Project No. 165-1-08-72 (Unit C-2), in preparing some of the graphs and tables is gratefully acknowledged.

Summary

The heat capacity of dimethylacetylene has been measured from 14°K. to room temperature. There is an anomaly in the heat capacity near 154°K.

The melting point of dimethylacetylene is 240.93 ± 0.05°K. (0°C. = 273.16°K.), the heat of fusion is 2207 ± 2 cal./mole, and the heat of vaporization is 6440 ± 6 cal./mole at 291.00°K. and 536 mm.

The entropy of the ideal gas from the calorimetric data is 67.48 ± 0.20 cal./deg./mole and 67.93 cal./deg./mole at 1 atm., 291.00°K. and 298.16°K., respectively. That of the liquid at 298.16°K. is 46.63 ± 0.1 cal./deg./mole.

Comparison of the statistical and calorimetric entropies indicates that the barrier restricting rotation of the methyl groups is not more than 500 cal./mole.

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The Heat Capacity, Entropy, Heats of Fusion and Vaporization and Vapor Pressure of Fluorotrichloromethane

BY DARRELL W. OSBORNE, CLIFFORD S. GARNER, RUSSELL N. DOESCHER AND DON M. YOST

Introduction

Because of the interesting properties of the fluorochloromethanes and their increasing use as refrigerants, they have received attention[1] with the view of determining their thermodynamic properties. These investigations, however, have not been of such a character as to permit the calculation of the entropies of these substances.

This paper presents the results of a low temperature calorimetric investigation of fluorotrichloromethane, CCl_3F, together with a comparison of the calorimetric entropy of this substance with that calculated from spectroscopic and electron-diffraction data. Since in the fluorotrichloromethane molecule there is no possibility of hindered internal rotation of the type found in ethane and similar molecules or little probability of randomness of molecular orientation in the crystals of the solid, the excellent agreement found in this comparison is an indication of the reliability of measurements[2] made with the low temperature calorimeters recently constructed in this Laboratory.

Experimental

Purification of the Fluorotrichloromethane Sample.—Commercial fluorotrichloromethane, manufactured by Kinetic Chemicals, Inc., Wilmington, Delaware, was purified by fractionation at atmospheric pressure in a 70 cm. column packed with glass helices. It was fractionated twice (reflux ratio of about 15 to 1), and only the middle cut of the last fractionation was utilized further. This portion was distilled through phosphorus pentoxide into a glass vessel in which it was repeatedly frozen and melted under high vacuum. Some of this purified sample was then distilled into an evacuated, weighed sample bulb, from which it was condensed into the evacuated calorimeter.

An impurity of 0.050 mole per cent. in the sample was estimated from measurements on its melting point.

Heat Capacity Measurements.—The heat capacities were determined with the adiabatic calorimeter (gold-plated copper calorimeter I) and strain-free platinum resistance thermometer CT-26 described elsewhere.[3] Our vapor pressure measurements and the data of Benning and McHarness[1] on the density of the liquid were used to correct for vaporization into the gas space. This correction amounted at most to 0.3%.

The results of these measurements are given in Table I and are shown graphically in Fig. 1. They are expressed in defined calories (1 cal. = 4.1833 international joules). In Table II are presented heat capacities at rounded temperatures read from a smooth curve through the experimental points; those given for temperatures just below the melting point have been corrected for premelting, using Raoult's law and the mole fraction of liquid-soluble, solid-insoluble impurity found in the melting point determination. The probable accuracy of the heat capacities is about 0.5% at 15°K. due to decreased sensitivity of the

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(1) A. Benning and R. McHarness, *Ind. Eng. Chem.*, **31**, 912 (1939); *ibid.*, **32**, 497, 698 and 814 (1940); A. Benning, R. McHarness, W. Markwood and W. Smith, *ibid.*, **32**, 976 (1940).

(2) (a) D. Osborne, C. Garner and D. Yost, *J. Chem. Phys.*, **8**, 131 (1940); (b) D. Osborne, R. Doescher and D. Yost, *ibid.*, **8**, 506 (1940); (c) D. Yost, D. Osborne and C. Garner, THIS JOURNAL, **63**, 3492 (1941).

(3) D. Yost, C. Garner, D. Osborne, T. Rubin and H. Russell, THIS JOURNAL, **63**, 3488 (1941).

TABLE I

THE MOLAL HEAT CAPACITIES OF FLUOROTRICHLOROMETHANE

0 °C. = 273.16 °K.; molecular weight = 137.38; 1.1567 moles in calorimeter.

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
14.74	3.052	109.78	15.73
15.83	3.517	115.52	16.24
17.13	4.026	121.09	16.78[a]
19.07	4.792	126.81	17.34[a]
21.34	5.589	132.54	17.93[a]
23.52	6.310	138.51	18.62[a]
25.74	6.955	144.66	19.42[a]
28.27	7.574	150.77	20.36[a]
31.21	8.208	155.89	21.80[a]
34.51	8.782	162.68	M. p.
38.12	9.322	170.55	26.19
42.10	9.819	179.99	26.38
46.78	10.36	189.61	26.57
52.07	10.91	199.76	26.76
56.78	11.30	210.10	26.98
57.67	11.37	220.22	27.18
61.69	11.71	230.19	27.41
66.76	12.14	240.34	27.62
72.10	12.56	250.34	27.84
77.79	13.06	259.90	28.07
84.00	13.55	269.33	28.31
90.65	14.12	278.63	28.53
97.34	14.67	287.82	28.79
103.72	15.21		

[a] Including premelting

TABLE II

THE MOLAL HEAT CAPACITIES OF FLUOROTRICHLOROMETHANE AT ROUNDED TEMPERATURES[a]

0 °C. = 273.16 °K.; molecular weight = 137.38

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}
15	3.163	150	20.05
20	5.114	160	21.54
25	6.751	162.68	M. p.
30	7.959	170	26.18
35	8.860	180	26.38
40	9.572	190	26.57
45	10.16	200	26.77
50	10.68	210	26.97
60	11.57	220	27.18
70	12.40	230	27.40
80	13.23	240	27.61
90	14.06	250	27.83
100	14.89	260	28.06
110	15.75	270	28.32
120	16.67	280	28.58
130	17.64	290	28.84
140	18.75	300	29.10

[a] Corrected for premelting.

resistance thermometer and increased heat losses by conduction, and is about 0.1% above 25 °K.

The heat capacities of the liquid have been determined recently[4] at four temperatures with a non-adiabatic calorimeter having appreciable heat losses, and the values reported in this paper differ from them by approximately 2%.

The Melting Point and Heat of Fusion.—In Table III are shown the equilibrium temperatures with various amounts of the sample melted, together with the temperatures calculated assuming Raoult's law, and assuming that there are no solid solutions, that the melting point is 162.68 °K. (−110.48 °C.), and that the proportion of impurity is 0.050 mole per cent. The value of the melting point reported in the literature is 162 °K.[5]

The results of measurements on the heat of fusion are given in Table IV. The procedure used was essentially the same as for the heat capacities. The premelting was calculated on the basis of the 0.050 mole per cent. impurity. Since the heat capacities of the solid were corrected in the same manner, any error in the premelting correction, as well as any error in the extrapolation of the heat capacities to the m. p., will nearly cancel out in the calculation of the entropy.

The Heat of Vaporization.—The results of measurements on the heat of vaporization are summarized in Table V. The procedure was essentially that used for similar studies on dimethyl acetylene,[2c] and will not be discussed here. In Table VI is presented the vapor pressure equation

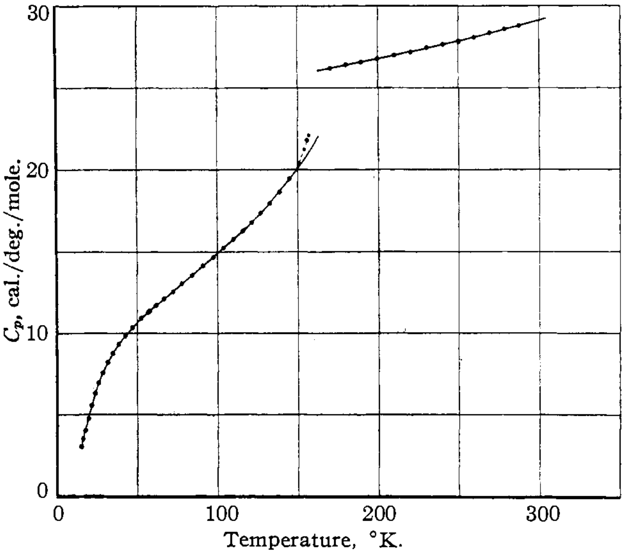

Fig. 1.—The molal heat capacity of fluorotrichloromethane, CCl_3F.

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(4) A. Benning, R. McHarness, W. Markwood and W. Smith, *Ind. Eng. Chem.*, **32**, 976 (1940).

(5) O. Ruff and R. Keim, *Z. anorg. allgem. Chem.*, **201**, 245 (1931).

TABLE III

THE MELTING POINT OF FLUOROTRICHLOROMETHANE

0°C. = 273.16°K.

Mole per cent. melted	$T_{\text{obs.}}$, °K.	$T_{\text{calcd.}}$, °K.[a]
24.72	162.613	162.613
47.80	162.644	162.645
64.77	162.654	162.653

M. p. this sample, 162.66 ± 0.05°K.

M. p. pure compound, 162.68 ± 0.05°K.

[a] Assuming mole per cent. impurity = 0.050.

TABLE IV

THE MOLAL HEAT OF FUSION OF FLUOROTRICHLOROMETHANE

0°C. = 273.16°K., molecular weight = 137.38, 1.1567 moles in calorimeter, m. p. = 162.68°K.

Temperature interval, °K.	Heat input, cal./mole	$\int C_p dT$ cal./mole	Pre-melting, cal./mole	ΔH fusion, cal./mole
158.024–165.297	1809.9	168.4	5.9	1647.4
157.571–165.821	1834.4	192.0	5.4	1647.8
			Mean	1647.6 ± 2

which was used to calculate the temperature of vaporization from the external pressure.

The heat of vaporization was also computed from this vapor pressure equation and the modified Berthelot equation of state. The values used for the critical temperature and pressure were 471.2°K. and 43.2 atm.[6] The molal heat of vaporization calculated in this manner is 6008 cal./mole at 290.40°K. and 602.5 mm., including a correction for gas imperfection amounting to −212 cal./mole. The agreement between the two values for the vaporization heat lends support to the later use of the same equation of state in correcting the entropy for gas imperfection.

TABLE V

THE MOLAL HEAT OF VAPORIZATION OF FLUOROTRICHLOROMETHANE AT 290.40°K. AND 602.5 MM.

0°C. = 273.16°K., molecular weight = 137.38

Moles vaporized	ΔH vaporization, cal./mole
0.10573	6027
0.11421	6023
Mean	6025 ± 6

The Vapor Pressure and the Boiling Point.—A summary of the results of measurements on the vapor pressure at various temperatures is given in Table VI. The measurements were made with a Henson cathetometer, with a scale calibrated in terms of a standard glass decimeter from the National Bureau of Standards, and a glass-contained mercury manometer described elsewhere.[3] By means of data given in the "International Critical Tables,"[7] the observed readings were corrected to international mm. of mercury. Corrections were made for the effect of temperature, gravity and the pressure exerted by the column of gas in the calorimeter tube leading to the manometer. The standard acceleration due to gravity was taken as 980.67 cm./sec.^{2} and the acceleration for this location as 979.57 cm./sec.[2,8]

Other vapor pressure data on fluorotrichloromethane are those of Ruff and Keim,[5] who report measurements at three temperatures which were recorded to the nearest degree only, and those of Benning and McHarness,[1] who made more extensive but less accurate measurements which are in substantial agreement with those presented here.

The normal boiling point calculated from our vapor pressure equation is 296.82°K. (23.66°C.). During the distillation of the sample, after it had been purified, the boiling point remained constant to within 0.1°, and the normal boiling point calculated from the distillation data is 296.8°K., in good agreement with the above value. Previous values which have been reported are 24.9°C.,[9] 24.1°C.,[5] and 23.71–23.77°C.[1] The first two values are too high probably because of impure samples or inaccuracies in the temperature scales used.

TABLE VI

THE VAPOR PRESSURE OF FLUOROTRICHLOROMETHANE

0°C. = 273.16°K.

T, °K.	$p_{\text{obs.}}$, mm.	$p_{\text{calcd.}}$, mm.[a]	$p_{\text{calcd.}} - p_{\text{obs.}}$, mm.
236.487	47.35	47.34	−0.01
251.335	108.13	108.17	+ .04
266.273	223.60	223.53	− .07
275.512	334.61	334.68	+ .07
283.522	463.46	463.33	− .13
288.268	556.15	556.25	+ .10
293.055	664.18	664.17	− .01
296.822		760.00	

[a] $\log_{10} p$ (Int. mm. Hg) = $18.54101 - (1841.72/T) - 3.82423 \log_{10} T$.

The Entropy of Fluorotrichloromethane.—In Table VII is summarized the calculation of the entropy from our calorimetric data. The extrapolation from 14.70° to 0°K. was made with a Debye function with six degrees of freedom and $h\nu/k = 90.1$, this function fitting the points up to 26°K. to 0.5% or better. The usual graphical

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(6) A. Benning and R. McHarness, *Ind. Eng. Chem.*, **32**, 814 (1940).

(7) "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1926, Vol. I.

(8) Measured at this Institute by the U. S. Coast and Geodetic Survey.

(9) F. Swarts, *Bull. Acad. Roy. Belg.*, [3] **24**, 309 (1892); *Ber.*, Ref. **26**, 291 (1893).

integrations of C_p *vs.* log T were made above 14.70°K. The correction for gas imperfection was made with the modified Berthelot equation of state and the critical constants previously referred to.

A summary of the calculation of the entropy from molecular data is given in Table VIII. The vibrations were taken to be harmonic, and the frequencies were those given by Glockler and Leader,[10] namely, 243.7(2), 349.5, 397.5(2), 535.3, 833.2(2) and 1067.2 cm.$^{-1}$. Numbers in parentheses adjoining the frequencies are the degeneracies of the mode of vibration in question as assigned by Kohbrausch and J. Wagner.[11] The moments of inertia were calculated using the following interatomic distances and bond angles[12]: C—F, 1.40 Å.; C—Cl, 1.76 Å.; ∠ F—C—Cl, 107.5°; the symmetry number is three.

TABLE VII

THE MOLAL ENTROPY OF FLUOROTRICHLOROMETHANE FROM CALORIMETRIC DATA

0°C. = 273.16°K.; molecular weight = 137.38

	ΔS, cal. deg.$^{-1}$ mole^{-1}
0–14.70°K. Debye extrapolation	1.197
14.70–162.68°K. graphical	26.053
Fusion (1647.6/162.68)	10.128
162.68–290.40°K. graphical	15.781
Vaporization (6025/290.40)	20.748
Entropy of actual gas at 290.40°K., 602.5 mm.	73.907 ± 0.1
Correction for gas imperfection[a]	0.13
Compression to 1 atm.	– .46
Entropy of ideal gas, 290.40°K., 1 atm.	73.58 ± 0.1
290.40–298.16° K. (molecular data)	0.49
Entropy of ideal gas at 25°C., 1 atm.	74.07 ± 0.1
Entropy of liquid, 25°C., 1 atm.	53.92 ± .1

[a] $S_{\text{ideal}} - S_{\text{actual}} = 27RT_c^3P/32T^3P_c$. $T_c = 471.2$°K., $P_c = 43.2$ atm.[1]

TABLE VIII

THE STANDARD MOLAL ENTROPY OF GASEOUS FLUOROTRICHLOROMETHANE FROM MOLECULAR DATA

0°C. = 273.16°K.; molecular wt. = 137.38

	S, cal. deg.$^{-1}$ mole^{-1} 290.40°K.	298.16°K.
Translational	40.53	40.66
Vibrational	7.40	7.68
Rotational	25.63	25.71
Total (P = 1 atm.)	73.56	74.05
Calorimetric (P = 1 atm.)	73.58	74.07

For the natural constants, the values recommended by Professor R. T. Birge in a private communication were employed, except for changes required by our conventional values of the ice point and calorie. The important values are 0°C. = 273.16°K., R = 1.9871 cal. deg.$^{-1}$ mole^{-1}, k = 1.3805 × 10^{-16} erg deg.$^{-1}$, N_0 = 6.023 × 10^{23}, h = 6.624 × 10^{-27} erg sec.

The excellent agreement of the calorimetric value with that calculated from molecular data serves as a check on the reliability of our temperature scale and of the low temperature calorimeter used in this investigation.

We wish to express here our indebtedness to Professor Hugh M. Huffman for the many helpful suggestions that he made in connection with the construction of apparatus and the methods for making measurements. The liquid hydrogen necessary for this investigation was kindly furnished by Professor A. Goetz of this Institute.

Summary

The heat capacity of fluorotrichloromethane has been measured from 14°K. to room temperature.

The melting point of fluorotrichloromethane is 162.68 ± 0.05°K. (0°C. = 273.16°K.), the heat of fusion is 1648 ± 2 cal./mole, and the heat of vaporization is 6025 ± 6 cal./mole at 290.40°K. and 602.5 mm.

The vapor pressures are given by the relation $\log_{10} p$ (Int. mm. Hg) = 18.54101 – (1841.72/T) – 3.82423 $\log_{10} T$ in the range 236–293°K. The normal boiling point of fluorotrichloromethane, as calculated from this vapor pressure equation, is 296.82°K.

The entropy of the ideal gas from the calorimetric data is 73.58 ± 0.1 cal. deg.$^{-1}$ mole^{-1} and 74.07 ± 0.1 cal. deg.$^{-1}$ mole^{-1} at 1 atm., 290.40°K. and 298.16°K, respectively. These values agree to within 0.02 cal. deg.$^{-1}$ mole^{-1} with those computed from molecular data. The entropy of the liquid is 53.92 ± 0.1 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. and 1 atm.

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(10) G. Glockler and G. Leader, *J. Chem. Phys.*, **7**, 278 (1939).

(11) K. W. F. Kohlrausch and J. Wagner, *Z. physik. Chem.*, **B45**, 93 (1939).

(12) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 and **747** (1937); see also J. Wouters and M. deHemptinne, *Nature*, **141**, 412 (1938).