Heat Capacity, Heats of Transitions, Fusion, and Vaporization, and Vapor Pressure of Octafluorocyclobutane [1]

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The heat capacity of octafluorocyclobutane of 99.98_9-mole-percent purity was determined in an adiabatic calorimeter from 17° to 270° K. The heat of fusion is 2768.2 ± 2.0 abs j mole^{-1} at the triple-point temperature of 232.96 ± 0.05° K. The three heat-of-vaporization experiments at the vapor pressure of 590.9 mm Hg and 261.25° K gave an average value of 23721 ± 20 abs j mole^{-1}. Four solid-solid transitions were observed with the heat-capacity peaks at 141.3 ± 0.2°, 174.6 ± 0.2°, 214.84 ± 0.05°, and 216.99 ± 0.05° K. The anomalous behavior in the heat capacity at about 97° K, where the heat capacity changes its slope abruptly, is attributed to glass transformation. The vapor pressure was measured from 177° to 274° K. The results of this measurement from the triple-point temperature to 274° K can be represented within ± 0.5 mm Hg in most cases by the equation

$$\log_{10} p(\text{mm Hg}) = 6.70267 - \frac{1315.906}{T} + 8.778482 \times 10^{-3} T - 1.739691 \times 10^{-5} T^2.$$

The entropy of octafluorocyclobutane in the ideal gas state at 261.25° K and 1 atm was computed from the experimental data to be 380.52 ± 0.71 abs j deg^{-1} mole^{-1} or 90.95 ± 0.17 cal deg^{-1} mole^{-1} (1 cal = 4.1840 abs j). The entropy computed from the spectroscopic assignments by Claassen and the molecular constants based on the D_{4h} model amounted to 87.83 cal deg^{-1} mole^{-1}.

1. Introduction

Octafluorocyclobutane can be prepared by pyrolysis of polytetrafluoroethylene [2] and by cyclic dimerization of tetrafluoroethylene.[3] The latter material has come into importance in the recent years as the monomer in the production of polytetrafluoroethylene plastic (Teflon), which has a remarkably high chemical and thermal stability. In order to obtain a wider thermodynamic knowledge regarding the fluorocarbons, fluorocarbon polymers, and monomers or prototype molecules, calorimetric and vapor-pressure measurements have been made with octafluorocyclobutane. This material is interesting also from the viewpoint of its structure; some [4][5] of the investigators have interpreted its vibrational spectra in terms of a planar ring model (D_{4h}). More recent spectral [6] and electron diffraction [7] studies seem to favor the nonplanar ring structure (V_d). There is at present an investigation being conducted at the Bureau to make spectral assignments in light of the evidence for a V_d structure.

Calorimetric studies with the tetrafluoroethylene [8] and the polytetrafluoroethylene [9] have been reported recently by the National Bureau of Standards.

2. Apparatus and Method

The heat-capacity, the heat-of-fusion, and the vapor-pressure measurements with the octafluorocyclobutane were carried out in the adiabatic calorimeter described previously by R. B. Scott, et al.[10] For the vapor-pressure measurements the calorimeter valve was opened to a mercury manometer, which was read by means of a mirror-backed glass scale. The calorimeter served as a thermostated container. No provision was made to stir the sample. The pressure readings were converted to standard mm Hg ($g = 980.665$ cm sec^{-2}, temperature $= 0$° C.) on the basis that the local gravity is 980.076 cm sec^{-2}.

The heat-of-vaporization measurements were made in another adiabatic calorimeter similar in design to those described by Osborne and Ginnings [11] and by Aston, et al.[12] This calorimeter contained a throttle valve within the space enclosed by the adiabatic shield. During the vaporization experiments, the vapor was removed isothermally by controlling the valve and introducing a known electric energy continuously. A nickel resistance thermometer wound on the tube between the valve and the calorimeter container served to sense the temperature of the vapor removed. When a desired quantity of the material was collected, the electric power was cut off and the valve closed. The heat of vaporization per mole, L, was computed from the total energy

[1] This paper is based on research sponsored by the Ordnance Corps, U. S. Department of the Army.
[2] United States Patent 2384821.
[3] United States Patent 2404374.
[4] W. F. Edgell, J. Am. Chem. Soc. **69**, 660 (1947).
[5] H. H. Claassen, J. Chem. Phys. **18**, 543 (1950).
[6] W. F. Edgell and D. G. Weiblen, J. Chem. Phys. **18**, 571 (1950).
[7] H. P. Lemaire and R. L. Livinston, J. Chem. Phys. **18**, 569 (1950).
[8] G. T. Furukawa, R. E. McCoskey, and M. L. Reilly, J. Research NBS, **51**, (1953) RP2432.
[9] G. T. Furukawa, R. E. McCoskey, and G. J. King, J. Research NBS **49**, 273 (1952) RP2364.

[10] R. B. Scott, C. H. Meyers, R. D. Rands, Jr., F. G. Brickwedde, and N. Bekkedahl, J. Research NBS **35**, 39 (1945) RP1661.
[11] N. S. Osborne and D. C. Ginnings, J. Research NBS **39**, 453 (1947) RP1841.
[12] J. G. Aston, H. L. Fink, G. J. Janz, and K. E. Russell, J. Am. Chem. Soc. **73**, 1939 (1951).

nput, Q, and the mass, m, of material collected by the relation

$$L = \frac{MQ}{m}\left(1 - \frac{u}{u'}\right), \qquad (1)$$

in which u and u' are the specific volumes of the liquid and vapor, respectively, at the vaporization temperature and M is the molecular weight.

All temperature measurements are in accordance with the International Temperature Scale [13] and below 90° K in accordance with a provisional scale [14] based on a set of platinum resistance thermometers calibrated against a helium-gas thermometer.

3. Material

The octafluorocyclobutane used in this investigation was kindly furnished by the E. I. du Pont de Nemours & Co. Although the sample was considered quite pure, the possible impurities were tetrafluoroethylene (C_2F_4) and chlorodifluoromethane ($CHClF_2$). The material was purified further by fractional crystallization. The procedure was similar to that described by Schwab and Wichers.[15] The purity of the material so treated was determined prior to the heat-capacity experiments from the equilibrium melting temperatures [16] and was found to be 99.98_9 mole percent. The equilibrium temperatures and the corresponding reciprocal of the fraction melted, F, are given in table 1. The triple-point temperature (obtained by extrapolating the temperature versus $1/F$ plot to $1/F=0$) was found to be $232.96 \pm 0.05°$ K. (In this paper, unless defined otherwise, the figure following the plus or minus is the authors' best estimate of the uncertainty.) A second purity measurement at the end of the heat-capacity studies gave essentially the same result.

TABLE 1. *Equilibrium melting temperatures of octafluorocyclobutane*

Mole fraction impurity=0.00613 ΔT,
°K $=273.16+$°C

Reciprocal of fraction melted, $1/F$	T
	°K
12.74	[a] 232.7587
8.33	232.8012
6.74	232.8215
3.93	232.8676
2.05	232.9114
1.55	232.9278
1.22	232.9420
0.00	[b] 232.9580

Triple-point temperature, $232.96 \pm 0.05°$ K. Purity, 99.98_9 mole percent.

[a] The temperatures given are accurate to $\pm 0.01°$ K. Wherever temperatures are given to the fourth decimal, the last two figures are significant only insofar as small temperature differences are concerned.
[b] Extrapolated.

[13] H. F. Stimson, J. Research NBS **42**, 209 (1949) RP1962.
[14] H. J. Hoge and F. G. Brickwedde, J. Research NBS **22**, 351 (1939) RP1188.
[15] F. W. Schwab and E. Wichers, J. Research NBS **32**, 253 (1944) RP588.
[16] G. T. Furukawa, D. C. Ginnings, R. E. McCoskey, and R. A. Nelson, J. Research NBS **46**, 195 (1951) RP2191.

In these purity determinations the system was assumed to behave ideally and to form no solid solution.

4. Heat Capacity

The heat-capacity measurements were carried out from 17° to 270° K. The observed values are given in table 2 and are also plotted in figure 1 to show the four solid-solid transitions observed. The temperatures given in the table are the mean temperatures of heating intervals. The temperature rise associated with each heating interval is also given. The corresponding heat-capacity values, which are under conditions of saturation have been corrected for curvature (see footnote 16) and vapor saturation [17] wherever applicable.

The heat capacity in the temperature range of each transition was carefully investigated. Of the four solid-solid transitions, two were found very close together, similar to those in hydrogen bromide.[18] Equilibrium was attained within these two transitions (214.84° and 216.99° K) in the usual time of 6 to 10 min. On the other hand, the relaxation time for the transitions at the two lower temperatures (141.3° and 174.6° K) was found to be extremely long; small but definite temperature drifts were observed even 2 hr after the end of heating. On account of this long relaxation time, the heat capacity in these transition ranges was dependent somewhat upon the thermal history or the rate of cooling prior to the experiments. Thus, the results in the transition region are scattered, up to as much as 0.3 percent. The peaks of the heat capacities within the four transitions were found to be $141.3 \pm 0.2°$, $174.6 \pm 0.2°$, $214.84 \pm 0.05°$, and $216.99 \pm 0.05°$ K. The heat of transition was not determined for any given temperature; instead, the enthalpy change was determined for an interval of convenient temperatures, which included the transition. These results are given in section 5.

Figure 1 shows an anomalous behavior in the region of 97° K, in which the heat capacity undergoes a rather abrupt change in slope. Also, a longer time (about 30 min) was required for temperature equilibrium. A magnified plot of this temperature range is shown in figure 2. The cooling rate prior to the heat-capacity measurements had a decided effect upon the results in this temperature range. Slow cooling yielded significantly higher values. As pointed out in section 5, the increase in the enthalpy change corresponding to the higher heat-capacity values in this temperature range seems to be offset by an almost equal enthalpy change decrease in the interval 130° to 150° K.

Although not as pronounced, the heat-capacity behavior of the substance near 97° K is similar to the glass transformation found in organic glasses,[19] high polymers,[20] and other noncrystalline solids. Similar

[17] H. J. Hoge, J. Research NBS **36**, 111 (1946) RP1693.
[18] W. F. Giauque and R. W. Wiebe, J. Am. Chem. Soc. **50**, 2193 (1928).
[19] G. S. Parks, H. M. Huffman, and F. R. Cattoir, J. Phys. Chem. **32**, 1366 (1928).
[20] G. T. Furukawa, R. E. McCoskey, and G. J. King, J. Research NBS **50**, 357 (1953) RP2425.

TABLE 2. *Observed molal heat capacities of octafluorocyclobutane*

Molecular weight=200.04; $°K=273.16 +°C$

T	$C_{satd.}$	ΔT	T	$C_{satd.}$	ΔT	T	$C_{satd.}$	ΔT
RUN 1			RUN 6			RUN 12		
$°K$	abs j deg $^{-1}$ mole^{-1}	$°K$	$°K$	abs j deg $^{-1}$ mole^{-1}	$°K$	$°K$	abs j deg $^{-1}$ mole^{-1}	$°K$
221.27	188.13	4.0158	181.58	159.24	7.3718	92.25	87.06	2.5503
225.27	190.01	3.9845	189.74	166.45	8.9346	94.77	88.50	2.5009
229.23	191.99	3.9511	198.52	175.39	8.6249	97.25	90.29	2.4518
Fusion			205.40	184.12	5.1513	99.67	93.09	2.3915
234.73	199.00	3.1500	208.87	189.66	1.7764	95.49	89.18	2.5237
237.87	199.87	3.1335	210.70	193.13	1.8886			
241.00	200.70	3.1194	211.43	193.57	1.6146	RUN 13		
246.04	202.28	6.9656	212.83	199.60	1.1887	223.41	191.64	1.9694
253.35	204.48	7.6644	213.82	202.47	0.7842	229.92	192.72	1.0460
260.98	207.05	7.5822	Transition			Fusion		
268.52	209.77	7.5034	216.32	215.00	.5659	237.23	200.02	4.7629
RUN 2			Transition			241.97	201.47	4.7318
210.25	191.77	1.6640	RUN 7			RUN 14		
211.95	195.46	1.7359	55.86	57.77	5.8959	86.06	82.37	2.5249
213.80	252.55	1.9638	61.45	62.25	5.2849	88.62	84.46	2.6105
Transition			66.52	66.36	4.8475	91.13	86.26	2.4014
215.78	273.48	1.8586	71.20	69.94	4.5216	93.89	88.03	3.1275
Transition			75.59	73.45	4.2568	96.61	89.48	2.2982
219.71	187.58	2.3583	80.13	77.26	4.8230	99.25	92.32	2.9847
222.06	188.58	2.3493	84.83	81.22	4.5657	101.83	95.50	2.1792
226.60	190.70	2.3288	89.29	84.90	4.3577	104.34	98.17	2.8383
229.82	192.53	4.1002	93.57	87.92	4.1982	107.14	100.97	2.7717
RUN 3			98.17	91.30	5.0130	RUN 15		
126.76	125.18	9.1535	103.07	96.60	4.7848	87.34	83.47	2.1532
134.47	143.70	6.2668	RUN 8			89.65	85.24	2.4628
138.99	174.84	2.7702	18.13	17.18	0.1117	92.09	87.05	2.4078
Transition			18.56	18.14	.7424	94.47	88.86	2.3574
144.24	157.16	3.9023	19.49	19.90	1.1328	96.80	90.86	2.3098
148.23	143.83	4.0824	21.69	23.59	3.2563	99.09	93.14	2.2602
154.30	145.00	8.0648	24.64	28.17	2.6484	101.69	96.06	2.9378
RUN 4			27.11	31.60	2.2921	104.65	98.98	2.9830
111.38	105.60	6.6270	29.92	35.06	3.3206	RUN 16		
118.42	113.37	7.4492	32.89	38.40	2.6231	82.82	79.59	2.7401
126.77	124.99	9.2458	36.49	41.97	4.5760	85.95	82.23	3.5220
135.03	147.21	7.2735	40.89	46.00	4.2323	89.41	85.06	3.3966
139.90	210.26	2.4853	46.20	50.27	6.3786	92.76	87.58	3.2929
Transition			52.43	55.34	6.0745	96.00	90.14	3.1997
142.02	264.30	1.0615	58.16	59.72	5.3968	99.16	93.18	3.1057
143.26	169.51	1.4173	63.31	63.86	4.8957	102.22	96.70	3.0126
144.98	151.79	2.0136	RUN 9			106.89	101.06	2.8944
147.02	145.33	2.0588	17.45	16.21	1.4819	110.69	104.94	4.7038
149.08	143.23	2.0686	18.83	18.69	1.2747	115.31	109.68	4.5350
151.15	142.75	2.0665	20.03	20.84	1.1343	120.30	115.56	5.4474
157.23	146.69	10.1044	21.24	22.87	1.2789	126.13	123.93	6.2149
171.49	159.08	0.9510	22.57	24.96	1.3893	Transition		
172.52	160.67	1.1034	RUN 10			153.42	144.17	3.6295
173.50	189.08	0.8580	82.20	79.04	5.7036			
RUN 5			86.41	82.66	2.7175			
163.21	151.63	9.8138	89.09	84.79	2.6443			
169.55	157.59	2.8631	91.71	86.69	2.5828			
172.12	159.45	2.3639	RUN 11					
173.77	210.46	0.9319	93.29	87.49	2.9379			
Transition			95.99	89.05	2.4637			
175.84	154.63	.9589	98.43	90.72	2.4207			
176.71	155.28	.7965	100.82	94.44	2.3531			
178.06	156.72	1.8992	103.53	97.38	3.0604			
179.96	158.21	1.8869						
185.59	162.94	9.3856						
194.74	171.42	8.9116						

FIGURE 1. *Observed heat capacities of octafluorocyclobutane.*

FIGURE 2. *Observed heat capacities of octafluorocyclobutane from 85° to 113° K.*

behavior was reported by Huffman, et al.[21] for cyclopentene and other compounds.

The heat-capacity values given in table 2 are probably accurate to 0.2 percent, except in the transition regions of 141.3° and 174.6° K, the anomalous region of 97° K, and the temperature range below 50° K, where larger tolerances must be allowed.

5. Heats of Fusion and Transitions

The heat of fusion was determined in the usual manner by introducing a known electric energy from a temperature just below the triple point to just above it and correcting for the premelting and heat capacity. The results of three measurements are summarized in table 3. The values given in the fourth column are the total heats required to melt 141.9302 g of the sample in the calorimeter. Considering the precision of the measurements and various sources of error, the uncertainty of the heat of fusion is believed to be ±2.0 abs j mole⁻¹.

TABLE 3. *Molal heat of fusion of octafluorocyclobutane*

Molecular weight—200.04; mass of sample—141.9302 g; triple-point temperature= 232.96° K; °K=273.16+°C

Temperature interval	Heat input	Heat capacity and premelting correction	ΔH	ΔH_f
°K	abs j	abs j	abs j	abs j mole⁻¹
227.6435 to 237.3363	4199.9	2236.9	1963.0	2766.7
227.7655 to 234.7512	3567.3	1602.2	1965.1	2769.8
227.4253 to 234.8109	3657.7	1693.9	1963.8	2768.0
Mean heat of fusion				2768.2
Standard deviation				±0.7

[21] H. M. Huffman, M. Eaton, and G. D. Oliver, J. Am. Chem. Soc. **70**, 2911 (1948).

TABLE 4. *Molal enthalpy changes over even temperature intervals, including the solid-solid transitions and the anomalous region*

Molecular weight=200.04; °K=273.16+°C

Temperature interval	Total energy input	Heat capacity correction	ΔH
$H_{153°K} - H_{130°K}$			
°K	abs j mole⁻¹	abs j mole⁻¹	abs j mole⁻¹
122.1832 to 150.2725 [a]	5095.7	−1010.0	4085.7
133.2603 to 150.6635 [b]	3739.7	+346.0	4085.7
		Mean	4085.7
129.2400 to 151.6058 [b][c]	4405.2	−328.8	4076.4
$H_{180°K} - H_{170°K}$			
170.9367 to 180.8963 [a]	5002.3	+6.0	5008.3
168.7525 to 177.2341 [b]	4768.1	+237.8	5005.9
		Mean	5007.1
$H_{220°K} - H_{210°K}$			
209.4137 to 220.8877 [a]	4878.4	−278.9	4599.5
212.4227 to 222.1278 [b]	4529.9	+70.0	4599.9
		Mean	4599.7
$H_{105°K} - H_{90°K}$			
87.1084 to 105.4621 [a]	1659.0	−289.9	1369.1
89.9824 to 105.7577 [a]	1450.4	−81.2	1369.2
		Mean	1369.2
88.4184 to 106.1372 [a][c]	1626.9	−247.7	1379.2
87.7140 to 103.7215 [a][c]	1446.5	−67.3	1379.2
		Mean	1379.2

[a] Heated in increments over this temperature interval under adiabatic conditions.
[b] Heated continuously over this temperature interval under adiabatic conditions.
[c] The sample was cooled slowly over 1 week from 230° to 80° K prior to the heat-capacity measurements.

As mentioned in section 4, in the temperature range of the four solid-solid transitions, small increments of heat were added to obtain the shape of the heat-capacity curve. Instead of attempting to determine the heat of transition at a given temperature, the enthalpy change was determined over an interval of convenient temperatures. This was done both by summing the increments of heats added in the determination of the shape of the heat-capacity curve and by heating continuously through this interval. The results of both experimental methods are summarized in table 4. The values given in the third column are corrections used to reduce the enthalpy changes to the even temperature intervals indicated. The anomalous region was treated in a similar manner by summing the heats added in the interval from 90° to 105° K. In one series of measurements (see table 2, runs 15 and 16), the material was cooled slowly over a period of 1 week from 230° to 80° K. The enthalpy change, as well as the heat capacity in the interval 90° to 105° K, was higher. The enthalpy change from 90° to 105° K was 10.0 abs j mole^{-1} higher. Also, there was found a decrease in the enthalpy change in the interval 130° to 150° K of 9.3 abs j mole^{-1}.

6. Heat of Vaporization

Three heat of vaporization experiments were made at 261.25° K ($p=590.9$ mm Hg). The experimentally observed quantity, MQ/m, the conversion factor, $1-u/u'$, and the heat of vaporization, L, are given in table 5. The specific volumes, u and u', for this material were kindly furnished by the E. I. du Pont de Nemours & Co. Considering the precision obtained and various sources of error, the uncertainty of the heat-of-vaporization value is believed to be ±20 abs j mole^{-1}.

Table 5. *Molal heat of vaporization of octafluorocyclobutane at 261.25° K*

Pressure=590.9 mm Hg; molecular weight=200.04; °K=273.16+°C

MQ/m	$1-u/u'$	L
abs j mole^{-1}		*abs j mole*$^{-1}$
23,842	0.99550	23,735
23,823	.99550	23,716
23,818	.99550	23,711
Mean		23,721
Standard deviation		±6

7. Vapor Pressure

As there was no provision made to stir the sample, several series of vapor-pressure measurements were made under different conditions to make certain that temperature equilibrium was attained. The measurements were made going down the temperature scale as well as up. The close agreement in the results given in table 6 indicates that good temperature equilibrium existed. The results above the triple-point temperature (232.96° K) were

fitted to an equation given by

$$\log_{10} p(\text{mm Hg}) = 6.70267 - \frac{1315.906}{T}$$
$$+ 8.778482 \times 10^{-3}T - 1.739691 \times 10^{-5}T^2.$$

The observations are compared with this equation in table 6. The equation gives the normal boiling temperature as 267.17 ± 0.01° K and the triple-point pressure as 142.8 ± 0.3 mm Hg.

Table 6. *Vapor pressure of octafluorocyclobutane*

° K=273.16+° C

$T_{obs.}$	$p_{obs.}$	$p_{calc.}$	$p_{obs.}-p_{calc.}$	$T_{obs.}$	$p_{obs.}$	$p_{calc.}$	$p_{obs.}-p_{calc.}$
Series I				°K	*mm* Hg	*mm* Hg	*mm* Hg
				241.32	226.3	226.5	−.2
°K	*mm* Hg	*mm* Hg	*mm* Hg	246.99	303.3	303.3	.0
				253.01	406.5	406.5	.0
267.89	782.6	782.9	−0.3	259.51	547.3	547.6	−.3
270.95	886.2	885.9	.3	263.88	661.9	662.2	−.3
273.63	984.8	984.2	.6	266.65	743.7	743.9	−.2
Series II				Series III			
179.16	5.0	---	--------	177.36	4.9	---	--------
191.94	8.2	---	--------	191.82	8.2	---	--------
201.23	14.7	---	--------	196.86	10.9	---	--------
215.30	43.4	---	--------	197.17	11.0	---	--------
223.60	77.7	---	--------	206.70	21.7	---	--------
230.81	125.7	---	--------	213.09	35.9	---	--------
232.91	142.4	142.5	−0.1	221.60	67.7	---	--------
233.16	144.6	144.5	.1	271.94	921.4	921.3	0.1

8. Experimental Entropy

The experimental data were used to calculate the entropy of the octafluorocyclobutane in the ideal gas state at 261.25° K and 1 atm. The results of the various calculations are summarized in table 7. In the temperature intervals in which the transitions occurred, the entropy change was evaluated by summing the various experimentally observed $C\Delta T/T$'s, where C is the observed heat capacity, ΔT the temperature rise, and T the midtemperature of the heating interval. The entropy change so obtained was corrected to the even temperatures indicated in table 7. Below 180° K, the results from the slow-cooling experiments were used to evaluate the en-

Table 7. *Summary of the experimental molal entropy of octafluorocyclobutane*

Molecular weight=200.04; °K=273.16+°C

	abs j deg^{-1} *mole*$^{-1}$
$S_{15°}$, Debye	4.38±0.04
$\Delta S_{15°-90°}$, numerical	78.24±0.16
$\Delta S_{90°-105°}$, transition	14.15±0.10
$\Delta S_{105°-130°}$, numerical	24.03±0.05
$\Delta S_{130°-150°}$, transition	29.14±0.06
$\Delta S_{150°-170°}$, numerical	18.67±0.04
$\Delta S_{170°-180°}$, transition	28.65±0.03
$\Delta S_{180°-210°}$, numerical	26.54±0.05
$\Delta S_{210°-220°}$, transition	21.32±0.02
$\Delta S_{220°-232.96°}$, numerical	10.92±0.02
$\Delta S_{232.96°}$, fusion, 2768.2/232.96	11.88±0.01
$\Delta S_{232.96°-261.25°}$, numerical	23.22±0.04
$\Delta S_{261.25°}$, vaporization, 23721/261.25	90.80±0.09
$\Delta S_{261.25°}$, gas imperfection	0.67
$\Delta S_{261.25°}$, compression	−2.09
Entropy, ideal gas at 261.25° K and 1 atm	380.5₂±0.71

tropy. The gas-imperfection correction was computed on the assumption that the octafluorocyclobutane vapor can be represented by the Berthelot equation of state. The critical constants used were those reported by Renfrew and Lewis.[22]

The uncertainties given in table 7 were based on the precision, the probable nonreproducibility of the physical state below 180° K, and various other sources of error. The absolute entropy obtained is probably in error by more than is given in the table because the results of the measurements indicate a certain degree of glassy state or randomness in the solid at the lower extreme of our measurements.

9. Entropy From Molecular and Spectroscopic Data

The entropy of the gaseous octafluorocyclobutane was computed from the molecular and spectroscopic data based on the D_{4h} structure. The results are summarized and compared with the calorimetric entropy in table 8. The rotational entropy was computed directly from the principal moments of inertia given by Smith, et al.[23] in which the C—C and C—F bond distances and C—C—C and F—C—F angles were 1.53 A and 1.36 A and 90 deg. and 112

deg., respectively. The moments of inertia were $I_x = I_y = 796 \times 10^{-40}$ g-cm^2 and $I_z = 951 \times 10^{-40}$ g-cm^2. The vibrational entropy was calculated on the basis of the assignments by Classen (see footnote 5).

On the basis of the existence of residual entropy in the calorimetric work, the discrepancy in the two results given in table 8 would be increased. Work is now in progress at the Bureau for the reassignment of the frequencies on the basis of the recent evidence for a V_d structure.

TABLE 8. *Molal entropy of octafluorocyclobutane at 261.25° K from molecular and spectroscopic data*

Molecular weight=200.04; °K=273.16+°C; 1 cal=4.1840 abs _

	cal deg⁻¹ mole⁻¹
S, translation	41.13
S, rotation	25.65
S, vibration	21.05
S, total, ideal gas at 261.25° K and 1 atm	87.83
S, calorimetric	90.95

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