About 10 ml. of liquid sample was contained in a glass Raman tube whose irradiated volume was 9 ml. This Raman tube was held in place inside a standard Lane–Wells glass double compartment jacket. The inner cylindrical jacket contained the filter solution, while tap water was circulated in the outer jacket to keep the sample and filter solution at room temperature.

The spectrum was recorded on Eastman Kodak Co. spectroscopic film, type 103-AJ. A number of pictures were taken with slit widths varying from 100 to 150 microns and exposures varying from one to four hours. No polarization data were secured.

Figure 2 shows a microphotometer tracing of a typical picture. All Raman lines indicated, whose frequencies are not enclosed in parentheses, have been observed in more than one picture.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS DIVISION, UNION CARBIDE AND CARBON CORPORATION]

Thermal Data, Vapor Pressure and Entropy of Chlorine Trifluoride[1]

BY J. W. GRISARD, H. A. BERNHARDT AND GEORGE D. OLIVER

Heat capacity measurements were made on chlorine trifluoride from 14 °K. to the boiling point, 284.91 °K. An isothermal transition at 190.50 °K. absorbed 360.5 cal./mole. The heat of fusion, 1819.3 cal./mole, was measured at a triple point of 196.84 ± 0.05 °K. Vapor pressure measurements which covered the pressure range up to 2 atmospheres and a temperature range of −47 to 30° are represented by the equation: $\log_{10} P\text{mm} = 7.37611 - 1096.917/(t + 232.75)$. The calculated heat of vaporization at the b.p. is 6580 cal./mole. Entropy values calculated from these data for the liquid and ideal gas state at the b.p. are 43.66 ± 0.10 and 66.87 cal./deg. mole, respectively.

Chlorine trifluoride is the first of a series of interhalogen compounds being studied at the present time. This compound was first prepared by Ruff and Krug,[2] who roughly determined some of its chemical and physical properties including the vapor pressure. Schafer and Wicke,[3] using the spectroscopic data of Schmitz and Schumacher,[4] calculated the thermodynamic properties from 298 to 1500°K. Unfortunately, the chemical reactivity of chlorine trifluoride precludes the accurate measurement of some of its properties at high temperatures. The thermal data in this report include heat capacity from 14°K. to the boiling point, heats of transition and fusion, and the calculated heat of vaporization.

Experimental

Material.—The chlorine trifluoride was prepared by combining the elements in a nickel reactor at a temperature of 280°. About 200 cc. of the liquid, containing an impurity of 0.3 mole %, was purified by distillation in an all nickel column at 760 mm. pressure. A portion of the middle fraction was used for the measurements and an estimate of its impurity, from a study of the melting point, was 0.04 ± 0.02 mole %.

Apparatus and Methods.—A brief description of the low-temperature adiabatic cryostat, fully described elsewhere,[5] follows. Approximately 0.65 mole of the material was placed in a copper calorimeter by bulb to bulb distillation. The copper filling tube, silver-soldered to the calorimeter, was pinched flat then cut off and sealed with Pb–Sn solder at the end of the flat portion. This method of closing the calorimeter apparently prevented contact of the chlorine trifluoride with the soft solder. The calorimeter, heater and thermometer were assembled and mounted in the calorimetric cryostat. Typical heat capacity and fusion measurements were made by supplying a measured amount of electrical energy to the calorimeter and measuring the initial and final temperatures with a certified platinum resistance thermometer. To prevent heat interchange between the calorimeter and its environment, the temperature difference between the two was kept as small as possible by means of an electrically heated shield and differential thermocouples. All electrical measurements needed to determine the temperatures and energy involved were made on a White double potentiometer in conjunction with a high-sensitivity galvanometer and calibrated resistances. An Eppley cell certified by the National Bureau of Standards served as a potential reference. Time measurements were made with an electric stopclock which was frequently checked against a calibrated stopwatch. Energy measurements made in terms of the absolute joule were converted to calories by dividing by 4.1840. The precision, 0.1%, and the over-all accuracy, 0.2%, of the measurements were the same as previously reported.[5]

Liquid nitrogen was used as a refrigerant in the cryostat above 50°K. Below 50°K. another refrigerant such as liquid hydrogen was necessary; consequently, a small Hampson type hydrogen liquefier was constructed. The designs published by Ahlberg, Estermann and Lundberg,[6] and Fairbanks[7] were combined in an apparatus which would produce an adequate amount of liquid hydrogen from approximately 600 cubic feet of gas having an initial pressure of 1800 pounds per square inch.

A boiling point apparatus previously used for measurements on fluorocarbons[5] was used to measure the vapor pressure of chlorine trifluoride. Briefly, it was composed of a nickel boiler similar to that described by Willingham, *et al.*,[8] which was connected to a simple mercury manometer by helium filled lines. The helium was used as an inert buffer and its pressure was controlled by valves and a sensitive relay system. Manometric measurements were made with Gaertner cathetometers and a calibrated metal scale. The platinum resistance thermometer used to measure the boiling points at the selected pressures had been calibrated by the National Bureau of Standards; its resistance was measured by means of a G-2 Mueller bridge and a sensitive galvanometer.

Results and Discussion

Melting points were determined on three samples varying in purity. The equilibrium temperatures, 196.731, 196.795, 196.812 and 196.820°K. and the reciprocal of respective percentages melted,

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[1] This document is based on work performed for the atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

[2] O. Ruff and H. Krug, *Z. anorg. allgem. Chem.*, **190**, 270 (1930).

[3] K. Schafer and E. Wicke, *Z. Elektrochem.*, **52**, 205 (1948).

[4] H. Schmitz and H. J. Schumacher, *Z. Naturforscher*, **2A**, 357 (1947).

[5] G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).

[6] J. E. Ahlberg, I. Estermann and W. O. Lundberg, *Rev. Sci. Instruments*, **8**, 422 (1937).

[7] H. A. Fairbanks, *ibid.*, **17**, 473 (1946).

[8] C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

TABLE I

MOLAL HEAT CAPACITY, CAL./DEG.: 0° = 273.16°K., mol. wt. 92.457

				Crystals I				
T, °K.	14.04	15.28	16.60	18.03	20.10	22.74	25.88	29.11
$C_{\text{satd.}}$	1.03	1.23	1.50	1.74	2.13	2.67	3.36	4.05
T, °K.	32.59	36.42	40.67	45.88	51.29	51.89	56.27	56.30
$C_{\text{satd.}}$	4.75	5.48	6.22	7.05	7.78	7.85	8.39	8.42
T, °K.	62.07	67.82	73.16	78.96	82.94	88.44	90.94	95.62
$C_{\text{satd.}}$	9.07	9.60	10.10	10.62	10.96	11.49	11.66	12.03
T, °K.	97.01	102.84	103.44	108.47	111.35	119.00	126.54	134.34
$C_{\text{satd.}}$	12.10	12.43	12.47	12.85	13.03	13.60	14.16	14.72
T, °K.	141.87	149.15	156.22	160.61	163.57	167.80	171.20	
$C_{\text{satd.}}$	15.28	15.78	16.28	16.59	16.83	17.08	17.36	
T, °K.	175.20	178.62	180.60	182.33	184.96	187.56	196.84	
$C_{\text{satd.}}$	17.63	17.88	18.04	18.21	18.46	18.78	19.18[a]	
				Liquid				
T, °K.	196.84	202.76	204.83	207.69	216.53	219.84		
$C_{\text{satd.}}$	26.68[a]	26.76	26.78	26.81	26.94	26.96		
T, °K.	226.95	237.83	248.61	259.30	269.86	278.25		
$C_{\text{satd.}}$	27.05	27.22	27.38	27.61	27.84	28.02		

[a] Extrapolated values.

15.7, 37.4, 61.3 and 85.1%, of the best sample are represented by line A, Fig. 1. Similar data on the initial material, line B, and on commercial material, line C, are also plotted in Fig. 1. If Raoult's law is obeyed, plots of this type would give a straight line whose slope is proportional to the mole fraction of impurity and whose intercept is the triple point for pure material. The triple point of pure material is 196.84 ± 0.05°K. Line C is drawn as a straight line through two points; however, data which lie below the limits of the plot make line C concave upward thus indicating non-ideal solution in the sample containing an estimated 1.8 mole % impurity. The points on lines A and B follow the theoretical linear relationship and extrapolate to the same triple point within experimental error, while the estimated triple point of sample C is 0.3° higher. Experimental data similar to those given for sample A were used in the simplified expression,[9] $N_x = K\Delta T$, where $K = 0.0236$, to estimate the mole fraction impurity for each sample.

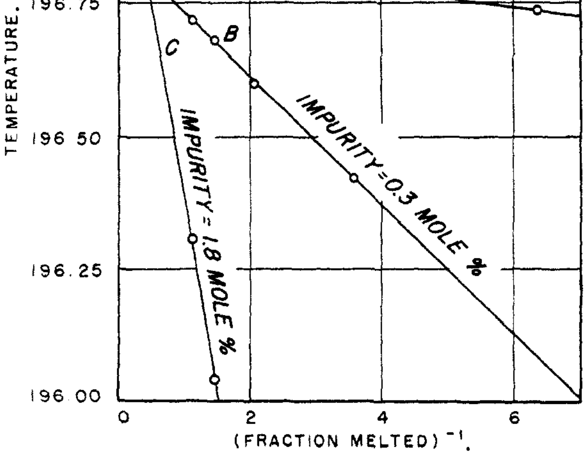

Fig. 1.—Chlorine trifluoride melting point.

The experimental heat capacities of the saturated crystals and liquid from 14°K. to near the boiling point are listed in Table I. Liquid heat capacity values were corrected for vapor saturation by the method outlined by Hoge,[10] using vapor pressure data of this report and the density data of Banks and Rudge.[11] The size of the correction ranged up to 0.8% of the heat capacity at the boiling point.

An isothermal transition occurred at 190.50 ± 0.05°K., only 6.3° below the triple point. Heat of transition measurements given in column 4 of Table II were made by starting several degrees below the transition temperature but were ended approximately 1° above it in order to reduce premelting uncertainties. Because of premelting in the narrow temperature range between the transition and triple points, it was also impractical to measure the heat capacity of the high temperature crystals II with any reliability. Consequently, the extrapolated heat capacity of the low temperature crystals I was used in the following procedure to calculate the heats of transition and fusion as listed in Table II. Each measurement of the fusion was started below the transition and necessarily included its heat, any fusion premelting effects, and the heat of fusion. The values of column 3 were calculated in the usual manner by subtracting from the corrected total heat input that portion of heat, $\int C_p dT$, adsorbed by the solid and liquid. Finally, the average heat of transition

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(9) B. J. Mair, A. R. Glasgow and F. D. Rossini, *J. Research Natl. Bur. Standards*, **26**, 594 (1941).

(10) H. F. Hoge, *ibid.*, **36**, 111 (1946).

(11) A. A. Banks and A. J. Rudge, *J. Chem. Soc.*, **191** (1950).

TABLE II

SUMMARY OF TRANSITION AND FUSION DATA, ΔH, CAL./MOLE

Transition temperature = 190.50 ± 0.05°K.

Expt.	Temperature interval, °K.	Fusion and transition	$\Delta H_{tr.}$	ΔH_f
1	180.08-201.48	2179.8[a]	359.7	1819.3
2	187.64-199.41	2179.8	361.3	1819.3
3	181.07-198.40	2179.9		1819.4
	Mean	2179.8	360.5	1819.3

[a] Melting point determination.

value was subtracted from the values of column 3 to obtain the heat of fusion in column 5. By this method, any heat not accounted for in the transition is included in the fusion which is necessarily larger than the true value by a small amount because the heat capacity of crystals I would be slightly smaller than that of crystals II. The heat of fusion and transition data in column 3 of Table II were precisely measured, but due to the experimental difficulties encountered in measuring each value separately their estimated accuracies are lowered.

The observed temperature and vapor pressure data given in Table III were used to calculate the constants of the Antoine equation by a method of least squares.[8] The resulting equation is

$$\log_{10} P_{\text{mm}} = 7.36711 - 1096.917/(t + 232.75) \quad (1)$$

Deviations of the data from this equation are given in columns 3 and 6 of Table III. The precision of the results was established by calculating 95% confidence limits on the temperatures. These limits were calculated for a straight line, log P *vs.* $1/(t + C)$ where C was treated as a known value. Below 18° (1000 mm.) the limits were approximately ± 0.01°, increasing to ± 0.02° above. Our value of 11.75° for the boiling point is approximately a mean value between the values of 11.3° reported by Ruff and Krug,[2] and 12.0° reported by Banks and Rudge.[11] Ruff and Krug gave a pressure value of 490 ± 5 mm. at 0° as a criterion of purity whereas by equation (1) the pressure at 0° is 451 ± 0.2 mm.

TABLE III

VAPOR PRESSURE OF CHLORINE TRIFLUORIDE

$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$
−46.97	29.06[a]	0.03	−1.58	419.44	0.54
−41.51	42.81[a]	.04	2.37	503.67	0.47
−35.59	63.59[a]	− .01	6.40	603.60	0.49
−33.14	74.31	− .13	9.85	701.23	0.40
−30.75	86.43[a]	− .05	12.24	775.88	0.28
−27.17	107.60	.09	13.78	827.84	0.36
−24.15	128.12[a]	− .27	17.46	962.07	0.21
−19.25	169.51[a]	− .04	17.76	974.00[a]	0.34
−17.63	185.01	− .33	21.02	1107.6	−0.5
−13.93	226.31	.19	24.97	1289.5	−1.4
− 9.72	281.37	.24	25.67	1324.7[a]	−0.9
− 5.63	345.06	.42	29.55	1530.6[a]	−1.0

[a] Data obtained on second sample.

A value for the heat of vaporization at the boiling point was calculated from the vapor pressure and auxiliary data by means of the exact Clapeyron equation. The molar volume of the liquid was obtained from density data.[11] A vapor volume of 22.623 liters/mole was calculated by means of equation (2).

$$V = 2RT/[(4P + 1/K_p) - \sqrt{(4P + 1/K_p)/K_p}] \quad (2)$$

This equation was developed from related equations published by Ritter and Simons,[12] and provided a correction for the dimerization of chlorine trifluoride in the vapor state at the boiling point by incorporating the following association data.[4]

$$\text{ClF}_3 + \text{ClF}_3 \rightleftarrows (\text{ClF}_3)_2 \quad (3)$$

$$K_p = P_{(\text{ClF}_3)_2}/P^2_{\text{ClF}_3} = 1/28 \quad (4)$$

The calculated heat of vaporization at 11.75° is 6580 cal./mole.

Entropy values calculated for the liquid and ideal gas at the boiling point are summarized in Table IV. Uncertainties introduced into the heats of fusion and transition by the method of calculation did not significantly affect the total entropy value; however, for reasons previously stated, the reported entropy of fusion is perhaps slightly larger than the true value. No equation of state or values of the critical constants are available for chlorine trifluoride; therefore, a critical temperature of 174° was estimated from liquid density data.[11] Using the calculated molar volume, a critical pressure of 57 atm. was estimated. These data were employed in a variation of the Berthelot equation to estimate a gas imperfection correction for the entropy.

TABLE IV

ENTROPY OF CHLORINE TRIFLUORIDE IN CAL./DEG. MOLE

$S_{14°}$ (3° freedom, θ = 102.65)	0.373
$S_{14-190.50°}$ solid, graphical	21.436
$S_{190.50°}$ transition, 360.5/190.50	1.892
$S_{190.50-196.84°}$ solid, graphical	0.621
$S_{196.84°}$ fusion, 1819.3/196.84	9.243
$S_{196.84-284.91°}$ liquid, grapical	10.090
Entropy of liquid at b.p., 284.91°K.	43.66 ± 0.10
$S_{284.91°}$ vaporization, 6580/284.91	23.10
Correction for gas imperfection	0.11
Entropy of the ideal gas at the b.p.	66.87

Acknowledgments.—The authors are indebted to Parkhurst B. Wood for statistical calculation of the vapor pressure equation.

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(12) H. L. Ritter and J. H. Simons, THIS JOURNAL, **67**, 757 (1945).