22.92	0.42
342.55	25.07	25.09	–0.10
343.17	25.34	25.41	–0.28
345.55	26.61	26.66	–0.19
		Av.	0.33

[a] Data taken from (*1*).

Table IV. Liquid Density of Pentafluoromonochloroethane

	Density, G./Cc.		
Temp., ° K.	Obsd.	Calcd.	% Dev.
197.41	1.6654	1.6649	0.03
253.31	1.4762	1.4781	–0.13
264.50	1.4341	1.4344	–0.02
280.32	1.3685	1.3679	0.04
290.11	1.3252	1.3233	0.14
298.14	1.2842	1.2844	–0.02
303.12	1.2584	1.2590	–0.05
308.13	1.2335	1.2323	0.10
312.75	1.2074	1.2064	0.08
318.14	1.1744	1.1745	–0.01
327.79	1.1083	1.1111	–0.25
335.66	1.0499	1.0500	–0.01
338.30	1.0256	1.0263	–0.07
340.77	1.0037	1.0020	0.17
		Av.	0.08

Table V. Critical Values for Pentafluoromonochloroethane

Critical temp., ° K.	353.1 ± 0.1
Critical density, g./cc.	0.6131 ± 0.0035
Critical pressure, atm.	31.16 ± 0.05
Critical volume, cc./g.	1.631 ± 0.009

age error of ±0.08% and has a maximum error of 0.25%.

A rectilinear diameter equation was derived from the experimental liquid density data and calculated vapor density data.

$$\rho_{\text{av.}} = 0.9688 - 1.0074 \times 10^{-3} \times T\text{° K.} \qquad (5)$$

A critical density was calculated from this equation and the critical temperature. The liquid density may be expressed as a function of temperature using Equation 4.

The critical data, determined both experimentally and by calculation, are given in Table V.

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Solubility of Niobic Oxide and Niobium Dioxyfluoride in Nitric Acid–Hydrofluoric Acid Solutions at 25° C.

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The solubilities of niobic oxide and niobium dioxyfluoride were determined at 25° C. in hydrofluoric acid solutions that initially were up to 25*M* in HF and in nitric acid–hydrofluoric acid solutions that initially were up to ~20*M* in HNO_3 and 5*M* in HF. In all cases, the niobium concentration in the saturated solution was about one fifth the total fluorine concentration, indicating that niobium was present in these solutions primarily as the $NbOF_5^{-2}$ ion. The solid phases at equilibrium always contained NbO_2F, indicating that the equilibria involved were $2NbO_2F_{(s)} + 8HF_{(aq)} \leftrightarrows 2H_2NbOF_{5(aq)} + 2H_2O$ and $Nb_2O_{5(s)} + 6HF_{(aq)} \leftrightarrows NbO_2F_{(s)} + H_2NbOF_{5(aq)} + 2H_2O$, depending on the initial compound used.

A PRIOR STUDY of the solubility of niobic oxide in hydrofluoric acid solutions was made by Nikolaev and Buslaev (*9*), who concluded that the oxide reacted with 0 to 25*M* HF according to the equation $Nb_2O_{5(s)} + 10HF_{(aq)} \leftrightarrows 2H_2NbOF_{5(aq)} + 3H_2O$, and that $Nb_2O_5 \cdot 2H_2O$ was the solid phase at equilibrium. During studies at this laboratory on the dissolution of niobium oxide in nitric acid–hydrofluoric acid solutions (*2*), it was noted that a solid, identified as NbO_2F by x-ray diffraction analysis, precipitated under certain conditions. This observation prompted the present investigation of the solubility of niobic oxide and the dioxyfluoride in HF-HNO_3 solutions.

EXPERIMENTAL

Materials Used. Hydrous niobic oxide was obtained by dissolving sintered Nb_2O_5 (Kawecki Chemical Co.; total metal impurities, less than 300 p.p.m.) in hydrofluoric acid, then precipitating the hydrous oxide with ammonium hydroxide. The precipitate was washed alternately with water and 0.1*M* HNO_3 and then air-dried at room temperature before use. The hydrous oxide contained about 50% niobium, 25% water, 0.1% fluorine, and less than 0.5% nitrogen.

Hydrated dioxyfluoride was obtained by allowing high purity niobium metal to react with boiling 16*M* HNO_3–1*M* HF (F/Nb atom ratio of less than 5). The hydrated dioxyfluoride flaked off the surface of the metal and settled to the bottom of the Teflon reaction vessel; it was then collected by filtration, washed with acetone, air-dried, and finally dried over Drierite in a desiccator. Analyses: Nb, 61.6%; F, 12.4%; H_2O, 5.12%. Calculated for $NbO_2F \cdot \frac{1}{2}H_2O$: Nb, 60.8%; F, 12.4%; H_2O, 5.89%. The existence of a hydrate was confirmed by infrared analysis. The water deformation band appeared at 1630 cm.$^{-1}$ and the –OH stretching bands at 3240 and 3360 cm.$^{-1}$. The x-ray powder pattern of $NbO_2F \cdot \frac{1}{2}H_2O$ was the same as that reported for NbO_2F by Frevel and Tinn (*3*). This is not surprising, since Frevel and Rinn found no change in lattice parameter with NbO_2F having water contents between 1.9 and 5.7%. The formula NbO_2F is used throughout this paper since, in general, the presence of the dioxyfluoride in equilibrium solid phases was confirmed by x-ray diffraction and not by chemical analysis. The hydrated dioxyfluoride was fairly stable on heating in dry helium at about 3° per minute in a thermobalance. Noticeable weight loss occurred only above about 200° C. On heating to 900° C., complete decomposition of the dioxyfluoride to Nb_2O_5 occurred.

All solutions were prepared from reagent grade acids and distilled water.

Procedure. Series of samples were prepared by adding excess oxide or dioxyfluoride to hydrofluoric acid or HF-HNO_3 solutions. The samples were equilibrated at 25° ± 1° C. Periodic analyses showed that samples originally containing the hydrous oxide attained equilibrium in a few days, but equilibration in samples initially containing the dioxyfluoride required nearly 2 years. After equilibration, samples of the saturated solutions were removed, clarified by centrifugation at 25° C., and analyzed. In some cases, wet residues were removed to allow determination of the equilibrium solid phase by the method of Schreinemakers (*10*). In all cases, the residual solids were recovered by filtration, washed with water, and subjected to x-ray diffraction and chemical analyses. No detectable hydrolysis of the dioxyfluoride occurred during washing.

Analytical. Niobium was determined both by an x-ray absorption method (*1*) and by ignition of samples to Nb_2O_5 at 900° C. The results from the two methods generally agreed within 3%. Total fluorine in solution and in wet residues was determined by differential potentiometric titration using standard NaOH as the titrant. This method is similar to the one used by Nikolaev and Buslaev (*9*). The over-all reaction (with the end point at pH 7 to 8) is: $2H_2NbOF_5 + 10NaOH \rightarrow Nb_2O_5 + 10NaF + 7H_2O$. Pyrohydrolysis (*4, 8*), after drying of the sample in the presence