Physical Properties of Perfluoropropane

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A Martin-Hou equation of state has been obtained for perfluoropropane applicable to 58 atm. 165° C., and to a molar volume of 0.30 liters/gram mole. Vapor pressure has been determined from −60° C. to 71.9° C., and measured critical temperature. Densities of liquid and saturated vapor have also been determined between −50° C. and the critical temperature. From this information, the rectilinear diameter line and the heats of vaporization have been computed.

THIS LABORATORY has for several years investigated the physical properties of fluorine-containing molecules (*6*). As part of this work, a Martin-Hou (*4*) equation of state has been obtained for perfluoropropane. Vapor pressure and density data have been determined over a wide temperature range. Finally, heats of vaporization and the rectilinear diameter line have been computed.

MATERIAL

The C_3F_8 sample used was prepared in a jet reactor by burning C_3H_8 in fluorine (*9*). The product was then distilled in a column having approximately 50 theoretical plates. The fore and end cuts were discarded. In this process, because of the high fluorine-propane ratio, and product recycling, the most probable impurities are the C_3F_7H isomers (*5*). Cleavage and polymerization are at a minimum (*5*). The purity of the sample was determined by infrared spectrographic and gas chromatographic analyses.

The gas chromatograph used was a Perkin-Elmer Model 154 unit. This instrument contained a 15-foot column packed with 40- to 60-mesh firebrick as the stationary phase and filled with 2*N* butyl maleate as the liquid adsorbent Helium served as the carrier gas. A sample of mixed C_3F_7H isomers containing C_3F_8 and other C_3 compounds with higher hydrogen content was easily resolved by this chromatograph, as would be predicted by the differences in boiling points (*5*). The C_3F_8 used showed a total of 0.06 mole % impurity, according to this chromatograph. The sensitivity of this chromatograph detector was increased 100-fold prior to and immediately following the peak of the main compound (C_3F_8).

The infrared curves of both liquid and vapor samples were checked between 625 and 5000 cm.$^{-1}$ on a Baird recording infrared spectrometer and were found to coincide throughout this frequency range within the error of the instrument. The curves were fully comparable with those of Edgell (*3*).

The perfluoropropane was 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. The process was repeated until no pressure was observed on a manometer upon cooling the sample in liquid nitrogen. In view of these findings, it is believed that the sample of perfluoropropane used in this work is of a purity of 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 (*1, 6*).

The equipment was completely constructed with high pressure fittings and was equipped with a 1000-p.s.i. Heise gage having 1-pound subdivisions. Its volume was found to be 1537.5 ± 1.0 cc. at 25 C. The methods used in calibrating this equipment and determining its volume have been described (*1*). Corrections were made for the expansion of the equipment with temperature fluctuation of <0.05° C. Measurements below 25° C. were made in a methanol thermostat with a temperature fluctuation of <0.05° C.

Except for vapor pressures below 25° C., all temperature measurements in this work were made using a Chromel-constantan thermocouple in conjunction with a Wenner potentiometer. The thermocouple was calibrated by comparison with a Leeds & Northrup platinum resistance thermometer which had been compared to a certified National Bureau of Standards thermometer by the manufacturer. To measure vapor pressures below 25° C., the platinum resistance thermometer was used directly. Resistance measurements were made using a Leeds & Northrup Speedomax high precision resistance recorder.

In carrying out either a vapor pressure or isochor determination, a weighed amount of C_3F_8 was distilled into the

Table I. *PVT* Experimental Points and Deviations from Derived Equation for Perfluoropropane

Volume, L./G. Mole	Temp., ° C.	Pressure (Obsd.), Atm.	Dev., Atm., Obsd. − Calcd.
0.30389	74.63	28.03	+0.02
	84.90	33.94	+0.06
	94.56	39.55	+0.10
	103.72	44.76	−0.01
	114.74	51.27	+0.08
	125.98	57.88	+0.10
0.33301	73.12	27.01	−0.07
	81.51	31.37	−0.05
	94.74	38.20	−0.04
	109.49	45.66	−0.15
	112.65	47.33	−0.10
	132.44	57.35	−0.22
0.39177	74.56	27.39	−0.12
	80.73	30.07	−0.06
	86.01	32.31	−0.04
	89.05	33.56	−0.07
	102.06	39.03	+0.01
	117.60	45.27	−0.09
	149.04	57.93	−0.02
0.50104	92.90	31.99	−0.06
	107.13	36.22	−0.01
	130.16	42.86	+0.05
	166.24	53.08	+0.30
1.00120	59.82	17.78	−0.01
	82.58	20.65	+0.04
	102.11	22.97	+0.05
	120.94	25.20	+0.13
	135.46	26.88	+0.19

apparatus from a tared sample bomb. Upon completion of a run, the material was distilled back into the original container. The weight of sample recovered agreed with that delievered to the apparatus to within 0.1 gram. In the sample bomb and again in the apparatus, noncondensables were removed using the technique mentioned. Vapor pressure and isochor determinations were carried out in thermostats, allowing a 2-hour equilibrium time for vapor pressure points and approximately one-half hour for vapor density points.

Liquid densities were determined by the method of Cork (*2*). Two tubes of heavy-walled annealed glass 30 cm. in length and 13 mm. in inside diameter were used. To calculate volume of these two tubes, using water, the height of the liquid in each tube was measured using a cathetometer. A scratch on the side of each tube served as a reference point. Measurements were made with the tubes containing varying amounts of water. A linear equation was derived for each tube, using the method of least squares. These equations expressed volume as a function of meniscus distance from the reference point. In the density determination a different quantity of C_3F_8 was distilled into each tube and the tubes were evacuated and sealed. Sample weight was determined by weighing the tubes before and after sealing. The tubes were placed in a thermostat at the desired temperatures and the liquid height was measured. The liquid volumes were determined using the equations mentioned above, then corrected for the meniscus difference between C_3F_8 and water and for the thermal expansion of the glass. For each tube the following relationship holds:

$$\text{Total weight of compound} = \text{volume of liquid} \times \text{density of liquid} + \text{volume of gas} \times \text{density of gas} \qquad (1)$$

From the two equations obtained, the densities of liquid and saturated vapor can be calculated algebraically. Because vapor densities determined in this manner are subject to error due to the small weight of the compound in the gas phase, the vapor densities as reported here were obtained by solving the equation of state implicity for vapor density at that vapor pressure which corresponded to the desired temperature.

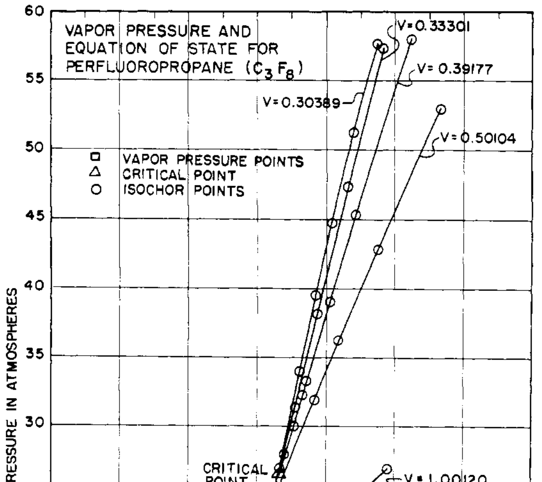

Figure 1. Vapor pressure and equation of state for perfluoropropane (C_3F_8)

The heats of vaporization were obtained by using the Clapeyron equation:

$$-\Delta H\,(\text{cal./g. mole}) = \left(\frac{dp}{dt}\right) T\,(V_L - V_G)\,24.206 \qquad (2)$$

where dp/dt was found by differentiating the vapor pressure equation with respect to temperature.

The critical temperature was found by using the usual sealed tube technique (*7*).

RESULTS AND DISCUSSION

The Martin-Hou (*4*) equation of state was used to correlate the *PVT* data. The various constants were evaluated and the following equation was derived:

$$P\,(\text{atm.}) = \frac{0.082054\ T\,^\circ\text{K.}}{(V-b)}$$

$$-\frac{15.126979 - 0.014656016\ T^\circ\,\text{K.} + 385.33552e^{-0.015866805\ T\,^\circ\text{K.}}}{(V-b)^2}$$

$$+\frac{1.7276043 + 0.34736373 \times 10^{-3}\,T\,^\circ\text{K.} + 104.35258e^{-0.015866805\ T\,^\circ\text{K.}}}{(V-b)^3}$$

$$-\frac{0.20515732}{(V-b)^4} + \frac{1.8182426 \times 10^{-5}\ T\,^\circ\text{K.}}{(V-b)^5} \pm 0.22\% \qquad (3)$$

where $b = 0.05332833$.

These constants are those as computed by the IBM 650 data-processing machine. Eight significant figures were kept for computation purposes only. These constants may be rounded to six significant figures without materially changing the computation.

A technique similar to that described earlier (*1*) was employed to determined the critical volume, critical pressure, and slope of the critical isochor. These constants are used in deriving the Martin-Hou equation. The equation constants were determined using an IBM 650 data-processing machine. The program developed to perform this calculation was designed to give us the best practical fit of the data to the equation. The equation of state data are shown in Table I and Figure 1.

The vapor pressure experimental data are shown in Table II.

Table II. Vapor Pressure of Perfluoropropane

Temp., °C.	Pressure (Obsd.), Atm.	Dev., Atm., Obsd. − Calcd.
−60.15	0.306	0.0
−52.03	0.477	0.0
−43.92	0.718	+0.003
−29.41	1.369	0.0
−14.27	2.51	0.0
−3.11	3.70	−0.01
−0.41	4.06	0.0
+14.58	6.50	+0.03
29.17	9.69	-0.04
43.66	13.96	−0.07
59.76	20.26	0.0
67.75	24.13	+0.14

A four-constant equation was derived to fit these data.

$$\text{Log } P(\text{atm.}) = 16.9953 - \frac{1435.89}{T\,^\circ\text{K.}} - 4.88280 \log T\,^\circ\text{K.} + 0.00282492\, T\,^\circ\text{K.} \pm 0.35\% \quad (4)$$

The experimental and calculated values for liquid and saturated vapor densities together with the heats of vaporization are shown in Table III and Figure 2.

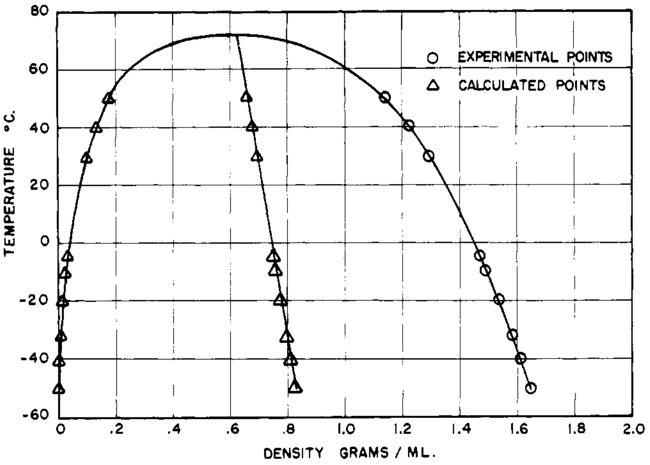

Figure 2. Liquid and saturated vapor density of perfluoropropane

Table III. Density Data and Heats of Vaporization for Perfluoropropane

Temp., ° C.	Saturated Vapor Density, G./Ml.	Liquid Density, G./Ml.	*H*, Cal./G. Mole
−60.0	0.0034	1.691	4960
−49.7[a]	0.0057	1.650	
−40.7[a]	0.0086	1.618	
−40.0	0.0089	1.612	4730
−36.7	0.0103	1.601	4690
−32.3[a]	0.0124	1.585	
−20.0[a]	0.0199	1.538	4450
−9.8[a]	0.0288	1.493	
−4.7[a]	0.0343	1.474	
0.0	0.0401	1.450	4090
+20.0	0.0749	1.350	3610
29.9[a]	0.1005	1.293	
40.0[a]	0.1353	1.225	2960
50.0[a]	0.1828	1.145	
60.0	0.2530	1.020	1990
71.9	0.628	0.628	0

[a] Experimental points.

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

$$\frac{\text{Density (vapor)} + \text{density (liquid)}}{2} = 0.7461 - 1.645 \times 10^{-3}\, T\,^\circ\text{C.} \quad (5)$$

A critical density was calculated using this equation and found to be 0.628 gram per ml.

The liquid density of C_3F_8 may be expressed as a function of temperature, using the following equation:

$$\text{Density (liquid), g./ml.} = 1.4531 - 4.5363 \times 10^{-3}\, T\,^\circ\text{C.} - 2.1518 \times 10^{-5}\, T\,^\circ\text{C.}^2 - 2.1174 \times 10^{-7}\, T\,^\circ\text{C.}^3 \pm 0.08\% \quad (6)$$

Range, −50° to 50° C.

The critical data determined both experimentally and by calculation are found in Table IV. The boiling point was calculated from the vapor pressure equation for C_3F_8 and is included for convenience.

Table IV. Boiling Point and Critical Values for Perfluoropropane

Critical temperature, ° C.	71.9 ± 0.2
Critical density, g./ml.	0.628
Critical pressure, atm.	26.45
Critical volume, l./g. mole	0.299
Boiling point (normal), ° C.	−36.7 ± 0.1 −38 (*8*)

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