

Physical and Thermodynamic Properties of Trifluoromethane

Y. C. HOU and J. J. MARTIN

The University of Michigan, Ann Arbor, Michigan

Trifluoromethane is commonly called fluoroform after the corresponding chloro-compound, chloroform. It is also known in the trade as Freon-23 refrigerant, and has various low-temperature applications. For the design of refrigeration units using trifluoromethane it is essential that the physical and thermodynamic properties of the compound be available over the desired ranges. The reported data on trifluoromethane are far from complete and are in some discrepancy among different investigators (1, 2).

The present investigation included determinations of the vapor pressure, saturated liquid density, critical constants, pressure-volume-temperature behavior, and heat capacity at zero pressure over the desirable ranges.

The sample of trifluoromethane, supplied by E. I. du Pont de Nemours and Company, was obtained from middle cuts in repeated fractionation processes and was therefore of very high purity. According to du Pont's analysis (3) the liquid phase had a moisture content of 0.0005 wt. %, and the vapor of the cylinder contained 0.021 vol. % noncondensables in liquid nitrogen.

EXPERIMENTAL WORK

Vapor Pressure

The measurements were made by a static method over the range of 254° to 537°R., which is equivalent to a pressure range of 0.25 to 690 lb./sq. in. abs. Two sets of equipment were designed for different pressure ranges. The low-pressure equipment, shown in Figure 1, was used for pressures up to 1.5 atm. abs. and was mostly made of glass. The high-pressure equipment, made of steel, as shown in Figure 2, was used for pressure determinations from 1.5 atm. to the critical point (about 700 lb./sq. in.).

Trifluoromethane was condensed in the isoteniscope at low temperature after the system had been evacuated down to a pressure of a few microns of mercury with a combination of Hyvac and mercury diffusion pumps. Then the isoteniscope was kept at constant temperature by submerging it in a constant-temperature bath. The temperature of the bath was measured by a platinum-resistance thermometer which had been calibrated by the National Bureau of Standards. The pressure was measured when the equilibrium between the vapor and liquid trifluoromethane was reached. The low-

boiling impurities such as air were removed by letting a part of the liquid boil off. The equilibrium pressure was again measured, and the boil off and pressure measurement were repeated until a constant equilibrium pressure was obtained. This constant pressure was taken to be the vapor pressure of trifluoromethane at the temperature of the surrounding bath. The pressure in the low-pressure equipment was measured by a mercury manometer, and that in the high-pressure equipment was measured by pressure gauges. The gauges were calibrated against a Mansfield and Green dead-weight tester before and after each charge of trifluoromethane was made to the isoteniscope.

Saturated Liquid Density and Critical Temperature

The saturated liquid density of trifluoromethane was determined from 370° to 538°R. by the method described by Benning and McHarness (4). The technique employed in the measurement was to find the temperature at which the density of the saturated liquid matched that of a precalibrated density float.

The critical temperature was determined as the average temperature at which the liquid meniscus would appear and disappear; it was found to be 538.33°R. for trifluoromethane.

Pressure-Volume-Temperature Behavior

The pressure-volume-temperature studies were carried out as a series of approximately constant density measurements. The ranges of variables were from

400° to 710°R. in temperature, 1 to 60 lb./cu. ft. in density, and 50 to 2,000 lb./sq. in. abs. pressure. The equipment is sketched in Figure 3. Trifluoromethane was charged into the steel bomb after it had been evacuated to a pressure of a few microns of mercury. The vapor in the connecting line was recovered into the recovery tube by cooling the latter with liquid nitrogen. The weight of trifluoromethane charged was calculated from the weights of the storage bulb and recovery tube before and after the charging. The whole system was kept submerged in a large constant-tempera-

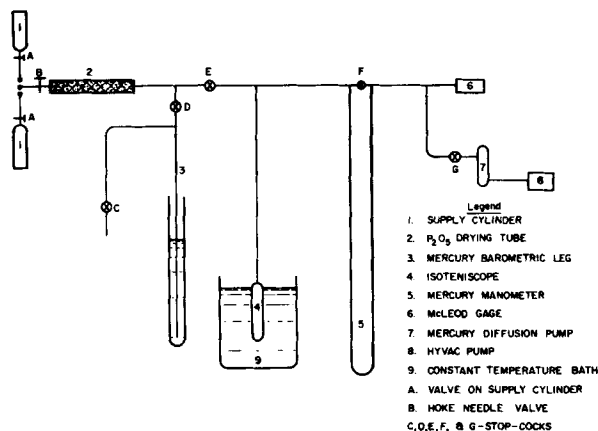


Fig. 1. Low-vapor-pressure equipment.

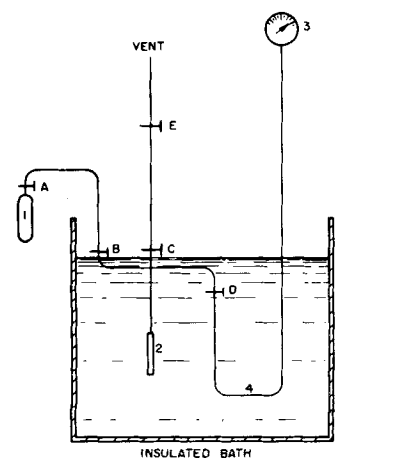


Fig. 2. High-vapor-pressure equipment.

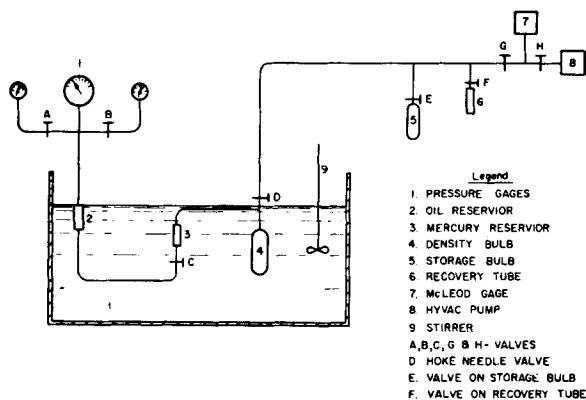


Fig. 3. Pressure-volume-temperature equipment.

TABLE 1. EXPERIMENTAL VAPOR-PRESSURE DATA

Temperature, °R.	Pressure, lb./sq. in.
253.91	0.2370
263.36	0.4306
278.25	0.9863
285.17	1.4068
287.68	1.5904
287.71	1.5964
300.37	2.8620
304.96	3.4713
309.60	4.2195
309.84	4.2454
309.87	4.2591
317.88	5.8852
327.91	8.5437
337.24	11.7875
337.27	11.788
341.24	13.437
348.98	17.187
352.31	19.029
357.02	21.957
361.84	25.275
368.19	30.213
375.15	36.60
382.61	44.40
391.11	54.60
398.22	64.55
403.92	73.40
404.97	74.97
411.91	87.52
417.86	98.92
424.64	113.92
425.48	115.57
433.98	136.92
443.22	162.52
450.81	186.42
457.97	211.72
465.30	239.19
473.53	273.70
481.61	310.78
491.69	363.3
501.52	418.2
509.60	472.3
518.22	533.3
526.50	595.4
527.35	604.3
527.36	604.3
533.52	656.3
536.74	687.3

ture bath. The reading on the pressure gauge was taken when the system reached thermal equilibrium with the bath. The corresponding temperature of the bath was measured by the platinum-resist-

ance thermometer. A series of pressure and temperature measurements for one charging of trifluoromethane gives an approximate isometric. (If the bomb were perfectly rigid for all temperatures and pressures, a true isometric would be obtained.)

After the isometric had been completed, the trifluoromethane in the system was recovered and replaced in the storage bulb and recovery tube. From the weights of the bulb and the tube before and after the recovery the weight of trifluoromethane recovered from the system is known. The weight of trifluoromethane charged and recovered had to agree within a few hundredths of a per cent or the run was rejected because of apparent leakage. Two steel isometric bombs were used in this work. One, with a volume of about 600 cc., was used for higher density isometrics, and the other, with a volume of about 4,100 cc., was used for lower density runs when the pressure did not exceed 300 lb./sq. in. The volume of each bomb was calibrated carefully by weighing when evacuated and when filled with distilled water. Pressure gauges with suitable ranges were used for measuring all pressures. Each gauge was calibrated against the Mansfield and Green dead-weight gauge tester before and after each isometric run.

RESULTS AND CORRELATIONS

Vapor Pressure

The data are plotted as $\ln P$ vs. $1/T$ in Figure 4 and tabulated in Table 1. The curve shows a definite S shape as emphasized by Thodos (5). For this reason the simple Clausius-Clapeyron equation, the Antoine equation (6), or even the Kirchoff-Rankine-Dupré equation (7, 8) would not give satisfactory representations of the data, since the inflection of the curve is not predicted by these algebraic forms. It was concluded that at least one more term must be added to modify the Kirchoff-Rankine-

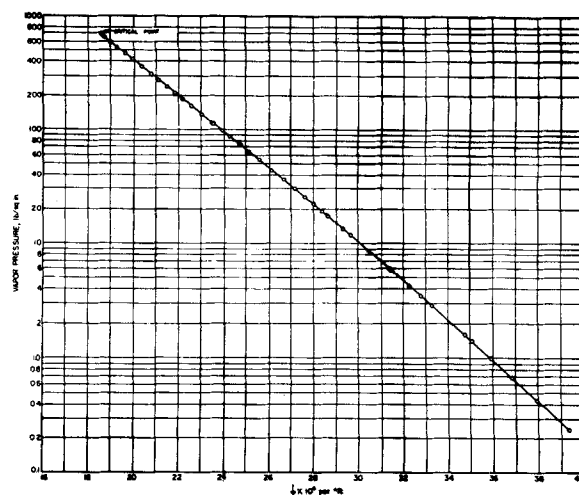


Fig. 4. Vapor-pressure data.

TABLE 2. EXPERIMENTAL SATURATED LIQUID-DENSITY DATA

Temperature, °R.	d_l , lb./cu. ft.
370.79	86.587
454.14	73.037
466.70	70.317
480.73	67.195
*498.1	62.285
512.77	57.429
529.76	49.322
*529.8	49.233
*533.1	46.459
*534.9	44.172
536.69	41.827
537.60	39.763

*Obtained from the extrapolation of isometric curves to saturation temperatures.

Dupré equation to take care of the reversal of the curvature. The following equation:

$$\ln P = 757.3398770 - \frac{18311.92765}{T} - 144.5142304 \ln T + 0.5574904317 T - 4.900054254 \times 10^{-4} T^2 + 2.17247877 \times 10^{-7} T^3 \quad (1)$$

with P in pounds per square inch absolute and T in degrees Rankine satisfactorily represents both the data and the general characteristics of the vapor-pressure behavior over this wide range. The average deviation between the equation and the data is 0.19%, and the maximum deviation is 0.58% and occurs at the lowest pressure.

Saturated Liquid Density and Critical Constants

The data on saturated liquid densities were corrected for thermal expansion of the density float. The data are presented in Table 2 and plotted in Figure 5 as

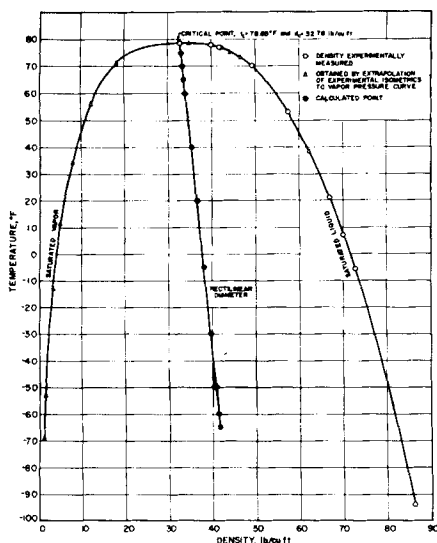


Fig. 5. Saturated liquid and vapor density plot.

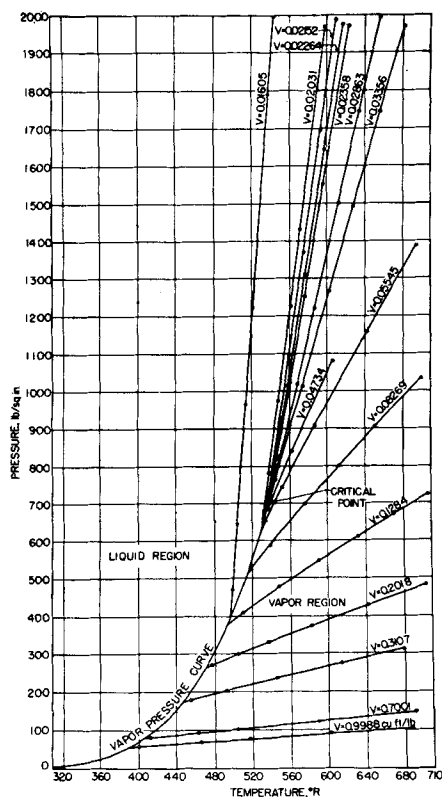


Fig. 6. Pressure-volume-temperature data for trifluoromethane.

liquid density d_l vs. temperature T . Different types of equations were studied for representing the data. The possibility of equations with density expressed as functions containing only integer powers of temperature was ruled out because such forms cannot give zero slope at the critical point ($dT/dd_l = 0$), as do the experimental data.

A combination of the equations

$$\frac{d_l + d_v}{2 d_c} = 1 + \frac{3}{4} \left(1 - \frac{T}{T_c}\right) \quad (2)$$

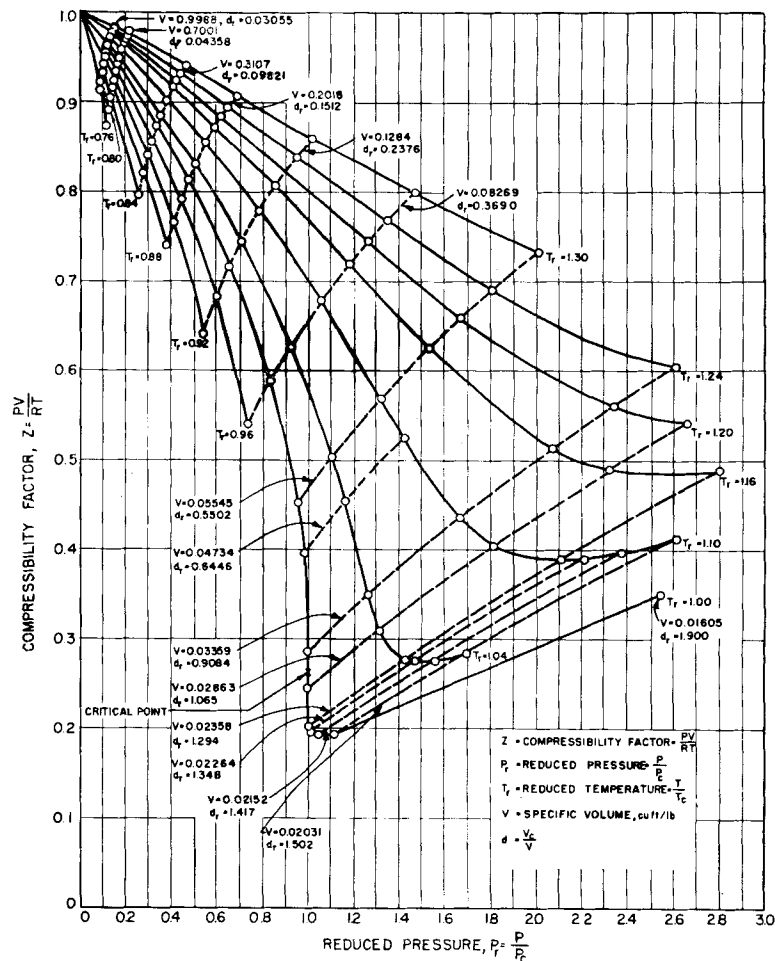


Fig. 7. Compressibility factor for trifluoromethane.

and

$$\frac{d_l - d_v}{d_c} = \frac{7}{2} \left(1 - \frac{T}{T_c}\right)^{\frac{1}{3}} \quad (3)$$

given by Guggenheim (9) yields an equation for the saturated liquid density of the form

$$d_l = d_c + a \left(1 - \frac{T}{T_c}\right)^{\frac{1}{3}} + b \left(1 - \frac{T}{T_c}\right) \quad (4)$$

With a parametric power of n replacing $\frac{1}{3}$ in the second term, the correlation was not significantly improved. One way of generalizing Equation (4) is to consider d_l as a function of $[1 - (T/T_c)]^{n/3}$,

$$d_l = \phi \left(1 - \frac{T}{T_c}\right)^{n/3} \quad (5)$$

or in a power series form,

$$d_l = \sum_{n=0}^{\infty} a_n \left(1 - \frac{T}{T_c}\right)^{n/3} \quad (6)$$

It is readily seen that a_0 must be identical with the critical density. Equation (4) may be considered as a sort of special case of Equation (6) obtained by setting all the coefficients, except a_0 , a_1 , and a_3 , equal to zero. Testing the data showed that equations with a_0 , a_1 , a_3 , and any

other two a 's (all the rest of the a 's were put equal to zero) gave correlations with almost equally high degrees of precision. It was decided that only a_0 , a_1 , a_2 , a_3 , and a_4 would be used. Therefore the saturated liquid density data were finally fitted by the equation

$$\begin{aligned} d_l = & 32.7758 \\ & + 63.37784 \left(1 - \frac{T}{T_c}\right)^{1/3} \\ & - 25.30533 \left(1 - \frac{T}{T_c}\right)^{2/3} \\ & + 144.16182 \left(1 - \frac{T}{T_c}\right) \\ & - 106.13280 \left(1 - \frac{T}{T_c}\right)^{4/3} \end{aligned} \quad (7)$$

lb. mass/cu. ft.

Equation (7) represents the data with an average deviation of 0.24% and a maximum deviation of 0.67%. The use of more terms after a_4 in Equation (6) may be justified for more precise work.

The critical temperature of trifluoromethane was found to be 538.33°R. Inserting this value into the vapor-pressure equation (1), one calculates the critical pressure as 701.4 lb./sq. in. abs. The critical density was determined

TABLE 3. EXPERIMENTAL PVT DATA

Volume, cu. ft./lb.	Temperature, °R.	Pressure, lb./sq. in.
0.99879	400.10	55.61
	466.40	67.20
	517.66	76.30
	602.60	90.25
	687.91	104.17
0.70008	412.49	79.45
	463.35	92.46
	504.59	103.13
	590.22	123.92
	691.63	148.08
0.31066	455.44	179.78
	493.07	203.82
	546.04	236.26
	614.02	276.15
	679.54	313.09
0.20158	479.89	270.8
	505.55	298.0
	536.95	330.7
	538.33	332.2
	582.52	375.2
	642.47	430.3
	703.64	484.3
0.12836	510.78	409.0
	548.42	476.9
	591.05	548.0
	632.09	612.2
	670.58	672.5
	705.91	725.5
0.082677	519.08	525.8
	539.42	589.9
	576.68	699.2
	613.11	802.0
	650.58	906.1
	700.06	1036.5
0.055465	534.86	654.3
	552.38	742.7
	587.93	910.0
	643.00	1162.6
	694.80	1392.5
0.047352*	537.68	684.3
	563.06	834.1
	606.44	1082.2
0.033604	545.67	764.1
	574.22	1014.7
	602.73	1268.9
	628.97	1496.4
	657.22	1748.6
	583.05	1973.1
0.028644	545.69	775.0
	568.67	1019.0
	587.21	1224.4
	613.06	1504.1
	634.82	1749.9
	656.98	1995.4
0.023589	538.33	705.8
	561.00	1024.3
	576.86	1254.5
	596.89	1555.7
	624.23	1974.3
0.022646	536.71	693.2
	538.33	715.7
	558.08	1014.3
	577.12	1313.6
	597.56	1649.1
	617.85	1978.2
0.021531	536.54	706.6
	538.33	736.6
	559.85	1097.5
	575.60	1374.6
	593.64	1698.1
	610.16	1991.0
0.020316	532.91	680.8
	538.33	781.1
	548.51	974.8
	561.74	1229.1

TABLE 3. (Continued)

Volume, cu. ft./lb.	Temperature, °R.	Pressure, lb./sq. in.
	572.13	1435.8
	598.68	1971.5
0.016045	500.02	467.8
	505.25	645.3
	514.58	965.4
	522.15	1226.6
	538.33	1793.4
	544.27	1997.9

*There was a leakage of trifluoromethane during the run.

from the rectilinear diagram described in the following section.

Pressure-Volume-Temperature Behavior

The data were corrected for the expansion of the density bombs, the mercury, and the oil in the whole equipment and then adjusted to true isometrics graphically with the aid of an approximate pressure-volume plot. The adjusted data were tabulated (Table 3) and then plotted as isometric curves in the pressure-temperature plane in Figure 6 and as compressibility curves in Figure 7. The isometric curves were extrapolated to intersect the vapor-pressure curve on the pressure-temperature diagram. The points of intersection gave the saturation temperatures for various vapor densities. These saturated vapor densities together with the saturated liquid density were plotted as temperature vs. density in Figure 5. The rectilinear diameter (average of saturated liquid and vapor densities) was constructed and appeared to be straight within the precision of the data. The critical density was determined from this diagram as 32.776 lb./cu. ft., with no greater precision than 0.05 lb./cu. ft.

The adjusted PVT data were then correlated with the generalized equation of state developed by Martin and Hou (10). A slight modification was made to the original equation by adding one more condition to improve it in the high-density liquid region. This was done by including a C_5 term and recognizing the fact that the isometric curve of trifluoromethane is practically straight at about twice the critical density (Figure 6). It was found for trifluoromethane that the condition of $(d^2P/dT^2)_V = 0$ at $V = V_c/2.1$ gave the best representation of the data. The equation of state has the form

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2e^{-(kT/T_c)}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-(kT/T_c)}}{(V-b)^3} + \frac{A_4}{(V-b)^4} \quad (8)$$

TABLE 4. ZERO PRESSURE HEAT CAPACITY

Temperature, °R.	C_p°
250	8.636
300	9.171
400	10.424
500	11.778
600	13.144
700	14.447
800	15.641

TABLE 5. COMPARISON OF CRITICAL CONSTANTS

	Critical tempera- ture, °R.	Critical Pressure, lb./sq. in.	Critical density, lb./cu. ft.
This investi- gation	538.33	701.42	32.78
Ruff et al.	550.8	691	32.2
Seger	518.7	—	32.21

$$+ \frac{B_5T + C_5e^{-(kT/T_c)}}{(V-b)^5}$$

Since sufficient data were taken in this investigation, the values estimated from the generalized correlations of certain parameters, β , T' , and $m = -MP_c/T_c$, were slightly adjusted, as described in Part III of the original paper (10), to give a better representation. The final value of the constants in the equation of state are as follows:

$$R = \text{gas law constant} \\ = 0.153266 \text{ (lb.-force)(cu. ft.)} \\ \text{/(lb.-mass)(°R.)(sq. in.)}$$

$$A_2 = -5.016053028$$

$$B_2 = 0.00310516248$$

$$C_2 = -130.8703305$$

$$A_3 = 0.09781899057$$

$$B_3 = -0.380613864 \times 10^{-4}$$

$$C_3 = 3.53359637$$

$$A_4 = -0.1094517281 \times 10^{-2}$$

$$B_5 = 1.112366387 \times 10^{-8}$$

$$C_5 = -0.000182469146$$

$$b = 0.00579112510$$

These constants result from using values of the parameters as follows: $\beta = 3.15$, $T' = 0.815 T_c$, $M = 7.65$, and $T_B = 1,256^\circ\text{R.}$, with P in pounds per square inch absolute and V in cubic feet per pound mass.

The equation was developed for densities up to about 1.5 times the critical density. Up to this density the average deviation between the equation and the data is only 0.45%, but right at this density the deviation is as great as 4.14%.

Heat Capacity at Zero Pressure

The heat capacities of trifluoromethane at zero pressure were calculated for the

range of 250° to 800°R. from the spectroscopic data reported in the literature. Among the various sets of assignments of fundamental vibrational frequencies given by different investigators (11, to 17), the infrared frequencies reported by Plyler and Benedict (15) with W_2 given by Edgell and May (17) were adopted. The final assignment of fundamental frequencies is as follows:

$$W_1 = 3,031$$

$$W_2 = 1,137$$

$$W_3 = 700$$

$$W_4 = W_7 = 1,372$$

$$W_5 = W_8 = 1,152$$

$$W_6 = W_9 = 507$$

The method of evaluating the harmonic vibrational contribution by the use of statistical mechanics is outlined by Wenner (18). The anharmonic contribution for this compound was arbitrarily estimated to be 0.75% of the harmonic contribution at 800°R. and 0.3% at 250°R. and was assumed to vary linearly with temperature in this range. The zero-pressure heat capacity at any temperature is the sum of the contributions due to harmonic and anharmonic vibrations and to translation and rotation. The results of adding the various contributions were represented by the equation

$$C_p^0 = 7.327 - 529.47 \times 10^{-6}T + 27.35341 \times 10^{-6}T^2 - 0.017189 \times 10^{-6}T^3 \text{ B.t.u.} / (\text{lb.-mole})(^\circ\text{R.}) \quad (9)$$

where T is in °R.

The cubic form of the equation was found desirable because the temperature range included the region where the heat-capacity curve shows a reversal of curvature. Table 4 gives a summary of the calculated heat capacities, which are represented by Equation (9) within a maximum deviation of 0.3%.

$$\Delta H = \int_{T_1}^{T_2} C_p^0 dT + \left[PV + \frac{A_2 + (1 + kT_r)C_2 e^{-kT_r}}{V - b} + \frac{A_3 + (1 + kT_r)C_3 e^{-kT_r}}{2(V - b)^2} + \frac{A_4}{3(V - b)^3} + \frac{(1 + kT_r)C_5 e^{-kT_r}}{4(V - b)^4} \right]_{V_1, T_1}^{V_2, T_2} \quad (10)$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p^0}{T} dT + \left[R \ln(V - b) - \frac{B_2}{V - b} - \frac{B_3}{2(V - b)^2} - \frac{B_5}{4(V - b)^4} + \left\{ \frac{C_2}{V - b} + \frac{C_2}{2(V - b)^2} + \frac{C_5}{4(V - b)^4} \right\} \frac{k}{T_c} e^{-kT_r} \right]_{V_1, T_1}^{V_2, T_2} \quad (11)$$

DISCUSSION

The data obtained in this investigation do not agree too well with those reported

by different investigators (1, 2, 19); however the disagreement between the earlier workers themselves is even greater. The purity of the trifluoromethane sample could be the factor that accounts for most of the discrepancies between all investigators.

The vapor pressures in the low-temperature region showed the slope of the curve of $\ln P$ vs. $1/T$ to be numerically smaller than that given by Ruff et al. (1). As a result the normal boiling point given by Ruff et al. is -84.4°C. instead of -81.8°C. from this investigation. Seger (2) estimated the normal boiling point to be -90°C.

The critical constants are compared with those of the other investigators in Table 5. It is apparent that the most significant discrepancy is in the critical temperature.

The internal consistency of the PVT data taken in this investigation is shown clearly by the smoothness of the curves in Figures 6 and 7. Unfortunately there are no published data with which to compare the PVT data taken in this work.

The statistical mechanical method of calculation of the heat capacity at zero pressure from the infrared and Raman frequencies is generally very satisfactory, if the fundamentals can be identified and the anharmonic effect is negligible. The assumptions made in this investigation on anharmonic contributions can be tested only when accurate calorimetric data are taken on the heat capacity. On the basis of other compounds it is believed that the final values of the heat capacity are probably not more than 1/2% in error.

The properties needed for evaluation of thermodynamic functions such as enthalpy and entropy have been determined in this investigation and represented in analytical form. The heat of vaporization can be calculated by using the Clapeyron equation with the vapor pressure and saturated liquid and vapor densities. The changes of enthalpy and entropy between any two gas states can be evaluated from the following formulas, derived for these thermodynamic properties:

values can therefore be easily evaluated from the information presented here.

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NOTATION

d_s	= density of saturated vapor
d_c	= critical density
k	= 5.475
A, B, C, a_n, b	= empirical constants
T_r	= T/T_c
C_p^0	= $C_p^0 + R$ = constant-pressure heat capacity of ideal gas
C_v^0	= constant-volume heat capacity of ideal gas

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