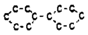
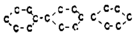
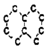
Table I. *(Continued)*

Compound	$-\Delta H$, B.t.u./Lb. (Net Value at 77° F.) Obsd.	Calcd.	Dev. calcd.−obsd.	% cis	% trans	Major Component, Mole %[a]	Estimated Purity of Desired Compound, Mole %[a]
Miscellaneous structures							
1,7,13,19-Eicosatetrayne[h]	18,690	18,720	+30				
1,3,5-Tricyclopentylcyclohexane	18,280	18,330	+50			99+	
1,1-Bis(4-methylcyclohexyl)ethane	18,530	18,470	−60				

[a] All purity checks made with aid of vapor phase chromatography. [b] Both cis- and trans-isomers eluted under one peak; this figure represents mole per cent of both isomers. [c] Vapor phase chromatography showed more than one major peak. Peaks are believed to be isomers of desired compound, and over-all purity of desired material has been estimated. [d] Low boiling isomer. [e] High boiling isomer. [f] Estimated purity of desired compound is minimum figure; actual purity may be higher. [g] Small quantity of ethyl Decalins may be present. [h] Material not investigated by vapor phase chromatography because it exhibited a tendency to explode on heating. [i] Vapor phase chromatography showed four unresolved peaks, probably isomers of desired compound. No purity calculation made.

Table II. Coefficients for Equation 2

Base value for liquid hydrocarbons, $a = 5.7$, $b = 52.08$

Functional group	a	b	Structure[a] (see rule 2)
Branched paraffin[b]	−3.7	+0.09	
Cyclopropane[b]	+16.2	−0.13	
Cyclobutane[b]	+10	+0.11	
Cyclopentane[b]	−1.7	0.00	
Cyclohexane[b]	−7.4	0.00	
Cycloheptane[b]	+17	−0.99	
Bicyclohexyl	−12.0	−0.01	
Tercyclohexyl	−27.6	+0.11	
Decalin	−13.9	0.0	
Hydrindan	−21.2	+0.25	

[a] All carbon atoms may have either hydrocarbon chain or hydrogen attached. [b] Values determined by Handrick (*3*).

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Thermodynamic Properties of Perfluorocyclobutane

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PERFLUOROCYCLOBUTANE, C_4F_8, is the completely fluorinated derivative of cyclobutane, alternatively known as octafluorocyclobutane and Freon-C318. The compound may be prepared either by cyclic dimerization of tetrafluoroethylene or by pyrolysis of polytetrafluoroethylene. For many potential applications of this compound in refrigeration, heat transfer, and propellents, it is desirable to know the thermodynamic properties. So far one table of such properties has been published (*1*). This is in the German literature, where the units are not those commonly employed in this country, and is based on data that are in some disagreement with the results of this study. Other properties have been investigated and are compared with this work where appropriate. In the work reported here data and equations are developed for the basic properties from which tables and graphs of the thermodynamic properties can easily be calculated.

EXPERIMENTAL WORK AND RESULTS

Experimental measurements were made to determine the vapor pressure, *PVT* behavior of the gas, saturated liquid density, and critical properties. The techniques used were those previously described (*6*). The perfluorocyclobutane was a fractionated material which contained no impurities detectable by infrared analysis. The moisture content was about 0.0005% by weight and the air content of the vapor phase was 0.11% by volume. The heat capacity of the gas was calculated from published spectroscopic data and compared with some experimental data, but no experiments on heat capacity were made in this study.

Vapor Pressure. Data were taken on vapor pressure over the temperature range from 419.94° to 698.85° R. The results have been correlated with an equation which has been shown (*11*) to fit the vapor pressure characteristics of pure compounds with an exceptionally high degree of precision. The equation with the specific constants for perfluorocyclobutane is

$$\log_{10} P = 15.63242 - \frac{4301.063}{T} - 2.128401 \log_{10} T - 0.00119759\,T + 0.6625898 \left(\frac{714 - T}{T}\right) \log_{10}(714 - T) \qquad (1)$$

where T is in ° R. (° F. + 459.69) and P is in pounds per square inch absolute. If a pressure of 14.696 p.s.i.a. is inserted into this equation and the temperature solved for implicitly, the normal boiling point is obtained as 481.16° R. or 21.47° F. This compares closely with a boiling point of 480.91° R. predicted by an equation presented by Furukawa, McCoskey, and Reilly (*5*), but is more than 1° above a value of 480.13° R. given by Bambach (*1*). It is not at the boiling point alone, however, that considerable disagreement exists in the vapor pressure, for, as shown in Table I, serious discrepancies exist over the whole temperature range, particularly below about 490° R. Table I compares all available experimental pressures with those calculated from Equation 1. Since the equation has been fitted to the data obtained in this study, one can see quickly the degree of agreement with other authors. For example, in the higher temperature range from about 545° R. to the critical, the pressures obtained by Douslin, Moore, and Waddington (*4*) are fairly close, but usually a little lower than those obtained here. Over the same temperature range Bambach reported significantly higher pressures. From 480° to 545° R. Bambach continues to be high, except for one point at 522.45° R. where there may be a typographical error in his paper. At the lower end of this range the data of Whipple (*14*) also appear high, being in fair agreement with Bambach's data, while the Furukawa data agree fairly well, being only slightly higher than the equation. At low temperatures below 480° R. the situation is bad; both Bambach and Whipple show pressures that run 4 to 9% higher than the equation, while Furukawa's results corroborate the equation better than in any other range. It is difficult to state the reason for such poor agreement, but low-temperature, low-pressure measurements are difficult to make. Also differences in the purity of the samples used by the different investigators may have contributed to differences in vapor pressures. Until more data are obtained, it is believed that Equation 1 represents the closest approach to the truth. One reason for this is that comparisons were made on a reduced vapor pressure plot in a manner previously described (*9*), and the equation and data presented here seemed to be in better agreement with those of other compounds than the data of Bambach and Whipple that are not represented well by the equation.

PVT Behavior of Gas. The volumetric behavior of gaseous perfluorocyclobutane was determined from 571° to 875° R. and from 60 to 2000 p.s.i.a. This corresponded to a range of volumes from 0.466 to 0.0179 cu. foot per pound. The Martin-Hou (*9, 10*) equation of state was fitted to these data, with the following specific form and constants:

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

where

P = p.s.i.a.
T = ° R.—i.e., ° F. + 459.69
V = cu. feet per pound
$B_2 = 0.98484745 \times 10^{-3}$
$C_2 = -28.542156$
$A_3 = 0.26479892 \times 10^{-1}$

Table I. Comparison of Calculated Vapor Pressures with Experimental Data

	Pressure, P.S.I.A.			
Temp., ° R.	Exptl.	Calcd., Eq. 1	% Deviation	Source
419.24	2.754	2.754	-0.00	(*5*)
419.49	3.071	2.776	9.61	(*1*)
419.69	2.796	2.793	0.11	(*5*)
419.94	2.793	2.815	−0.78	A[a]
420.75	3.188	2.888	9.40	(*1*)
424.69	3.264	3.264	−0.00	A
426.53	3.732	3.452	7.49	(*14*)
428.80	3.708	3.698	0.29	A
430.85	4.235	3.931	7.17	(*14*)
434.38	4.376	4.362	0.32	(*5*)
437.69	4.912	4.800	2.27	(*14*)
437.99	4.852	4.842	0.21	A
443.36	5.859	5.634	3.83	(*14*)
444.58	5.865	5.829	0.62	(*5*)
445.43	6.304	5.967	5.34	(*14*)
451.42	7.389	7.020	4.99	(*1*)
455.42	7.860	7.804	0.72	(*5*)
457.13	8.528	8.160	4.32	(*14*)
465.95	10.597	10.209	3.66	(*14*)
466.13	10.205	10.255	−0.49	A
467.12	10.583	10.510	0.69	(*5*)
472.36	12.298	11.943	2.89	(*14*)
474.52	12.956	12.577	2.93	(*1*)
474.98	12.799	12.716	0.65	(*5*)
477.24	13.807	13.414	2.85	(*14*)
479.14	14.024	14.024	0.00	A
479.97	14.380	14.297	0.58	(*5*)
480.53	14.393	14.484	0.63	A
482.20	15.133	15.053	0.53	(*5*)
482.17	14.969	15.043	−0.49	A
482.51	15.489	15.160	2.12	(*14*)
487.71	17.363	17.055	0.48	(*5*)
489.49	17.817	17.745	0.40	(*5*)
489.80	18.312	17.868	2.42	(*14*)
492.53	19.043	18.974	0.36	(*5*)
494.64	20.210	19.866	1.70	(*1*)
498.19	21.391	21.440	−0.23	A
520.67	34.300	33.790	1.49	A
522.45	34.133	34.962	−2.43	(*1*)
522.74	35.232	35.156	0.22	(*14*)
523.55	36.121	35.701	1.16	(*14*)
531.55	41.880	41.447	1.04	A
545.69	53.009	53.291	−0.53	(*4*)
548.46	56.535	55.882	1.16	(*1*)
549.36	57.190	56.744	0.78	A
549.70	57.830	57.072	1.31	A
571.88	81.740	81.740	−0.00	A
578.32	91.402	90.191	1.33	(*1*)
581.69	93.662	94.861	−0.95	(*4*)
594.02	113.09	113.48	−0.34	A
600.59	124.59	124.43	0.13	A
601.85	128.72	126.61	1.64	(*1*)
619.36	159.46	159.96	−0.31	A
626.69	174.18	175.67	−0.86	(*4*)
629.46	184.90	181.89	1.63	(*1*)
637.85	201.26	201.72	−0.23	A
646.00	226.86	222.48	1.93	(*1*)
654.18	242.06	242.06	−0.00	A
662.63	276.65	269.80	2.47	(*1*)
668.81	294.42	289.24	1.76	(*1*)
669.62	291.46	291.87	−0.14	A
671,69	297.89	298.68	−0.26	(*4*)
674.01	312.20	306.46	1.84	(*1*)
677.09	317.14	317.05	0.03	A
682.67	343.50	337.02	1.88	(*1*)
687.98	358.33	357.06	0.35	A
690.32	371.23	366.24	1.35	(*1*)
696.69	393.03	392.43	0.15	A
696.98	397.54	393.67	0.98	(*1*)
697.79	397.13	297.15	−0.01	(*4*)
698.69	401.11	401.06	0.01	(*4*)
698.85	402.83	401.76	0.27	A
698.87	401.89	401.84	0.01	(*4*)
699.05	402.67	402.63	0.01	(*4*)
699.27		403.60	Calcd. crit. pt.	

[a] Author.

$R = 10.7315/\text{mol. wt.}$
$= 10.7315/200.044$
$= 0.05364569$
$T_c = 699.27° \text{ R.}$
$b = 0.60114165 \times 10^{-2}$
$A_2 = -1.8947374$
$\bar{B}_3 = -0.6862101 \times 10^{-5}$
$C_3 = 0.66384636$
$A_4 = -0.24565234 \times 10^{-3}$
$A_5 = 0.60887086 \times 10^{-6}$
$B_5 = 0.8269634 \times 10^{-9}$
$C_5 = -0.3849145 \times 10^{-4}$

Equation 2 is compared in Table II with the *PVT* data of this investigation and with those of Douslin, Moore, and Waddington and Bambach. The data of Douslin go to much higher temperatures than in this work, while the data of Bambach go to lower temperatures. The deviations between the equation and the data of Bambach are of the same order of magnitude as between the equation and the data reported here, indicating experimental errors of the same size in the two sets of determinations. In comparison with Douslin's data, however, the deviations are much less, because in fitting the equation of state to the data of this study the Douslin data were taken to be of greater precision. Douslin reported that the Benedict, Webb, Rubin (B-W-R) (3) equation and the Beattie-Bridgeman (B-B) (2) equation

Table II. Comparison of *PVT* Equation with Experimental Results

Vol., Cu. Ft./Lb.	Temp., ° R.	Pressure, P.S.I.A. Exptl.	Pressure, P.S.I.A. Calcd., Eq. 2	% Deviation	Source
7.12657	459.94	3.411	3.416	−0.15	(1)
7.14259	528.03	3.907	3.929	−0.57	(1)
7.1650	635.31	4.278	4.730	−0.05	(1)
7.17783	689.65	5.118	5.131	−0.26	(1)
2.87850	474.34	8.503	8.571	−0.80	(1)
2.88811	581.67	10.57	10.62	−0.41	(1)
2.89772	689.90	12.61	12.63	−0.15	(1)
1.37518	491.78	17.80	18.08	−1.60	(1)
1.37758	545.24	20.11	20.31	−1.01	(1)
1.38062	617.24	23.09	23.24	−0.64	(1)
1.38351	682.92	25.73	25.85	−0.45	(1)
0.680781	527.69	36.92	37.61	−0.89	(1)
0.682863	618.14	45.05	45.53	−1.07	(1)
0.684305	688.25	51.11	51.42	−0.60	(1)
0.465549	572.63	58.40	58.63	−0.40	A
	641.52	69.20	67.82	1.98	A
	711.18	77.20	76.79	0.53	A
	785.07	86.50	86.08	0.49	A
	862.42	96.70	95.66	1.07	A
0.411692	571.32	65.37	65.03	0.51	A
	710.19	87.95	85.95	2.28	A
	781.52	97.47	96.20	1.29	A
	851.83	107.70	106.15	1.43	A
0.406226	559.62	62.62	63.90	−2.05	(1)
0.407187	618.10	71.92	72.99	−1.48	(1)
0.408148	689.15	82.73	83.53	−0.97	(1)
0.218651	596.02	113.79	115.72	−1.71	(1)
0.218971	638.28	127.30	129.30	−1.49	(1)
0.219291	689.96	143.09	144.93	−1.29	(1)
0.126033	634.03	187.75	189.69	−1.03	(1)
0.126177	670.19	208.37	211.93	−1.71	(1)
0.126257	689.60	219.33	223.46	−1.88	(1)
0.126582	651.44	199.50	200.04	−0.27	A
	768.55	266.70	268.15	−0.54	A
	849.84	312.00	312.39	−0.12	A
0.106771	699.08	257.91	257.70	0.08	(4)
	761.69	302.15	301.97	0.06	(4)
	851.69	362.81	362.45	0.10	(4)
	941.69	421.53	420.83	0.17	(4)
	1031.69	479.11	478.11	0.21	(4)
	1121.69	535.95	534.80	0.22	(4)
0.080078	699.08	308.29	307.99	0.10	(4)
	761.69	372.55	372.28	0.07	(4)
	851.69	459.77	459.47	0.07	(4)
	941.69	543.76	543.18	0.11	(4)
	1031.69	625.90	625.07	0.13	(4)
	1121.69	706.80	705.99	0.12	(4)
0.0751582	666.56	276.22	280.46	−1.54	(1)
0.0752062	691.31	308.36	309.66	−0.42	(1)
0.0665336	680.89	313.40	313.60	−0.06	A
	761.67	419.00	420.84	−0.44	A
	820.86	495.50	494.65	0.17	A
	875.49	558.90	560.56	−0.30	A
0.0589957	677.77	321.45	321.92	−0.15	(1)
0.0590277	686.32	336.53	335.84	0.20	(1)
0.0590437	699.03	355.59	356.27	−0.19	(1)
0.0533853	699.08	369.97	369.53	0.12	(4)
	761.69	480.62	480.23	0.08	(4)
	851.69	629.04	629.72	−0.11	(4)
	896.69	700.80	701.82	−0.15	(4)
	986.69	841.84	842.90	−0.13	(4)
	1076.69	980.21	981.53	−0.13	(4)
	1121.69	1048.81	1050.31	−0.14	(4)
0.0448229	694.68	376.00	377.19	−0.32	A
	769.11	544.00	543.77	0.04	A
	864.33	742.00	743.57	−0.21	A
0.0400390	699.08	395.48	395.13	0.09	(4)
	861.69	558.11	558.37	−0.05	(4)
	851.69	777.54	780.46	−0.38	(4)
	941.69	990.26	994.15	−0.39	(4)
	1031.69	1199.28	1203.43	−0.35	(4)
	1121.69	1405.68	1410.39	−0.34	(4)
0.0371786	693.86	384.03	383.08	0.25	(1)
0.0371786	697.90	397.12	395.07	0.51	(1)
0.0371947	705.60	416.46	417.77	−0.32	(1)
0.0320312	699.08	402.18	402.11	0.02	(4)
	761.69	619.08	620.97	−0.31	(4)
	851.69	919.72	924.39	−0.51	(4)
	941.59	1215.53	1220.33	−0.39	(4)
	1031.69	1508.26	1512.34	−0.27	(4)
	1121.69	1798.83	1802.28	−0.19	(4)
0.0300300	699.52	403.90	404.31	−0.10	A
	738.79	555.40	554.18	0.22	A
	776.94	695.40	697.31	−0.27	A
	852.59	973.40	976.09	−0.28	A
0.0266927	716.69	479.28	480.66	−0.29	(4)
	806.69	873.64	876.44	−0.32	(4)
	896.69	1269.80	1269.73	0.05	(4)
	986.69	1665.45	1661.72	0.22	(4)
	1076.69	2059.57	2053.02	0.32	(4)
	1121.69	2256.82	2248.52	0.37	(4)
0.0228794	699.08	403.00	402.70	0.07	(4)
	761.69	741.70	743.03	−0.18	(4)
	851.69	1253.79	1246.51	0.58	(4)
	941.69	1773.29	1759.52	0.78	(4)
	1031.69	2295.64	2277.54	0.79	(4)
	1121.69	2817.53	2798.20	0.69	(4)
0.0224971	707.28	453.00	447.72	1.16	A
	782.89	873.40	872.65	0.09	A
	857.52	1313.40	1304.64	0.67	A
0.0200195	699.08	406.94	405.63	0.32	(4)
	761.69	835.89	839.21	−0.40	(4)
	851.69	1497.04	1498.36	−0.09	(4)
	941.69	2171.80	2181.49	−0.45	(4)
	1031.69	2854.76	2877.21	−0.79	(4)
	1121.69	3536.41	3579.56	−1.22	(4)
0.0196695	698.80	402.00	405.19	−0.79	A
	752.14	781.40	788.51	−0.91	A
	796.81	1111.40	1123.68	−1.10	A
	838.86	1430.40	1447.61	−1.20	A
	862.04	1612.40	1628.86	−1.02	A
0.0179308	695.95	405.90	404.36	0.38	A
	763.76	987.40	1055.40	−6.89	A
	801.60	1338.40	1433.39	−7.10	A
	861.36	1895.40	2044.78	−7.88	A
0.0177951	699.08	434.15	438.25	−0.94	(4)
	761.69	991.76	1057.80	−6.66	(4)
	851.69	1847.64	1993.07	−7.87	(4)
	941.69	2720.79	2958.21	−8.73	(4)
	1031.69	3607.03	3939.04	−9.20	(4)
	1121.69	4493.49	4928.11	−9.67	(4)

were fitted to the data more precisely than the Martin-Hou (M-H) equation. Knowing that the latter equation was developed to fit the characteristics of *PVT* behavior in a manner not accomplished by either of the two former equations, it was simple to adjust the constants slightly and obtain a much better fit. The modified form of the equation was used, since it had been shown (*10*) to do a better job in the high density range than the original equation, though the modification had little to do with obtaining the better fit. Table III compares the average and maximum deviations at different densities of Douslin's data from those of the several equations. Over the range of density for which it was developed—i.e., up to about 1.5 times the critical density—Equation 2 is evidently superior to either the B-B or the B-W-R equation for all except the smallest volume of 0.0177951 cu. ft./lb. In the neighborhood of this volume the equation starts to deviate rapidly and should not be used for smaller volumes. Not only are the average deviations for Equation 2 usually lower, but the maximum deviations are lower than for the B-W-R equation. This means that Equation 2 is more consistent and should give more precise derivatives. For these reasons Equation 2 is recommended for calculations of thermodynamic properties that depend upon *PVT* behavior. Only if one wishes to go about twice the critical density is the B-W-R equation recommended and even here the deviations get up to more than 12%, so the equation cannot be considered too reliable.

At low pressure and relatively low temperatures—i.e., well below the critical temperature—Equation 2 is further substantiated by its prediction of the variation of the constant pressure heat capacity with pressure. Masi (*12*) experimentally measured the variation at three temperatures and at pressures approaching zero. His results in B.t.u./lb.-° R.-p.s.i.a. were: at 509.69° R., 2.5×10^{-4}, at 581.67° R., 1.4×10^{-4}, and at 653.69° R., 0.8×10^{-4}. Using the well-known thermodynamic relation, $(dC_p/dP)_T = -T(d^2V/dT^2)_P$, in Equation 2, gives the corresponding results: at 509.69° R., 2.7×10^{-4}, at 581.67° R., 1.6×10^{-4}, and at 653.69° R., 1.0×10^{-4}. Equation 2 predicts both the right order of magnitude and the right trend with temperature in the variation of the constant pressure heat capacity with pressure. The prediction is always a little high, but this is an extremely severe test of an equation of state.

Another interesting fact concerning Equation 2 is that it fits the critical point of this work exactly and has the first two derivatives of pressure with respect to volume vanish at this point. This means that the isotherms have the right shape in this region and that calculation of thermodynamic properties in the neighborhood of the critical point is dependable if carried out with this equation. Heretofore, in most tables of thermodynamic properties, such as the steam tables (*7*), for example, it has been necessary to use graphical techniques to obtain accurate *PVT* and thermodynamic behavior around the critical point.

Saturated Liquid Density. The measured saturated liquid densities have been correlated with the equation,

$$d_l = 38.70 + 70.858318\,(1 - T/T_c)^{1/3} + 23.609759\,(1 - T/T_c)^{2/3} + 15.989182\,(1 - T/T_c) - 8.9243856\,(1 - T/T_c)^{4/3} \text{ lb./cu. ft.} \tag{3}$$

where $T_c = 699.27°$ R. Table IV compares this equation with the experimental data of this work and with the data of Bambach. At lower temperatures Bambach's densities are higher than the equation, while at higher temperatures his densities are considerably lower. A possible explanation, as with the vapor pressure discrepancies, may lie in different sample purities, though usually small amounts of impurities have little effect on density.

Critical Properties. The critical temperature was determined by noting the disappearance and reappearance of the meniscus. The average of the two observations was 699.27° R. (239.58° F.). The critical pressure was determined by inserting this temperature into the vapor pressure equation, Equation 1, yielding a value of 403.6 p.s.i.a. The critical density was obtained from the rectilinear line on a saturated liquid and vapor density *vs.* temperature plot. The saturated liquid densities came from the experimental data directly, while the saturated vapor densities resulted from the simultaneous solution of the *PVT* equation (Equation 2) with the vapor pressure equation (Equation 1). The critical density was found to be 38.70 lb./cu. ft. All of the critical properties are compared with those of both Bambach and Douslin in Table V. In each instance the results of this work lie between those of the other two investigators, though usually closer to Douslin.

Heat Capacity of Gas at Zero Pressure. The heat capacity of the gas has been calculated by the usual statistical mechanical equations (*8*), utilizing the fundamental vibrational frequencies reported by Nielsen, Berryman, Claasen, and Hudson (*13*). Table VI shows the active

Table III. Comparison of Deviations of Several Equations of State from Data of Douslin, Moore, and Waddington

Spec. Vol., Cu. Ft./Lb.	Equations Fitted by Douslin, Others (*4*): B-B eq., av. dev.	M-H eq., av. dev.	B-W-R Eq. Av. dev.	B-W-R Eq. Max. dev.	Equation 2 Av. dev.	Equation 2 Max. dev.
0.10677	0.27	0.59	0.22	0.60	0.14	0.22
0.080078	0.32	0.64	0.23	0.64	0.10	0.13
0.053385	0.31	0.55	0.22	0.56	0.13	0.22
0.040039	0.21	0.30	0.18	0.89	0.29	0.42
0.032031	0.58	0.29	0.36	1.30	0.30	0.51
0.0266927	1.37	0.48	0.57	0.93	0.23	0.46
0.0228794		0.36	0.55	0.94	0.57	0.81
0.0200195		0.99	0.59	4.25	0.53	1.22
0.0177951		4.21	2.06	9.50	7.40	9.67

Table IV. Comparison of Saturated Liquid Density Equation with Experimental Data

Temp., ° R.	Density, Lb./Cu. Ft. Exptl.	Density, Lb./Cu. Ft. Calcd.	% Deviation	Source
698.67	45.237	45.659	−0.93	A
697.27	49.276	49.276	0.00	A
696.98	48.193	49.791	−3.32	(*1*)
690.32	56.209	56.745	−0.95	(*1*)
688.91	57.386	57.732	−0.60	A
682.67	60.641	61.334	−1.14	(*1*)
674.01	64.936	65.175	−0.37	(*1*)
668.81	67.096	67.114	−0.03	(*1*)
664.43	69.281	68.603	0.98	(*1*)
659.20	70.246	70.246	0.00	A
650.07	72.692	72.842	−0.16	A
646.00	74.456	73.911	0.73	(*1*)
629.46	78.564	77.835	0.93	(*1*)
601.85	84.358	83.361	1.18	(*1*)
583.97	86.484	86.484	0.00	A
578.32	88.552	87.415	1.28	(*1*)
548.46	93.278	91.978	1.39	(*1*)
532.15	94.132	94.263	−0.14	A
522.45	96.936	95.565	1.41	(*1*)
494.64	100.476	99.095	1.37	(*1*)
474.52	102.904	101.490	1.38	(*1*)
473.04	101.661	101.661	0.00	A
451.42	105.763	104.100	1.57	(*1*)
420.75	109.222	107.369	1.70	(*1*)
419.49	109.421	107.499	1.76	(*1*)

Table V. Critical Constants

	This Work	Bambach (*1*)	Douslin, Others (*4*)
Crit. temp., ° R.	699.27	699.39	699.08
Crit. pressure, p.s.i.a.	403.6	406.79	402.85
Crit. density, lb./cu. ft.	38.70	39.42	38.45
Z_c	0.27800	0.27504	0.27937

vibrations observed experimentally and inactive vibrations which Nielsen and others calculated. All of the active fundamentals were used directly, while one inactive assignment was changed to obtain better agreement between this calculated heat capacity and the experimental heat capacity of Masi (*12*). Bambach also calculated the heat capacity from a set of fundamental vibrational frequencies which he did not report. An empirical equation was developed to represent the heat capacities calculated in this work:

$$C_p^0 = 6.590444 + 7.399784 \times 10^{-2}\, T - 3.297576 \times 10^{-5}\, T^2 + 4.306509 \times 10^{-9}\, T^3 \text{ B.t.u./lb. mole-}^\circ\text{ R.} \qquad (4)$$

where T is in ° R.

Table VII gives a comparison of Equation 4 with the statistical heat capacity calculated here, the statistical heat capacity calculated by Bambach, and the calorimetrically measured heat capacity of Masi. Taking the extraordinarily precise work of Masi (a precision of 0.1% is given for this measurement) as the truth, it is clear that Equation 4 can be used with a high degree of confidence. Bambach's heat capacity is good, considering that it is estimated from fundamental frequencies alone, but it runs from 1.5 to 2.0% higher than Equation 4.

CONCLUSIONS

Equations 1 to 4 represent the best data on perfluorocyclobutane with a uniform high degree of precision. Consequently, they can be used to calculate the desired tables of thermodynamic properties over wide ranges of temperature and pressure. The method of utilizing these equations in exact thermodynamic relations has been discussed thoroughly (*8*). Time did not permit calculating any tables of thermodynamic properties for this article even though such calculation is routine once the basic equations (1 through 4) have been established.

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. mole-° R.
d = density, lb./cu. ft.
M.W. = molecular weight (200.004)
P = pressure, p.s.i.a.
R = gas constant, 10.7315 p.s.i.a.-cu. ft./lb. mole-° R.
T = absolute temperature, ° R. (° F. + 459.69)
V = volume, cu. ft./lb.
Z_c = P_cV_c/RT_c

Subscripts

c = critical property
l = saturated liquid
p = constant pressure

Superscripts

0 = ideal gas state or zero pressure

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Table VI. Fundamental Vibration Frequencies of Perfluorocyclobutane

		Wave Number, Cm.$^{-1}$	
Symmetry Species	Approximate[b] Character	Infrared (gas)	Raman (gas)
	Active Vibrations[a]		
A_{1g}	CF stretching		1431.3
A_{1g}	Ring stretching		699.3
A_{1g}	CF_2 deformation		358.2
A_{2u}	CF stretching	1239	
A_{2u}	CF_2 rocking	338	
B_{1g}	CF stretching		1220
B_{1g}	CF_2 wagging		258
B_{2g}	CF stretching		1008
B_{2g}	CF_2 deformation		659.5
B_{2g}	In-plane ring bending		192
E_g	CF stretching		1285
E_g	CF_2 twisting		439
E_g	CF_2 twisting		273
E_u	CF stretching	1340	
E_u	Ring stretching	962	
E_u	CF_2 deformation	569	
E_u	CF_2 wagging	(285)	
	Inactive Vibrations		
		Calcd. Value	
A_{1u}	CF_2 twisting	(173)	
A_{2g}	CF_2 wagging	(745)	
B_{1u}	CF stretching	(1385)	
B_{1u}	CF_2 rocking	(972)[c]	
B_{1u}	Out of plane ring bending	(86)	

[a] Fundamentals not observed directly are enclosed in parentheses. [b] Only very rough meaning can be attached to terms used in this column. [c] Assignment modified. Original assignment reported is (613).

Table VII. Constant Pressure Heat Capacity at Zero Pressure

(B.t.u./Lb. Mole-° R.)

	Calcd. Heat Capacity		Exptl. Heat Capacity	Heat Capacity Equation
Temp., ° R.	This work	Bambach (*1*)	(*12*)	(*4*)
360	28.95			29.06
432	32.65	33.23		32.65
509.69	36.22		36.19	36.21
581.69	39.22	39.93	39.23	39.22
653.69	41.97	42.62	42.01	41.97
900	49.49			49.52
1260	56.27			55.99

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