Thermodynamic Properties of Dichlorotetrafluoroethane

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SYMMETRICAL dichlorotetrafluoroethane ($CClF_2$—$CClF_2$) is one of a series of halogenated hydrocarbons used as a refrigerant and heat transfer fluid. In industrial applications it is known as Freon 114. The compound has not been studied over wide ranges of conditions, and few articles have been published on its properties. Thornton, Burg, and Schlesinger (*14*) reported some measurements of vapor pressure from about 2 to 150 p.s.i.a. Locke, Brode, and Henne (*7*) determined several saturated liquid densities. Some vapor pressure, saturated liquid density, saturated liquid specific heat, and *P-V-T* data were obtained in the Jackson Laboratory of the Du Pont Co., but were not published (*11*). Benning and McHarness (*3*) measured a few vapor specific heats and developed a table of thermodynamic properties. Also, some saturated liquid specific heat data were taken in the Cryogenic Laboratory of the Pennsylvania State University but not published (*2*). The Raman spectra have been investigated by Glockler and Sage (*4*), and Smith, Nielsen, Berryman, Claassen, and Hudson (*13*) studied the infrared spectra, but no complete analysis of the structure of the $CClF_2$—$CClF_2$ molecule has been made to permit choosing the correct fundamental vibrational frequencies.

Table I. Vapor Pressure

T, ° R.	P, P.S.I.A. Exptl.	P, P.S.I.A. Calcd.	% Dev.	Exptl. Investigator
350.21	0.1276	0.1276	−0.00	A[a]
350.68	0.1265	0.1305	−3.14	(*11*)
381.17	0.4900	0.4894	0.12	(*11*)
381.56	0.4958	0.4970	−0.24	(*11*)
410.88	1.4333	1.4333	0.00	A
419.69	1.8752	1.9064	−1.66	(*14*)
454.59	5.2083	5.2116	−0.06	(*11*)
455.69	5.2215	5.3641	−2.73	(*14*)
495.14	13.786	13.683	0.74	(*3*)
498.89	14.505	14.825	−2.21	(*14*)
531.99	28.437	28.437	0.00	(*3*)
561.89	47.306	47.515	−0.44	(*3*)
563.83	49.584	49.020	1.14	(*11*)
602.50	86.530	87.088	−0.65	(*3*)
605.21	90.100	90.392	−0.32	A
630.20	125.20	125.37	−0.14	A
636.19	135.30	135.05	0.19	A
640.87	144.86	142.98	1.29	(*11*)
641.12	142.07	143.42	−0.95	(*3*)
646.70	153.60	153.35	0.17	A
663.91	187.70	187.18	0.28	A
671.04	202.40	202.72	−0.16	A
691.67	252.70	253.20	−0.20	A
694.53	256.74	260.89	−1.62	(*11*)
696.13	266.50	265.28	0.46	A
708.84	300.60	302.26	−0.55	A
724.46	356.90	353.45	0.96	A
743.13	426.80	424.90	0.45	A
743.65	430.89	427.08	0.88	(*11*)
750.26	454.00	456.00	−0.44	A
753.95	Critical point	473.19		

[a] A: Author, Tables I, II, and III.

EXPERIMENTAL WORK AND RESULTS

A purified sample of dichlorotetrafluoroethane was supplied by the Freon Products Division, Du Pont Co. Its analysis was stated to be approximately 95% $CClF_2$—$CClF_2$ and 5% CCl_2F—CF_3, a typical isomeric composition of the commercial product. Measurements were made of the vapor pressure, *P-V-T* behavior of the gas, saturated liquid density, and critical temperature by techniques previously described (*1*, *5*). The following sections summarize experimental results and comparisons with the particular correlating equations.

Vapor Pressure. The vapor pressure data of the several investigators have been represented by an algebraic equation of a form which has been shown (*9*) to fit the data for other compounds within experimental error from the triple point to the critical point. The vapor pressure equation is

$$\log_{10}P = 27.071306 - \frac{5113.7021}{T} - 6.3086761 \log_{10}T$$
$$+ 0.0006913003T + 600.40491 \left(\frac{768.35 - T}{768.35T}\right) \log_{10}(768.35 - T) \qquad (1)$$

where T is in ° R. (° F. + 459.69) and P is in p.s.i.a.

Table I compares some of the experimental points and those calculated from Equation 1. The scatter is in both the positive and negative directions with no obvious trends.

Pressure-Volume-Temperature Behavior of the Gas. Because previous data had been taken (*11*) for volumes greater than about 0.1 cubic foot pound, this study concentrated on lower volumes. All data were fitted with the Martin-Hou equation of state (*8*, *10*). Table II compares some of the experimental pressures with those calculated from the following equation:

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2T + C_2 \exp. - KT_r}{(V-b)^2} +$$
$$\frac{A_3 + B_3T + C_3 \exp. - KT_r}{(V-b)^3} + \frac{A_4}{(V-b)^2} +$$
$$\frac{A_5 + B_5T + C_5 \exp. - KT_r}{(V-b)^5} \qquad (2)$$

with

$R = 10.7351/\text{M.W.} = 10.7315/170.936$
$T_r = T/T_c = T/753.95$
$b = 0.005914907$
$k = 3.0$
$A_2 = -2.3856704$
$B_2 = 0.0010801207$
$C_2 = -6.5643648$
$A_3 = 0.034055687$
$B_3 = -5.3336494 \times 10^{-6}$
$C_3 = 0.16366057$
$A_4 = -3.857481 \times 10^{-4}$
$A_5 = 1.6017659 \times 10^{-6}$
$B_5 = 6.263234 \times 10^{-10}$
$C_5 = -1.0165314 \times 10^{-5}$

In addition to utilizing the critical *P-V-T*, the following values were put into the appropriate formulas (*8*, *10*) to obtain the above constants in the equation of state: $T_B = 1650$, $T' = 595$, $m = 4.82$, $n = 1.7$, $y = 3.5$.

Equation 2 represents the data well except for the very smallest volume which actually is beyond the range of applicability claimed for the equation.

Saturated Liquid Density. Saturated liquid densities were measured only at very low and very high temperatures, as the other temperatures had been adequately covered in previous investigations. The following equation was used to represent all of the data:

$$d_l = 36.32 + 0.021776(T_c - T) + 0.634649(T_c - T)^{1/2} + 6.71826(T_c - T)^{1/3} + 1.97 \times 10^{-6}(T_c - T)^2 \text{ lb./cu. ft.} \qquad (3)$$

where T_c is 753.95° R.

Table II. Pressure-Volume-Temperature Behavior of Gas

Vol., Cu. Ft./Lb.	Temp., ° R.	P, P.S.I.A. Exptl.	P, P.S.I.A. Calcd.	% Dev.	Exptl. Investigator
2.20310	536.88	14.78	14.81	−0.18	(*11*)
0.63371	573.78	51.39	51.39	0.00	(*11*)
0.63371	767.10	71.98	72.12	−0.20	(*11*)
0.39348	605.64	82.97	83.42	−0.54	(*11*)
0.39348	767.10	112.47	112.46	0.01	(*11*)
0.22302	648.84	146.22	145.38	0.58	(*11*)
0.22302	725.16	172.09	171.60	0.29	(*11*)
0.22302	799.32	197.51	196.46	0.53	(*11*)
0.15803	673.50	197.07	197.99	−0.46	(*11*)
0.15803	732.36	228.5	228.3	0.07	(*11*)
0.15803	799.50	263.6	262.1	0.57	(*11*)
0.12872	690.06	236.2	236.5	−0.12	(*11*)
0.12872	724.98	260.0	259.6	0.14	(*11*)
0.12872	764.04	286.0	285.1	0.32	(*11*)
0.12872	799.68	310.2	308.0	0.73	(*11*)
0.12225	702.98	245.2	253.2	−3.15	A
0.12225	757.36	289.3	291.2	−0.65	A
0.12225	812.35	331.5	328.8	0.83	A
0.12225	862.36	373.8	362.3	3.18	A
0.097876	707.50	278.2	291.1	−4.45	A
0.097876	770.48	342.3	349.3	−2.00	A
0.097876	855.14	421.8	424.9	−0.73	A
0.095886	708.24	293.5	294.9	−0.48	(*11*)
0.095886	724.98	311.0	311.0	0.01	(*11*)
0.079142	738.21	353.3	357.9	−1.29	A
0.079142	807.44	437.5	440.7	−0.72	A
0.079142	864.07	504.9	506.5	−0.31	A
0.073779	735.73	360.3	366.2	−1.60	A
0.073779	776.53	421.3	420.1	0.29	A
0.073779	804.88	456.5	456.9	−0.09	A
0.073779	862.43	532.3	530.3	0.39	A
0.064898	748.63	402.8	404.9	−0.53	A
0.064898	811.56	504.5	502.3	0.44	A
0.064898	864.10	587.0	581.5	0.95	A
0.056482	743.95	406.5	415.8	−2.25	A
0.056482	797.93	522.3	516.9	1.05	A
0.056482	864.01	653.9	637.1	2.64	A
0.052291	751.46	443.2	439.6	0.82	A
0.052291	804.27	557.3	548.8	1.54	A
0.052291	863.29	688.8	667.8	3.14	A
0.041708	770.57	515.2	512.1	0.61	A
0.041708	828.41	688.5	672.7	2.34	A
0.041708	874.31	818.0	797.8	2.54	A
0.034012	766.73	509.2	519.4	−1.97	A
0.034012	804.65	656.2	658.3	−0.32	A
0.034012	824.14	728.3	729.1	−0.12	A
0.034012	863.04	868.5	869.5	−0.12	A
0.028310	746.29	440.4	437.5	0.66	A
0.028310	785.89	620.4	621.8	−0.23	A
0.028310	825.37	806.5	805.2	0.16	A
0.028310	862.28	980.9	976.4	0.46	A
0.023752	753.40	475.3	470.3	1.07	A
0.023752	776.03	600.2	602.2	−0.34	A
0.023752	818.49	853.4	852.4	0.12	A
0.023752	862.81	1124.0	1116.5	0.67	A
0.019322	765.73	591.0	593.9	−0.48	A
0.019322	786.04	776.0	766.2	1.28	A
0.019322	804.95	942.2	928.7	1.46	A
0.019322	824.47	1124.6	1098.3	2.39	A
0.019322	862.97	1481.5	1438.1	3.02	A
0.017123	730.81	384.8	360.6	6.71	A
0.017123	772.09	857.8	882.7	−2.83	A
0.017123	804.49	1249.2	1298.3	−3.78	A
0.017123	832.35	1582.2	1659.2	−4.64	A

Table III shows that the equation fits the data within their probable experimental precision. The greatest deviation, of course, occurs in the neighborhood of the critical temperature, where the density changes extremely rapidly with temperature.

Critical Properties. The critical temperature was determined by observing the disappearance and reappearance of the meniscus. The average of two observations was 294.3° F., which agreed with an earlier (*11*) determination of 145.7° C. The latter value was converted to 753.95° R., which was used in the equations reported here.

The critical pressure was obtained by inserting the critical temperature into Equation 1. The result, 473.187 p.s.i.a., is slightly higher than that obtained earlier (*11*).

The critical density had been estimated (*11*) as 36.32 pounds per cubic foot. This value was checked on a rectilinear diameter plot of saturated density *vs.* temperature, and found to be within the precision of estimating from the plot.

Heat Capacity of Gas. The statistical heat capacity of the gas at zero pressure or infinite volume has been calculated by choosing a set of fundamental vibrational frequencies from the Raman and infrared spectra. The choice of the fundamentals was arbitrary, because there was no good analysis of structure of the molecule available. Table IV lists the major spectral lines that have been observed (*4*, *13*), and shows the 17 chosen as fundamentals. According to the number of degrees of freedom for this molecule there should be either one more fundamental vibrational frequency or a contribution due to internal rotation. The assumption was made that free internal rotation existed, contributing $R/2$ to the heat capacity. The ideal gas heat capacity was calculated from 360° to 900° R. using conventional techniques (*1*, *5*, *6*), and the calculated points fitted with a simple quadratic equation. For both the constant volume and constant pressure heat capacities the results are

Table III. Saturated Liquid Density

Temp., ° R.	d_L, Lb./Cu. Ft. Exptl.	d_L, Lb./Cu. Ft. Calcd.	% Dev.	Exptl. Investigator
753.80	39.90	40.14	−1.57	A
752.40	45.22	44.92	+0.47	A
747.65	50.77	50.46	+0.55	(*11*)
738.29	55.97	55.99	−0.07	(*11*)
737.00	56.56	56.57	−0.05	A
722.09	61.92	61.91	0.00	(*11*)
699.95	67.66	67.57	+0.12	(*11*)
665.07	74.25	74.25	−0.01	(*11*)
619.29	81.08	81.11	−0.04	(*11*)
574.42	86.69	86.73	−0.05	(*11*)
554.89	88.91	88.94	−0.03	(*11*)
554.69	88.76	88.97	−0.24	(*7*)
546.61	89.82	89.85	−0.03	(*11*)
536.69	90.84	90.92	−0.09	(*7*)
516.17	93.06	93.05	+0.01	(*11*)
491.74	95.52	95.48	+0.04	(*11*)
491.69	95.52	95.48	+0.04	(*3*)
491.69	95.59	95.48	+0.11	(*7*)
435.17	100.89	100.72	+0.16	(*11*)
424.64	101.69	101.65	+0.04	A
352,73	107.47	107.68	−0.20	A

$$C_v^0 = 0.0175 + 3.49 \times 10^{-4} T - 1.67 \times 10^{-7} T^2 \text{ B.t.u./lb.-° R.} \qquad (4)$$

$$C_p^0 = C_v^0 + 1.98589/170.936$$

$$= 0.029118 + 3.49 \times 10^{-4} T - 1.67 \times 10^{-7} T^2 \text{ B.t.u./lb.-° R.} \qquad (5)$$

where T is ° R.

It is interesting to compare the heat capacity of $CClF_2$—$CClF_2$ with that for the isomer CF_3—CCl_2F. The absorption frequencies and the fundamentals have been reported (*12*) for the latter compound along with the calculated heat capacity, assuming internal rotation to be one of the fundamental frequencies. At 298° K. the value of C_v^0 for this isomer is reported as 25.3 cal./gram mole-° K., whereas the frequencies chosen in this work for the symmetrical isomer give a value of 26.9 cal./gram mole-° K. This might indicate that the fundamentals chosen here give a heat capacity which is about 5% too high; however, the same authors (*12*) reported a value of the heat capacity for CF^3—$CClF_2$ of about 4% lower than a value measured by the present investigator. One other method of confirming the gas heat capacity is by calculating the saturated liquid heat capacity and comparing with some unpublished data (*2*). The technique of making this comparison has been previously described in detail (*6*). The results show that at 275.94° K. the heat capacity of the saturated liquid calculated from the heat capacity of the gas is 39.235 cal./gram mole-° K, whereas the experimentally measured value is 39.04 cal./gram mole-° K. At 237.05° K. the calculated heat capacity is 35.264, whereas the experimental value is 36.62. It must be understood that these checks involve the accuracy of the vapor pressure equation and the *P-V-T* equation, as well as the gas heat capacity. In view of these comparisons, the fundamentals selected in this work and the resulting calculated heat capacity are not out of line. Of course, the only way to settle the question is to have experimental measurements taken on the heat capacity of gaseous $CClF_2$—$CClF_2$.

Table IV. Infrared and Raman Spectra

(All values in $cm.^{-1}$)

Infrared	Raman	Infrared	Raman
	171.4[a]	772	
	207.4[a]	847	
	253.1[a]	849	
	309.5[a]	850	
	325.7[a]	864	
	360.0[a]	869	
	399.9[a]	883	
	443.9[a]	888	
475			914.7[a]
	497.7[a]	923	
	503	928	
505		943	
	542.3[a]	948	
	556.5[a]	981	
560		988	
565		1003	1043.5
590		1053	
617			1055.9
621			1063.7
	677.0[a]	1111	
678			1111.6
	699.9[a]	1140	
	723.4		1172.5[a]
731		1186	
	734.1[a]	1195	
735		1229	
740		1223	
762		1274	
768			1269.6[a]

[a] Selected as fundamental frequency.

CONCLUSIONS

Experimental data have been taken over wide ranges of temperature and pressure, and appropriate correlating equations have been developed to permit calculation of the thermodynamic properties of the saturated liquid, saturated vapor, and superheated vapor of dichlorotetrafluoroethane. The equations appear to represent the data within experimental accuracy. The techniques of using an electronic digital computer to calculate the various properties have been described (*1, 5, 6*), and are being applied to this compound by a group at Oak Ridge Gaseous Diffusion Plant.

NOMENCLATURE

A_2, A_3, etc. = constants in equation of state
b = constant in equation of state
B_2, B_3, etc. = constants in equation of state
C_2, C_3, etc. = constants in equation of state
C = heat capacity of gas, B.t.u./lb.-° R.
d = density, pounds per cubic foot
k = constant in equation of state
P = pressure, p.s.i.a.
R = gas constant, 1.98589 B.t.u./lb. mole-° R. or 10.7315 cu. ft.-lb./lb. mole-° R.-sq. inch
T = absolute temperature ° R. (° F. + 459.69)
V = volume, cubic feet per pound

Subscripts

c = critical property
l = saturated liquid
p = constant pressure
r = reduced condition, as $T_r = T/T_c$
v = constant volume

Superscripts

0 = ideal gas state

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