The results in Table II are represented (to within the average deviations indicated) by the equations

$Na_3AlF_6(\alpha)$

$$H_T - H_{298.15} = 45.95T + 14.73 \times 10^{-3}T^2 + 2.78 \times 10^5T^{-1} - 15{,}942$$
(0.2%, 298–845°K.)

$Na_3AlF_6(\beta)$

$$H_T - H_{298.15} = 52.15T + 7.93 \times 10^{-3}T^2 - 13{,}840$$
(0.1%, 845–1300°K.)

$Na_3AlF_6(l)$

$$H_T - H_{298.15} = 93.40T - 26{,}420$$
(0.2%, 1300–1400°K.)

$AlF_3(\alpha)$

$$H_T - H_{298.15} = 17.27T + 5.48 \times 10^{-3}T^2 + 2.30 \times 10^5 \cdot T^{-1} - 6408$$
(0.2%, 298–727°K.)

$AlF_3(\beta)$

$$H_T - H_{298.15} = 20.93T + 1.50 \times 10^{-3}T^2 - 6500$$
(0.1%, 727–1400°K.)

NaF(c)

$$H_T - H_{298.15} = 10.40T + 1.94 \times 10^{-3}T^2 + 0.33 \times 10^5 \cdot T^{-1} - 3384$$
(0.3%, 298–1285°K.)

NaF(l)

$$H_T - H_{298.15} = 16.40T + 170$$
(0.1%, 1285–1800°K.)

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[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Heat Capacity, Heat of Fusion, Heat of Transition and Heat of Vaporization of Chlorodifluoromethane between 16°K. and the Boiling Point[1,2]

BY ELEANOR F. NEILSON AND DAVID WHITE

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The heat capacity of 99.98 mole % pure chlorodifluoromethane has been determined from 16–230°K. A λ-type transition in the solid was observed at approximately 59°K. with a heat of transition of 16 ± 2 cal. The heat of fusion at the melting point, 115.73 ± 0.01°K., was found to be 985.47 ± 1.82 cal./mole. The heat of vaporization at the normal boiling point, 232.50 ± 0.07°K., was found to be 4832.5 ± 12.5 cal./mole. Thermodynamic functions of chlorodifluoromethane have been computed from 0 to 232.5°K. The entropy of the ideal gas at the normal boiling point, from the calorimetric measurements, is 63.92 ± 0.28 e.u. as compared with the spectroscopic value of 64.03 ± 0.02 e.u. The large uncertainty of the calorimetric entropy was due to difficulty in evaluating the Debye θ ($\theta = 70 \pm 5$) which was necessary for the extrapolation of the data to 0°K. From an agreement of the calorimetric and spectroscopic entropy it can be concluded that there is no appreciable hydrogen bonding in the gas phase.

Introduction

The thermodynamic properties of chlorodifluoromethane have in part been investigated over the past few years. Benning and McHarness have obtained P–V–T data,[3] vapor pressures[4] and the heat capacity of the liquid and gas[5] above the normal boiling point. Gelles and Pitzer[6] have calculated the heat capacity of the ideal gas from spectroscopic data. Their calculations agree with those of Benning and McHarness at high temperatures, but not at lower temperatures. The possibility of hydrogen bonding in the gas phase, as in the case of hydrogen fluoride, may result in discrepancies between calorimetric and spectroscopic values of the thermal functions. Recent investigations[7] of the vapor pressure of fluorocarbon mixtures indicates that large positive deviations from Raoult's Law are due to hydrogen bonding in the liquid. Whether these hydrogen bonds manifest themselves in the gas phase as they do in the liquid phase will be reflected in the agreement between the spectroscopic and calorimetric entropies. The object of this research was therefore to determine experimentally the heat capacity of chlorodifluoromethane so that such a comparison of the calorimetric and spectroscopic entropies could be made.

Material.—The chlorodifluoromethane was supplied through the courtesy of the General Electric Research Laboratories at Schenectady, New York. It was a high purity sample from the General Chemical Division of Allied Chemical and Dye Corporation at Morristown, New Jersey.

From the variation of the melting point with amount of sample melted the purity of the sample was estimated to be 99.98 mole %. The weight of sample was 92.9426 g. (1.0743 moles).

Apparatus.—The apparatus used in this research is similar to the condensed gas calorimeter system which has been described by Johnston and co-workers.[8] A high pressure calorimeter system[9] also was used for several heat of vaporization measurements, supplementing those made using the condensed gas calorimeter.

Experimental Procedures.—The experimental procedure for the determination of the heat capacity, heat of vaporization and the heat of fusion is identical to that described by Johnston and co-workers[8] in their paper on condensed gas calorimetry.

Experimental Data

I. Heat Capacities of the Solid and Liquid.—The experimental heat capacities are summarized in Table I and plotted in Fig. 1 along with the data of Benning and McHarness[4] for the heat capacity of the liquid above the normal boiling point. Three series of determinations were made: series

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[1] This work was supported in part by the General Electric Company, Schenectady, New York.

[2] This article contains in part material abstracted from a dissertation presented by Eleanor F. Neilson to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Master of Science.

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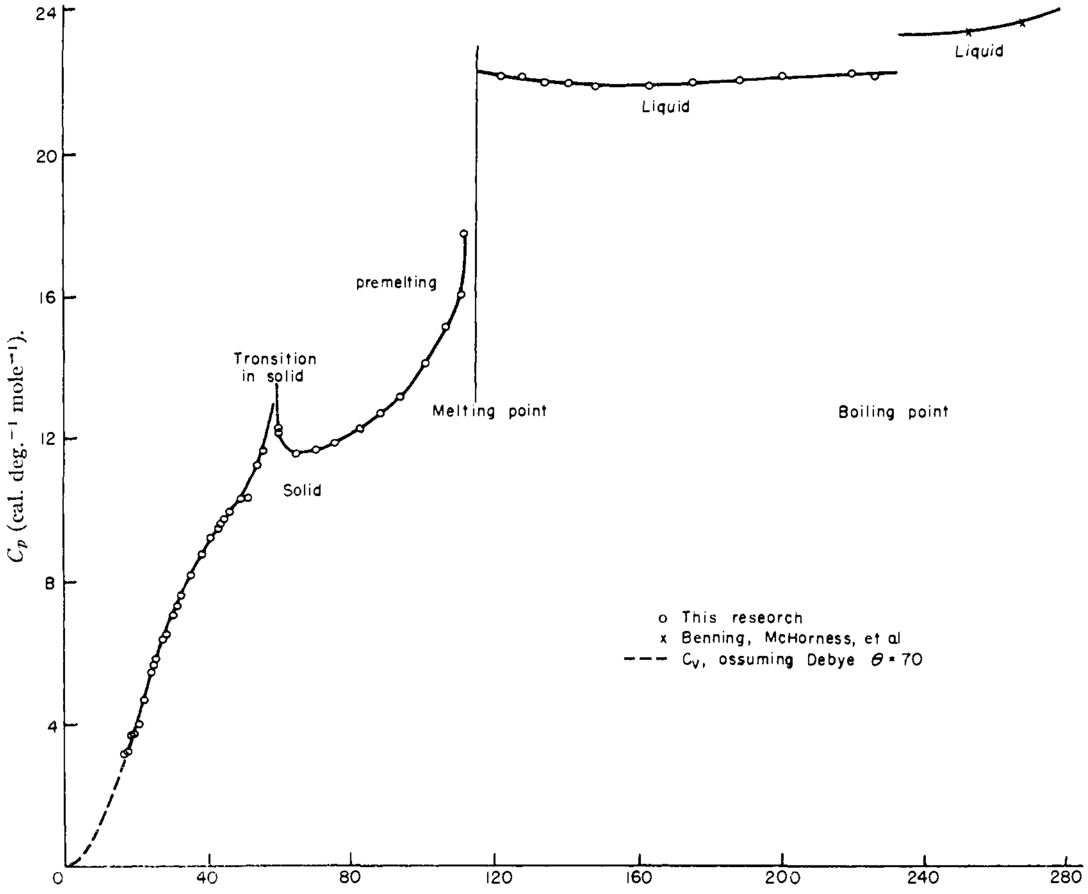

Temperature (°K).

Fig. 1.—Heat capacity of chlorodifluoromethane.

TABLE I

EXPERIMENTAL HEAT CAPACITY OF CHLORODIFLUOROMETHANE

T_{av}, °K.	C_p, cal./mole/deg.	T_{av}, °K.	C_p, cal./mole/deg.	T_{aq}, °K.	C_p, cal./mole/deg.
Series I		Series I		Series II	
Solid		Liquid		Solid	
16.77	3.162	121.84	22.081	25.57	5.720
18.43	3.586	127.82	22.037	27.66	6.369
20.49	3.971	134.16	21.951	31.18	7.253
24.92	5.663	140.85	21.943	43.15	9.507
27.52	6.395	148.87	21.847	46.87	9.949
30.19	7.032	163.01	21.868	50.97	10.312
32.89	7.620	175.64	21.961	55.38	11.627
35.71	8.165	188.50	22.050	59.58	12.224
38.76	8.787	194.33	22.113	16.75	3.184
42.70	9.464	200.18	22.068	18.79	3.695
Transition at 59°K.		220.04	22.191		
59.99	12.121	226.09	22.152	Series III	
64.62	11.539	B.p. at 232.50°K.		Solid	
69.79	11.635			20.13	3.942
75.40	11.822			22.25	4.619
82.32	12.228			24.56	5.472
88.05	12.690			28.62	6.456
93.57	13.123			40.82	9.212
100.68	14.025			44.56	9.691
106.34	15.049			49.04	10.282
110.94	15.992			53.84	11.252
111.82	17.664				
M.p. at 115.73°K.					

I (16–230°K.), series II (16–60°K.) and series III (16–60°K.). The heat capacity curve of the solid shows a λ-type transition at approximately 59°K. The heat of transition obtained from the integral $\int C_p$ (anomalous) dT, is 16 ± 2 cal., corresponding to an entropy of transition of 0.272 ± 0.02 e.u.

II. Melting Point and Heat of Fusion.—The melting point of chlorodifluoromethane was obtained by studying the temperature of the sample as a function of the amount of material melted and then extrapolating to an infinite amount melted. This extrapolation should give a value corresponding to the melting point of the pure substance. The experimental data can be expressed by the relation

$$T = 115.727 - (0.0039/x) \qquad (1)$$

where x is the amount of material melted (in moles). Putting $1/x = 0$, *i.e.*, for infinite dilution, one obtains the true melting point of pure chlorodifluoromethane, equal to 115.73 ± 0.01°K. The experimental values of the temperature and those calculated from eq. 1 for various amounts of solid melted are given in Table II.

From thermodynamic considerations, one would expect the melting point to vary with amount melted, according to the relationship

$$T = T_m - \frac{RT^2_m}{\Delta H_f}\frac{y}{x + y} \qquad (2)$$

where T and T_m are the apparent and true melting

TABLE II

MELTING POINT OF CHLORODIFLUOROMETHANE[a]

x, amount melted, moles	T, °K. Expt.	T, °K. Calcd.
0.233	115.710	115.710
.350	115.718	115.716
.467	115.721	115.719
.702	115.718	115.721
.819	115.718	115.722
.935	115.728	115.724

[a] Melting point of the pure substance is 115.727 ± 0.01°K.

points of the material, respectively; x, the number of moles of material melted; y, the number of moles of impurity; and ΔH_f the heat of fusion of the pure material. This relation holds provided that the impurities are completely soluble in the liquid phase, that the solution is sufficiently dilute to justify assumption of ideality, and that the difference between the true and apparent melting points is small. Since the solution is dilute this reduces to

$$T = T_m - K(y/x) \qquad (3)$$

where K is a constant equal to $RT^2_m/\Delta H_f$ or 27.006 for chlorodifluoromethane.

From a comparison of equations 1 and 3 we find that Ky is 0.0039, yielding a value of 0.14×10^{-3} for y, the moles of impurity. The purity of the sample is then estimated to be 99.98 mole %.

Three determinations were made of the heat of fusion and the results are summarized in Table III.

TABLE III

HEAT OF FUSION OF CHLORODIFLUOROMETHANE

Run no.	Temp. interval, °K.	ΔH_f, heat of fusion, cal./mole
1	108.76–119.25	983.92
2	104.24–118.24	985.36
3	105.80–117.93	987.12
	Av.	985.47 ± 1.82

III. Heat of Vaporization.—Four determinations of the heat of vaporization were made with the condensed gas calorimeter which had previously been used for the heat capacity measurements and the results are summarized in Table IV. The normal boiling point determined from vapor pressure measurements was found to be 232.50 ± 0.07°K. while the data of Benning and McHarness[4] yield a boiling point of 232.36°K.

TABLE IV

HEAT OF VAPORIZATION OF CHLORODIFLUOROMETHANE

Run no.	Amount vaporized, g.	ΔH_V at 232.50°K. (760 mm.), cal./mole
	(a) Condensed gas calorimeter	
1	7.5526	4818.5
2	7.2466	4830.8
3	7.8288	4828.3
4	7.6770	4852.4
	Av.	4832.5 ± 12.5

(b) High pressure calorimeter

Run no.	Amount vaporized, g.	ΔH_V at 222.00°K., cal./mole	ΔH_V cor. to 232.50°K., cal./mole
1	38.1619	4937.1	4838.4
2	38.1619	4934.3	4835.6
	Av.	4935.7 ± 1.4	4837.0 ± 1.4

Since it was impossible to avoid superheating of the liquid during the vaporization, it was found desirable to determine the heat of vaporization in the high pressure calorimeter[9] where the temperature of the liquid could be controlled to ± 0.05°K. The results of these two determinations at 222.00°K. were consistent with the heat of vaporization obtained at the normal boiling point.

Discussion of Results

(a) Comparison with Spectroscopic Data.—The calculations of the entropy of the ideal gas from the calorimetric measurements are given in Table V. The correction for gas imperfection is calculated from Berthelot's equation of state using the critical constants of Benning and McHarness.[3] To determine the entropy from 0–15°K. a Debye θ was estimated from the experimental data in the temperature range 16–20°K. This was found to be 70 ± 5 degrees. The large uncertainty is due to the fact that θ decreases with decreasing temperature. Using this value of θ the increase in entropy from 0 to 15°K. is found to be 1.1393 e.u. with an uncertainty of ± 0.2 e.u.

TABLE V

THE CALORIMETRIC VALUE OF THE ENTROPY OF CHLORODIFLUOROMETHANE AT ITS BOILING POINT

	Entropy, e.u.
1. Solid, 0–15°K. (Debye θ = 70)	1.1393 ± 0.2
2. Solid, 15–115.73°K. (Simpson's rule)	17.720 ± .003
3. Transition at 59°K. (graphical integration)	0.272 ± .02
4. Fusion at 115.73° (985.47/115.73)	8.516 ± .011
5. Liquid, 115.73–232.50°K. (Simpson's rule)	15.349 ± .001
6. Vaporization at 232.50°K. (4832.5/232.50)	20.785 ± .051
7. Corrn. for gas imperfection (Berthelot's eq.)	0.138
Entropy of ideal gas at 232.50°K. (760 mm.)	63.919 ± 0.28

This uncertainty is large in comparison with the uncertainty in the experimental data up to the boiling point. The total uncertainty in the entropy of chlorodifluoromethane at the boiling point is at most ± 0.28 e.u.

Pitzer and Gelles[6] have calculated the entropy of the ideal gas from spectroscopic data for chlorodifluoromethane. They obtain a value of S^0 = 64.03 ± 0.02 e.u. at the boiling point (232.50°K.). The vibrational contributions to the entropy were calculated by Pitzer and Gelles[10] using the frequency assignments of Plyler and Benedict.[11]

The calorimetric value of the entropy of the ideal gas at its boiling point, 63.919 ± 0.28 e.u. is in good agreement with the spectroscopic value of 64.03 ± 0.02 e.u. The difference between the two is 0.11, which is well within the uncertainty of the calorimetric value. It can be concluded therefore that there is no appreciable hydrogen bonding in the gas phase.

(b) Heat Capacity of the Liquid.—When the heat capacity data for the liquid chlorodifluoromethane are plotted *versus* temperature, there appears a broad flat minimum at about 150°K. This may suggest the possibility of polymers existing in the liquid phase. Since there is evidence in vapor pressure measurements of liquid mixtures of

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fluorocarbons[7] that association due to hydrogen bonding between molecules of partially fluorinated methanes occur in the liquid state, the above mentioned minimum could correspond to a shift in the equilibrium constant of the reaction polymers ⇄ monomers as the temperature is raised.

(c) **Heat Capacity of the Solid.**—An examination of the heat capacity of the solid state for various halogenated methanes reported in the literature indicates that except for methane[12] no λ-type transitions are observed. Carbon tetrafluoride,[13] carbon tetrabromide,[14] carbon tetrachloride[15] and bromomethane[16] show sharp transitions, characteristic of a first-order effect, while chloromethane[17] and trichlorofluoromethane[18] show no transitions.

The nature of the λ-type transition in chlorodifluoromethane cannot be ascertained solely on the basis of the heat capacity. This transition appears anomalous in comparison with other halogenated methanes, however, it should be pointed out that due to kinetic effects a first-order transition may be masked, resulting in what appears to be a λ-type transition.

Derived Thermodynamic Functions

The heat capacity and derived thermodynamic functions for chlorodifluoromethane at selected temperatures are given in Table VI.

TABLE VI

THERMODYNAMIC FUNCTIONS OF CHLORODIFLUOROMETHANE

Temp., °K.	C_p, cal./mole/deg.	S, cal./mole/deg.	$(H - H_0)/T$, cal./mole/deg.	$-(F - H_0)/T$, cal./mole/deg.
Solid				
15	2.470	1.1393	0.8120	0.3273
20	3.905	2.039	1.395	0.644
30	6.970	4.236	2.747	1.489
40	9.015	6.536	4.097	2.439
50	10.235	8.697	5.219	3.478
Transition in solid occurs 50–75°K. (entropy of transition is 0.272 cal./mole/deg.)				
80	12.080	14.215	8.648	6.567
90	12.845	15.681	8.185	7.496
100	13.645	17.070	8.688	8.382
110	14.442	18.395	9.175	9.220
115.73	14.900	19.131	9.447	9.684
Liquid				
115.73	22.142	27.647	17.963	9.684
120	22.100	28.449	18.111	10.338
140	21.904	31.841	18.666	13.175
160	21.856	34.760	19.066	15.694
180	21.978	37.341	19.382	17.959
200	22.104	39.663	19.649	20.014
220	22.184	41.774	19.875	21.899
232.50	22.234	42.996	20.001	22.995
232.50 (vapor)	....	63.781	40.786	22.995
232.50 (ideal gas)	....	63.919	....	....

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK STATE COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY, AND ALDRICH CHEMICAL CO.]

Addition of Methyl Radical to *cis* and *trans* Isomers

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The addition of methyl radicals to a series of *cis* and *trans* isomers has been studied. The kinetic data permit us to conclude that different transition states represent the addition to a *cis* and a *trans* isomer. This means that the transition state is rigid in respect to the central C–C bond. The difference in the reactivities of *cis* and *trans* isomers is satisfactorily accounted for. It is explained by the difference in the resonance energies of the respective transition states. Finally an attempt is made to solve the problem from which direction the radical approaches a C═C double bond. It is suggested tentatively that the most probable approach of a radical is along the C═C axis.

The object of the present investigation is to study the differences in the reactivities of *cis* and *trans* isomers and to explain the observed variations in reactivities in terms of structural changes of the molecule resulting from the isomerization process. To obtain the desired information we investigated the addition of methyl radicals to the respective isomers, *i.e.*, the reactions described by the general equation

$$\mathrm{CHX{:}CHX + CH_3 \longrightarrow \cdot CHX{\cdot}CHX{\cdot}CH_3}$$

These reactions are simple, easy to investigate, and their product—the radical $\cdot$CHX$\cdot$CHX$\cdot$CH$_3$— is common for both isomers.[1]

Although the addition to either isomer results in the same product, the transition states of the respective processes need not be the same. If the internal rotation in the transition state is free, then the reactions involving the *cis* or the *trans* isomer would both proceed through the same transition state. On the other hand, if the internal rotation is restricted, then the two reactions would proceed through different transition states. The results, discussed later in this paper, show that the addition of radicals to *cis* and to *trans* isomers proceeds through different transition states. Hence, it appears that the internal rotation in respect to the central C–C bond is restricted in the transition state.

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[1] See, *e.g.*, F. R. Mayo and K. E. Wilzbach, THIS JOURNAL, **71**, 1124 (1949).