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Pressure-Volume-Temperature Behavior of Difluoromethane

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The pressure-volume-temperature properties of difluoromethane are correlated using the Martin-Hou equation of state to within ±0.94% standard deviation over the experimental ranges: 25° to 200° C., 8 to 200 atm., and 47 to 1.8 cc. per gram. Vapor pressures have been determined from −83° to +78.4° C., the measured critical temperature. Using liquid densities measured between −25° and +78° C. and densities of saturated vapor computed from the Martin-Hou equation of this work, a rectilinear diameter line has been developed. The critical pressure is 57.54 atm., and the critical density is 0.430 grams per cc.

IN A cooperative program between the Bellevue Laboratory for High Pressure and the Industrial Chemicals Research Laboratory, Morristown, the physical properties of difluoromethane have been studied. These include the equation of state, vapor pressure, liquid density, and critical constants.

This compound has uses as a refrigerant (Refrigerant 32) and also as a component in refrigerant mixtures such as Refrigerant 504, which is an azeotrope of difluoromethane and pentafluorochloroethane. No experimental data on either vapor pressures, or *PVT* properties are available in the literature except the boiling point (*1*).

MATERIAL PURITY

The samples of CH_2F_2 (Genetron 32), were obtained from the Industrial Chemicals Division of Allied Chemical Corp. For the earlier samples, purification was made by a preparative scale gas chromatograph. The more recent samples were purified by distillation through a 50 x 1/2 inch vacuum jacketed column packed with nickel Helipaks. The entire sample was degassed several times by freezing the sample with liquid nitrogen and pumping off noncondensables (*4*). The purity was determined by gas chromatography to be 99.95 mole % or better for all samples used.

VAPOR PRESSURE MEASUREMENTS

Experimental Methods. Below room temperature where sample condensation was not a problem, and at pressures near or below atmospheric, the usual static manometric techniques served to measure the vapor pressure of the liquid. Here a manometer connects directly to an equilibrium cell located in a cryostat. The cryostat used at Bellevue consisted of a thermostatically controlled copper block. Its temperature was controlled to ±0.005° C. for periods up to 10 minutes by circulating chilled methanol through the block. A platinum resistance thermometer, calibrated by the U.S. National Bureau of Standards (degrees Centigrade. Int. 1948) (*6*) and monitored by a Type M-3 Mueller Bridge determined the temperature. For pressure observations, a cathetometer determined the mercury column height in the manometer to ±0.2 mm. At higher temperatures, the Bellevue *PVT* equipment, method I of

Table I. *PVT* Measurement Techniques

Measurement	Method	Ranges	Precision Temp.	 Press.	 Volume	 Weight
Vapor pressure	Manometric	−81 to −25° C 0 to 3 atm.	±0.02% ±0.05° C.	±0.1% ±0.2 mm	... ...	... ...
Vapor pressure	Allied static	−50 to +78.4° C. 1 to 57 atm.	±0.02% ±0.05° C.	±0.1%	...	...
Vapor pressure Equation of state Liquid compressibility	Mercury piston[a]	−25 to +100° C. 3 to 100 atm. 47 to 0.88 cc./g.	±0.02% ±0.05° C.	±0.1%	±0.05%	±0.03%
Equation of state Constant volume		100 to 200° C. 10 to 200 atm. 45 to 1.5 cc./g.	±0.12% ±0.03° C.	±0.2%	±0.2%	±0.1%

[a] Reference (5), method I.

reference (5), was also employed in the vapor pressure measurements (Table I).

The data taken by Allied used several techniques. At temperatures up to 20° C., the vapor pressure was measured by direct connection of a thermostatically controlled bomb to the pressure measuring device. A mercury manometer determined pressure up to 1 atm. and Heise gages of 0 to 3, 0 to 6, and 0 to 20 atm. ranges were used at higher pressures. Above 20° C. a high pressure bomb equipped with a hydraulic mercury-oil transmitter supplemented the gages (*4*).

Data. Equation 1, derived by a least square method, fits the experimental data of Table II within a standard deviation of ±0.21%. The equation is of the form:

$$\log_{10} P\ (\text{atm.}) = A + \frac{B}{T} + CT + DT^2 \qquad (1)$$

where $A = +8.43150\underline{44}$; $B = -1394.821$; $C = -0.0129338\underline{88}$; $D = +0.149021\underline{96} \times 10^{-4}$; and where $T = T$, °K. = t, °C. + 273.16. We can discard underlined digits for hand calculation.

The normal boiling point for difluoromethane, as calculated by Equation 1, is −51.69° C. compared with −51.6° C. (*1*), or with −51.63° to −51.68° C. measured at Industrial Chemicals Research Laboratory by boiling point tube methods. The data in Table II obtained by both laboratories show good agreement with Equation 1.

PVT MEASUREMENTS

Experimental. Several methods served to determine isotherm data for the equation of state and the liquid compressibilities. Table I presents these together with ranges and precisions of the measurements. Below 125° C., techniques developed at Bellevue and presented by Perraud, Lazarre, and Fournie (*5*) determined both vapor pressure and isotherm data. The mercury piston unit, method I (*5*), was the classical one in which mercury acts as the containing fluid for the sample and also as the support for a glass sample container of known volume. Here, a high pressure window permitted observation of critical phenomena. The visual observation of the disappearance or reappearance of the meniscus was taken as the critical temperature. Figure I is a schematic diagram of the Bellevue equipment used for method I. It consists of a cell *M* (volume 125 cc.) equipped with a high pressure window for observation of critical points and condensation. This is a rectangular parallelopiped (2.5 × 2.5 × 17 cm.) with two quartz plates placed in opposite walls and sealed with a metal gasket on Poly TFE joints. Its dead volume under valve *a* was 1 cc. This permitted rear lighting and telescopic observation through the window.

A 1000-cc. sample reservoir connects to cell *M* via pressure tubing and valve *a*. Two separate volumometers P_m and P_R separately control the mercury levels of the cell and of the sample volume. A mercury-oil separator device, equipped with two electrical contacts for level indication connects either volume to the pressure balance and thus permits separate observation of the pressure in each.

An air thermostat maintains this unit at the experimental temperature. It contains the platinum resistance thermometer and a suitable thermocouple located in the cell wall to ensure temperature equilibrium.

To fill cell *M*, one transfers a definite volume *V* of gaseous difluoromethane from the sample container via the interconnection and valve *a* replacing the mercury with which it was filled, simultaneously transferring the same volume of mercury from cell *M* to *R* by means of the volumometers, P_M and P_R. The method of direct weighing determines the density of the gas under the pressure and temperature conditions of reservoir *R*, and, thus, the density of the sample in *M*.

To obtain the isotherm data, *PVT* measurements and visual observations were made on the gas for each temperature at varying densities of filling.

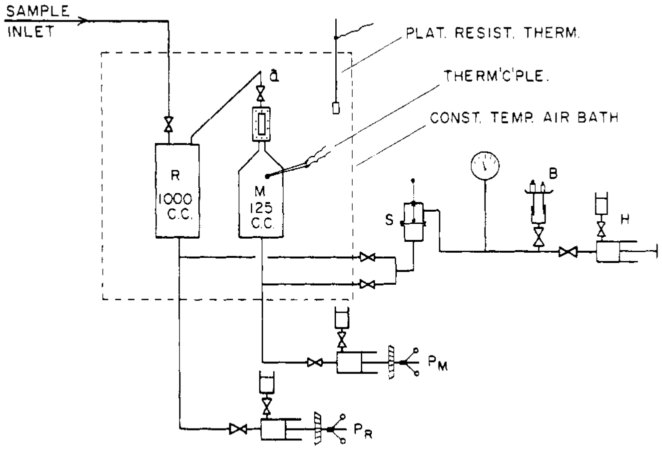

Figure 1. Mercury piston equipment

a. = Valve
B. = Deadweight gage
H. = Hydraulic piston
M. = Measurement cell
R. = Sample reservoir
S. = Mercury-oil separator
P_M, P_R. = Volumometers
PRT. = Platinum resistance thermometer
T_c. = Thermocouple

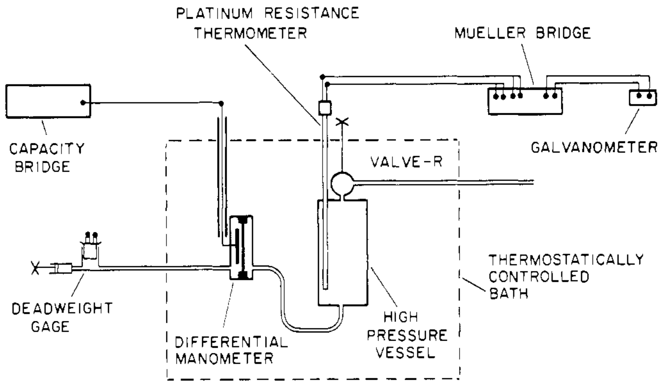

Figure 2. Constant volume *PVT* equipment

As temperature increases, use of the piston technique with or without mercury becomes less desirable because of the gasket or mercury vapor pressure complications. Therefore, for some 100° C. points and at 125° C. or above, a second method using a constant volume cell was employed (Figure 2). Here, a small high pressure vessel is connected via an oil-gas diaphragm differential manometer to an oil filled, dead weight gage and oil pressure pump. Valve *R* isolated the calibrated volume.

The differential manometer (Figure 3) is essentially composed of a plane diaphragm made of stainless steel (diameter, 40 mm.; thickness, 0.2 mm.). This is clamped on a metallic seal (to ensure no leakage between oil and gas) in such a way that the diaphragm can be submitted to a certain tension. On the oil side, an isolated plane electrode parallel to the diaphragm constitutes a condenser which is connected to a capacity bridge. The output of this bridge indicates the displacements of the diaphragm with respect to its equilibrium position. Before each experiment, a check run with argon was made with a conventional (Bourdon type) differential manometer, mounted (outside of the thermostatically controlled bath) in parallel with the diaphragm manometer. In this way, the corrections owing to the variations of the dielectric constant of the silicone oil with temperature and pressure were determined. The diaphragm differential manometer was very sensitive (± 1 mm. of Hg), and therefore, because of the corrections, an over-all accuracy, of the order of ±0.01 atm., was achieved for pressure measurements given in the paper, corresponding to a relative error of 1 or 2 × 10^{-4} for the average pressure measured. A thermostatically controlled bath, which contains the equipment, is composed of a metal tank thermally insulated and filled with a silicone oil, which resists oxidation up to 250° C. The heating is done by electrical resistances controlled by a contact thermometer regulator. The temperature is measured by the platinum resistance thermometer, which is lodged in the wall of the measurement vessel. The resistance bridge to which this thermometer is connected is the same as that used for the vapor pressure measurements.

Method of Operation for High Temperature Data. The amount of material admitted to the high temperature equipment is determined from the *PVT* data at 100° C. previously established by the mercury piston equipment, method I (5). After evacuation of the calibrated volume, this material is heated to 100° C. with the experimental sample. Opening the inlet valve permits the sample to expand into the calibrated volume, and then the valve is reclosed. Measurement of the equilibrium pressure at 100° C. with the known volume of the equipment and the available isotherm data permits computation of initial density of the material.

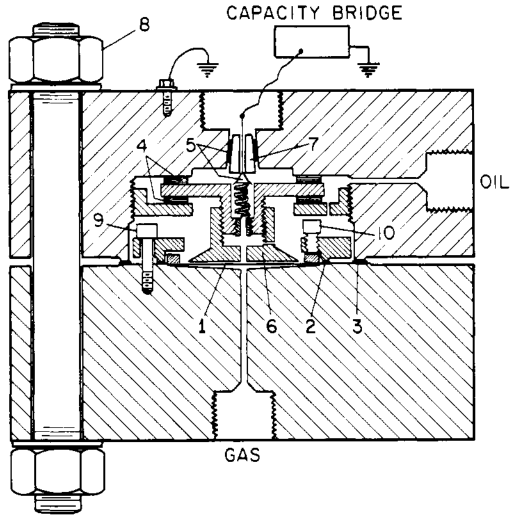

Figure 3. Differential manometer (scale – 1/2)

1. = Diaphragm
2. = Copper diaphragm seal
3, 5. = Copper seal
4. = Mica insulator
6. = Electrode
7. = Alumina insulator
8. = Eight clamping bolts
9. = Eighteen sealing screws
10. = Nine bending screws

Table II. Vapor Pressure of CH_2F_2

T, °C.	T, °K.	P_{obsd}, Atm.	P_{calcd}, Atm.	$(P_{obsd} - P_{calcd}/P_{calcd}) \times 100$
−81.96	191.20	0.1614[a]	0.16150	−0.05
−68.89	204.27	0.3830[a]	0.38280	0.05
−58.62	214.54	0.6948[a]	0.69360	0.17
−52.61	220.55	0.9562[a]	0.95395	0.23
−51.36	221.80	1.0171	1.01682	0.03
−49.91	223.25	1.0910	1.0938	−0.26
−32.64	240.52	2.4120[a]	2.4185	−0.28
−31.82	241.34	2.500	2.5034	−0.20
−25.73	247.43	3.201	3.2090	−0.26
−25.00	248.16	3.296	3.3030	−0.20
−22.86	250.30	3.599[a]	3.5907	0.23
−20.60	252.55	3.921[a]	3.9137	0.19
−6.89	266.27	6.422[a]	6.3942	0.46
−2.24	270.92	7.474[a]	7.4607	0.18
0.00	273.16	7.994	8.0203	−0.33
11.33	284.49	11.35	11.354	0.01
17.96	291.12	13.71[a]	13.739	−0.18
25.00	298.16	16.67	16.666	0.02
28.92	302.08	18.61[a]	18.489	0.66
40.09	313.25	24.56[a]	24.529	0.16
49.60	322.76	30.64	30.750	−0.35
50.03	323.19	31.12[a]	31.058	0.19
50.10	323.26	30.92[a]	31.108	−0.61
50.53	323.69	31.37[a]	31.419	0.16
56.01	329.17	35.68[a]	35.593	0.25
60.40	333.50	39.15[a]	39.238	−0.23
67.27	340.43	45.50[a]	45.524	−0.05
69.78	342.94	48.07[a]	48.010	0.14
75.00	348.16	53.47	53.525	−0.10
78.40 T_c	351.56	57.52	57.382	0.27
		Std. Dev.		± 0.28%

[a] Allied Chemical data, static method.

To obtain the high temperature isotherms, the thermostatically controlled bath is then heated to a temperature close to that of the isotherm to be determined (125°, 150°, 175°, or 200° C.) to facilitate the measurement at these whole values. The pressure and the temperature are measured after stabilization. By returning to the initial conditions, one can verify that the measurement vessel was air tight during the heating cycle.

Table III. CH_2F_2 Isotherms

V, Cc./G.	P_{obsd}, Atm.	P_{calcd}, Atm.	$(P_{obsd} - P_{calcd})/(P_{calcd})$
	t = [a]25.0$\underline{0}$° C., 298.16° K.		
47.03	$8.79\underline{3}$	8.831	−0.43
36.89	$10.80\underline{8}$	10.869	−0.57
29.98	$12.8\underline{30}$	12.874	−0.35
24.92	$14.8\underline{04}$	14.856	−0.35
	t = 50.0$\underline{0}$° C., 323.16° K.		
50.45[b]	$8.88\underline{3}$	9.210	−3.68
28.95	$14.7\underline{90}$	14.965	−1.18
19.09	$20.7\underline{25}$	20.819	−0.45
14.97	$24.6\underline{73}$	24.729	−0.22
11.77	$28.6\underline{21}$	28.730	−0.38
10.47	$30.5\underline{95}$	30.621	−0.09
10.17	$31.0\underline{89}$	31.072	+0.05
	t = 70.0$\underline{0}$° C., 343.16° K.		
21.58	$20.7\underline{25}$	20.853	−0.61
12.94	$30.5\underline{95}$	30.700	−0.34
8.164	$40.4\underline{64}$	40.508	−0.11
6.255	$45.3\underline{99}$	45.466	−0.15
5.465	$47.3\underline{74}$	47.442	−0.15
	t = 75.0$\underline{0}$° C., 348.16° K.		
22.11	$20.7\underline{25}$	20.888	−0.78
13.46	$30.5\underline{95}$	30.690	−0.31
8.738	$40.4\underline{64}$	40.506	−0.10
6.991	$45.3\underline{99}$	45.395	+0.01
5.368	$50.3\underline{33}$	50.252	+0.10
5.024	$51.3\underline{20}$	51.222	+0.19
4.650	$51.9\underline{67}$	52.199	+0.21
4.213	$53.2\underline{95}$	53.183	−0.21
	t = 77.0$\underline{0}$° C., 350.16° K.		
45.62[b]	$10.85\underline{6}$	11.149	−2.70
22.36	$20.7\underline{25}$	20.869	−0.69
11.10	$35.5\underline{29}$	35.433	+0.27
9.005	$40.4\underline{64}$	40.357	+0.27
7.265	$45.3\underline{99}$	45.291	+0.24
5.702	$50.3\underline{33}$	50.222	+0.22
5.671	$50.3\underline{33}$	50.321	+0.03
4.363	$54.2\underline{81}$	54.183	+0.18
3.948	$55.2\underline{68}$	55.137	+0.24
3.322	$56.2\underline{55}$	56.079	+0.31
	t = 78.0$\underline{0}$° C., 351.16° K.		
7.336	$45.3\underline{99}$	45.422	−0.05
5.776	$50.3\underline{33}$	50.453	−0.25
3.754	$56.2\underline{55}$	56.280	−0.04
	t = 80.0$\underline{0}$° C., 353.16° K.		
46.20[b]	$10.8\underline{56}$	11.134	−2.56
13.91	$30.5\underline{95}$	30.742	−0.48
6.018	$50.3\underline{33}$	50.540	−0.41
4.604	$55.2\underline{68}$	55.384	−0.21
3.981	$57.2\underline{42}$	57.248	−0.01
	t = 100.0$\underline{0}$° C., 373.16° K.		
49.47[b]	$10.8\underline{56}$	11.160	−2.80
24.85	$20.7\underline{25}$	20.863	−0.60
16.60 V[c]	$29.6\underline{58}$	29.351	+1.03
10.90 V	$41.2\underline{02}$	40.598	+1.46
7.998	$50.3\underline{33}$	50.107	+0.45
7.922	$50.3\underline{33}$	50.410	−0.15
7.150 V	$53.7\underline{88}$	53.681	+0.20
6.900 V	$54.9\underline{74}$	54.820	+0.28
6.789	$55.2\underline{68}$	55.338	−0.13
5.812	$60.2\underline{03}$	60.272	−0.11
4.952	$65.1\underline{37}$	65.199	−0.10
3.488	$75.0\underline{07}$	74.971	−0.05
3.400 V	$75.3\underline{04}$	75.628	−0.43
3.300 V	$76.0\underline{41}$	76.390	−0.46
1.776	$99.6\underline{86}$	99.605	+0.08
	t = 125.0$\underline{0}$° C., 398.16° K.		
22.24[b]	$25.6\underline{60}$	25.101	+2.18
17.78	$30.5\underline{95}$	30.510	+0.28
9.590	$50.3\underline{33}$	50.266	+0.13
6.100	$68.8\underline{42}$	68.956	−0.16
5.330	$75.0\underline{07}$	75.022	−0.02
3.176	$99.6\underline{80}$	99.767	−0.09
2.174	$124.\underline{35}$	124.045	+0.25
1.900	$139.\underline{11}$	139.013	+0.07
1.782	$149.\underline{03}$	149.178	−0.10
1.602	$173.\underline{70}$	173.868	−0.10
1.495	$198.\underline{37}$	198.273	+0.05
	t = 150.0$\underline{0}$° C., 423.16° K.		
16.60[b]	$35.\underline{97}$	35.288	+1.91
10.90	$50.6\underline{3}$	50.428	+0.41
7.150	$70.6\underline{2}$	70.196	+0.59
6.100	$78.9\underline{5}$	78.851	+0.13
3.400[b]	$117.\underline{45}$	116.552	+0.76
3.300[b]	$118.\underline{73}$	118.794	−0.06
1.900[b]	$181.\underline{00}$	184.112	−1.72
	t = 175.0$\underline{0}$° C., 448.16° K.		
10.90	$54.9\underline{74}$	55.190	−0.39
7.150	$78.2\underline{10}$	78.157	+0.07
6.100	$88.3\underline{0}$	88.536	+0.11
3.400	$138.\underline{32}$	136.474	+1.33
	t = 200.0$\underline{0}$° C., 473.16° K.		
16.60	$41.\underline{16}$	41.052	+0.25
10.90	$59.\underline{80}$	59.893	−0.15
7.150	$85.\underline{86}$	86.003	−0.16
6.900[b]	$87.1\underline{0}$	88.593	−1.72
6.100	$98.0\underline{5}$	98.077	−0.02
3.400	$159.\underline{39}$	156.186	+2.01
3.300	$161.\underline{96}$	159.934	+1.25

[a] Uncertain figures are underlined. [b] Points not included in Equation 2, Table IV derivation. [c] V = constant volume, high temperature method.

Average % deviation, all 86 points = ±0.53

Standard % deviation, all 86 points = ±0.94

Standard % deviation atm., all 86 points ±0.69

Standard % deviation atm., all 86 points but 4 above 100° C. and 100 atm. ±0.25.

Table IV. CH_2F_2 Martin-Hou Equation of State

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2 e^{\frac{-KT}{T_c}}}{(V-b)^2} + \frac{A_3 + B_3T + C_3 e^{\frac{-KT}{T_c}}}{(V-b)^3} + \frac{A_4}{(V-b)^4} + \frac{A_5 + B_5T + C_5 e^{\frac{-KT}{T}}}{(V-b)^5} \quad (2)$$

Where;

P = atmospheres
T = ° K. or 273.16 + t ° C.
V = cc. per gram, specific volume
T_c = 351.56° K. or 78.4° C.
K = 5.475
R = 1.577232 cc. atm. ° K.$^{-1}$ gram^{-1}
b = $0.0368\underline{5236}$
A_2 = $-3605.377\underline{0}$
B_2 = $+5.110136\underline{8}$
C_2 = $-64629.8\underline{99}$
A_3 = $+5533.040\underline{0}$
B_3 = $-6.989460\underline{0}$
C_3 = $+170602.4\underline{09}$
A_4 = $-3329.88\underline{77}$
A_5 = -3556.2514
B_5 = $14.5294\underline{23}$
C_5 = $-10458\underline{9.48}$

Results. The remarks previously made concerning the resistance thermometer indicate a precision of ±0.05° C. for the temperature values measured, allowing for the stability of the thermostatically controlled bath, which is of the order of ±0.03° C. The initial density is determined from the values obtained with the mercury apparatus, and thus, their accuracy is determined by the precision of this apparatus. The specific volumes above 100° C. are corrected for the effect of temperature on the vessel containing the volume of gas under study.

The accuracy of the pressure measurements would be the same as the accuracy of the pressure balance—i.e., 0.1%; but the inaccuracy in the determination of the density was equivalent to an error of the same order as the pressure—i.e., 0.1%. Therefore, the total error of the pressure is 0.2%, in the case of this third method.

Data. Table III presents the data used to derive the Martin-Hou equation of state, Equation 2 (*2, 3*). Table IV gives the form and constants for this relation.

The precision of the input variables based on information of the equipment section is 0.02% or better for temperature, 0.03% for weight of sample, and the volume accuracy in various methods was about 0.05%. For pressures, the accuracy is 0.1% in the case of the equipment of reference (*5*) essentially (method I) and 0.2% for the constant volume method.

Equation 2, Table IV fits the data with an average error of ±0.94%. Above 100° C. and 100 atm. the equation starts to diverge from the data. Evidence for this is the standard deviation of the calculated pressures which is ±0.65 atm. for all points but only ±0.25 atm. when the four points above 100° C. and above 100 atm. are not used. Of interest is the fit of the equation in the 100 to 200 atm. region at the higher temperature ranges, which is often surprisingly good. No attempt was made at this time to analyze the liquid compressibility data, which will be the subject of the future study and which served only to determine liquid densities as below.

LIQUID DENSITY

Experimental. The data on liquid compressibility (Table V) graphically extrapolated to the saturated vapor pressure, determined the orthobaric liquid density for temperatures up to 70° C. Above this temperature, the curvature of the isotherms near the saturation point becomes large, and the extrapolations become increasingly inaccurate. However, below 70° C., the density can be measured to within 0.001 gram per cc. and the temperature to ±0.2° C.

Between 70° C. and the critical temperature, a pycnometer method determined the liquid density. This apparatus consisted of a heavy-walled glass ampoule of approximately 12-cc. volume. Calibration with water measured the

Table V. Liquid Pressure Isotherms

$t = -25.0\underline{0}$° C.		$t = 10.0\underline{0}$° C.		$t = 25.0\underline{0}$° C.		$t = 50.0\underline{0}$° C.	
$P_{atm.}$	$V_{cc./g.}$	$P_{atm.}$	$V_{cc./g.}$	$P_{atm.}$	$V_{cc./g.}$	$P_{atm.}$	$V_{cc./g.}$
198.4	0.850	198.4	0.879	198.4	0.960	198.4	1.035
173.7	0.854	173.7	0.883	173.7	0.968	173.7	1.047
149.0	0.857	149.0	0.888	149.0	0.976	149.0	1.062
124.4	0.861	124.4	0.893	124.4	0.985	124.4	1.078
99.68	0.865	99.68	0.898	99.68	0.995	99.68	1.098
75.01	0.869	75.01	0.903	75.01	1.006	75.01	1.123
50.33	0.873	50.33	0.909	50.33	1.019	50.33	1.155
25.66	0.878	25.66	0.915	25.66	1.035	40.46	1.173
4.935	0.882	5.922	0.920	17.76	1.040	35.53	1.183
3.303[a]	0.8823	5.749[a]	0.9200	16.67[a]	1.0410	30.04[a]	1.1905

$t = 0.0\underline{0}$° C.		$t = 10.0\underline{0}$° C.		$t = 70.0\underline{0}$° C.	
198.4	0.900	198.4	0.923	99.68	1.231
173.7	0.905	173.7	0.929	60.20	1.369
149.0	0.911	149.0	0.935	50.33	1.443
124.4	0.916	124.4	0.942		
99.68	0.922	99.68	0.949	48.23[a]	1.4639
75.01	0.929	75.01	0.957		
50.33	0.936	50.33	0.966		
25.66	0.943	25.66	0.976		
9.869	0.950	11.84	0.983		
8.020[a]	0.9505	10.92[a]	0.9835		

[a] Extrapolated value.

Table VI. Density of CH_2F_2

t, °C.	d_{obsd}, G./Cc.	d_{calcd}, G./Cc.	$(d_{obsd} - d_{calcd}/d_{calcd}) \times 100$
$-25.\underline{00}$	1.133	1.134	−0.07
$-10.\underline{00}$	1.087	1.086	+0.09
$0.\underline{00}$	1.052	1.052	+0.00
$10.\underline{00}$	1.017	1.016	+0.07
$12.\underline{15}$	1.006^a	1.009	−0.30
$25.\underline{00}$	0.961	0.959	+0.20
$50.\underline{00}$	0.840	0.839	+0.12
$61.\underline{39}$	0.764^a	0.764	−0.00
$62.4\underline{0}$	0.756^a	0.756	−0.00
$65.1\underline{0}$	0.731^a	0.733	−0.29
$65.9\underline{6}$	0.723^a	0.725	−0.29
$70.\underline{00}$	0.683	0.682	+0.14
$73.\underline{17}$	0.640^a	0.639	+0.15
$73.8\underline{7}$	0.631^a	0.627	+0.64
$76.2\underline{2}$	0.575^a	0.578	−0.53
$78.4\underline{0}$	0.430^b		

Standard per cent deviation = 0.25%

[a] Allied Chemical sealed tube method. [b] From rectilinear diameter line.

ampoule volume with respect to a zero reference mark in the capillary neck and also variation of capillary volume with height. To carry out a measurement, a weighed quantity of sample was distilled into the ampoule, frozen in liquid nitrogen, and the ampoule sealed. After the seal off, the exact sample weight is taken, and the ampoule is heated until the liquid level reaches the zero reference line. The volume calibration was accurate to ±0.02 cc., the temperature to ±0.02° C., and the mass to 0.001 grams, giving an over-all accuracy for the measurements of 0.2% or better.

The equation used to correlate the data is that of Martin and Hou (2).

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

A_1 = +0.60501

A_2 = +1.44591

A_3 = −2.186346

A_4 = +1.56228

T_c = +351.56° K.

d_c = +0.4296 grams per cc. (computed from Equation 4)

Equation 3, derived by least squares, fits the experimental data to ±0.25% standard deviation with $n = 4$. Table VI gives the fit of the data.

Table VII. Critical Constants for CH_2F_2

Temperature, ° C.	=	+78.4
Pressure, atm.	=	57.54
Density, g./cc.	=	0.430

CRITICAL CONSTANTS AND RECTILINEAR DIAMETER EQUATION

The critical temperature measured by visual observation of the liquid meniscus in the window equipped mercury piston unit is +78.4° ± 0.2° C., in good agreement with an earlier value of 78.2° ± 0.1° C. obtained at Allied Chemical by the sealed tube method. The measured critical pressure is 57.54 atm.

A rectilinear diameter Equation 4 is shown below:

$$\frac{d_l + d_v}{2} \text{ g./cc.} = 0.9188 - 0.0013916T \qquad (4)$$

where T = ° K.; d_l = orthobaric liquid density; and d_v = orthobaric vapor density.

To make this computation, the liquid density at various selected temperatures was calculated. Then for these temperatures and their corresponding vapor pressures, the Martin-Hou Equation 2 was solved implicitly for the specific volume of the saturated vapors, from which one computes the density value. Extrapolating this line to the critical temperature results in a calculated value of 0.4296 gram per cc. for the critical density (Table VII).

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