phenyl)-chlorosilane with 0.1 g. (0.0027 mole) of lithium aluminum hydride in ether for 6 hours. The mixture was hydrolyzed by adding ether saturated with water, and the aluminum hydroxide was washed out with dilute aqueous acetic acid. The dried ether solution, on standing, deposited 0.9 g. (98%) of tris-(*p*-dimethylaminophenyl)-silane, m.p. 157°, without recrystallization. This was identified by a mixed melting point determination with the sample reported above.

Attempted Preparation of Hexakis-(*p*-dimethylaminophenyl)-disiloxane.—All attempts to prepare this compound from tris-(*p*-dimethylaminophenyl)-silanol were unsuccessful. Refluxing the silanol with glacial acetic acid,[7] 98% formic acid[7] or hydrochloric acid in methanol[12] gave glasses or oils with a strong blue color which suggests that cleavage of the *p*-dimethylaminophenyl group had taken place.[8]

One gram of tris-(*p*-dimethylaminophenyl)-silanol (0.0025 mole) was suspended in dry xylene and 0.5 g. (0.022 g. atom) of sodium metal was added. This was warmed until the silanol had completely dissolved and hydrogen was no longer evolved. The solution was then decanted into a xylene solution of 1 g. (0.0024 mole) of tris-(*p*-dimethylaminophenyl)-chlorosilane. This mixture was refluxed for 6 hours, then washed with water, and 0.4 g. of colorless insoluble material was filtered off. This solid did not melt, but slowly turned brown and decomposed when heated above 400°. A product with very similar properties was obtained when 5.22 g. (0.0183 mole) of hexachlorodisiloxane was refluxed in ether with 0.11 mole of *p*-dimethylaminophenyllithium until Color Test I became negative (15 hours). Purification of the crude product was attempted by dissolving it in dilute acid, washing the solution with ether, and reprecipitating with dilute aqueous ammonia. The material so obtained had a satisfactory silicon analysis for hexakis-(*p*-dimethylaminophenyl)-disiloxane (calcd. 7.07, found 6.96) but its cryoscopic molecular weight in nitrobenzene was much too low (calcd. 792, found 440 ± 30). In view of these anomalous results, we do not claim that this material is hexakis-(*p*-dimethylaminophenyl)-disiloxane.

AMES, IOWA

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[12] Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

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

Some Thermodynamic Properties of Hexadecafluoroheptane[1]

BY GEORGE D. OLIVER AND J. W. GRISARD

The heat capacity of hexadecafluoroheptane was measured over the temperature range of 18 to 310°K. A transition that absorbed 1594 ± 1.5 cal./mole was found at 180.46 ± 0.10°K. The triple point, 221.87 ± 0.05°K., and heat of fusion, 1660.5 ± 2 cal./mole were determined. Vapor pressure measurements were made for the temperature range −2 to 106° and are represented by the equation $\log_{10} P_{\text{mm.}} = 6.96493 - 1196.067/(t + 210.36)$. The calculated heat of vaporization is 7543 cal./mole at a boiling point of 82.50 ± 0.05°. The critical constants are: t_c, 201.7°, p_c, 16.0 atm. and d_c, 0.584 g./ml. Entropy values calculated from these data for the liquid and ideal gas state at 298.16°K. are 134.28 ± 0.27 and 158.88 cal./deg. mole, respectively.

Introduction

Very little work has been done on the thermodynamics of pure fluorocarbons, probably due to the difficulty of obtaining pure samples. Since fluorocarbons are becoming increasingly important in industrial and academic laboratories, it is desirable to obtain precise data which can be applied to practical as well as fundamental problems. Therefore, the vapor pressure and low temperature thermal properties of hexadecafluoroheptane have been measured and other properties have been calculated from the data.

Experimental

Materials.—The samples were part of a lot of technical grade material produced by the fluorination of *n*-heptane with cobalt trifluoride.[2] Most of the impurities were removed by fractional crystallization, while further purification was obtained by passing the best of this crystallized material through a 56-foot silica gel adsorption column.[3]

TABLE I

MELTING POINT SUMMARY

0°C. = 273.16°K.

Melted, %	21.9	39.8	44.9	72.1	84.7
$T_{\text{obsd.}}$, °K.	221.730	221.789	221.794	221.822	221.830

Triple point, 221.87 ± 0.05°K. $N_x = 0.0168\ \Delta T$. Impurity = 0.06 ± 0.02 mole per cent.

An estimate of the mole per cent. impurity in the purer sample as determined from melting point studies in this research is given in Table I. A different sample was used for vapor pressure measurements. Its purity was approximately 99.92 mole per cent. as deduced from time–temperature freezing curves.

Apparatus.—The calorimetric apparatus was similar to that described by Ruehrwein and Huffman,[4] who improved the design of Blue and Hicks,[5] mainly, by the addition of the vacuum windlass and by the use of alternating current in the shield heater circuits. Two modifications were made which should be mentioned[6]: The heater, made of size No. 36 Advance wire, was bifilarly wound on a copper sleeve which enveloped a 25.5 ohm commercial platinum resistance thermometer. The copper sleeve, greased with Apiezon N, fitted tightly in a well in the calorimeter and in turn the greased thermometer fitted tightly inside the heater. The other modification consisted of a separate differential couple between the shield and ring which indicated their temperature difference on an additional galvanometer and scale.

A brief description of the apparatus and procedure follows: Approximately 50 ml. of the material was sealed in a copper calorimeter and mounted in the adiabatic calorimetric system. To prevent heat interchange, the temperature of the environment was maintained at that of the calorimeter by means of an electrically heated shield as indicated by differential thermocouples. All electrical measurements needed to determine the temperature 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 National Bureau of Standards was used as a potential reference. Time measurements were made with an electric stop-clock which was frequently

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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] R. G. Benner, *et al.*, *Ind. Eng. Chem.*, **39**, 329 (1947).

[3] S. Blumkin, N. C. Orrick, J. W. Grisard and J. D. Gibson, "Purification of Hexadecafluoroheptane," to be published at a later date.

[4] R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

[5] R. W. Blue and J. F. G. Hicks, *ibid.*, **59**, 1962 (1937).

[6] G. D. Oliver, J. W. Grisard and V. E. Anderson, Instrumentation, K-550, Carbide and Carbon Chemicals Division, K-25 Plant, Oak Ridge, Tennessee, January 20, 1950. Detailed description and drawings of the apparatus are presented.

checked against a calibrated stop-watch. 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 National Bureau of Standards calibrated platinum resistance thermometer. Energy measurements made in terms of the absolute joule were converted to calories by dividing by 4.1840.

In order to establish an over-all accuracy for the apparatus, thermal data on *n*-hexane[6] were determined over the temperature range 50 to 300°K. A precision of 0.1% was obtained in both the heat capacity and heat of fusion measurements. The agreement between these data and the data of Douslin and Huffman[7] on *n*-hexane is better than 0.2% except at the lower temperatures.

A detailed description of apparatus and procedure used for measuring the vapor pressure of hexadecafluoroheptane will appear in a subsequent publication. A very brief description follows. Approximately 20 ml. of material was placed in a nickel boiler that was connected to a simple manometer by helium filled lines. The pressure of the helium gas could be adjusted to any predetermined value between 15 and 1500 mm. 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. These temperature measurements were similar to those reported by Willingham, *et al.*,[8] who used glass equipment. The manometer was read by means of Gaertner cathetometers up to 1000 mm., and by a meter scale with millimeter divisions in conjunction with a cathetometer at the higher pressures.

Results and Discussion

A study of the melting point was made by the customary procedure of introducing measured quantities of energy and allowing time for the temperature to become essentially constant.[9] The equilibrium temperatures, $T_{\text{obs.}}$, for the different liquid–crystal ratios are summarized in Table I. These experimental data were used in the simplified relation,[10] $N_x = K\Delta T$, to calculate the mole fraction of impurity present on the assumption that Raoult's law is obeyed.

Two series of heat capacity measurements were made on hexadecafluoroheptane over the temperature range of 18 to 310°K. Since the sample used for series I contained 0.4 mole % impurity which caused a large amount of premelting, it was decided to make similar measurements on a purer sample. Series II constitutes the measurements made on a sample containing 0.05 mole % impurity. As was expected there was no difference in the two series, except in the temperature regions just below the melting and transition points. For the sake of space economy and ease of comparison, only the molal heat capacity values at integral temperatures, read from a smooth curve through all the experimentally determined points, are listed in Table II. A total of 85 heat capacity measurements were made.

Hexadecafluoroheptane was found to have two crystalline forms. Observations were made on the equilibrium temperatures with different amounts of crystals I transposed to obtain the transition temperature. The heat of transition was 1594 ± 1.6 cal./mole at a transition temperature of 180.46 ± 0.10°K.

TABLE II

MOLAL HEAT CAPACITY VALUES AT INTEGRAL TEMPERATURES

Molecular weight = 388.07; 0°C. = 273.16°K.

T, °K.	$C_{\text{satd.}}$, cal./deg.	T, °K.	$C_{\text{satd.}}$, cal./deg.
Crystals I		150	57.43^a
18	9.22	160	60.86^a
20	10.62	170	64.29^a
22	11.94	180.46	67.86^a
25	13.80	Crystals II	
30	16.40		
35	18.77	180.46	71.67
40	20.77	190	73.75
45	22.61	200	75.91
50	24.41	210	78.07^a
55	26.15	220	80.23^a
60	27.86	221.87	80.65^a
65	29.53	Liquid	
70	31.16	221.87	89.73
75	32.79	230	90.86
80	34.44	240	92.25
85	36.09	250	93.61
90	37.71	260	94.93
95	39.33	270	96.25
100	40.95	280	97.58
110	44.12	290	98.91
120	47.38	300	100.26
130	50.67	310	101.61
140	54.00		

^{a} Corrected for premelting or pretransition.

Three measurements of the heat of fusion were made and the results are presented in Table III. The accuracy uncertainty is probably greater, due to premelting effects, than the precision uncertainty which is indicated in Table III.

TABLE III

HEAT OF FUSION OF HEXADECAFLUOROHEPTANE

Temperature interval, °K.	ΔH, cal./mole
213.734–224.051	1660.2
208.187–225.332	1661.5
213.437–223.213	1658.6
Mean	1660.5 ± 1.7

Only the heats of fusion and transition obtained on the purer sample are reported, since the sample containing 0.4 mole % impurity had a heat of fusion value about 1% lower. The lower value was attributed to the effect of premelting on the heat capacity of the pure crystals.

The vapor pressure of hexadecafluoroheptane has been measured previously on material of unknown purity.[11] Since a pure sample was available, measurements were made up to two atmospheres and the accuracy of the results established by calculating 95% confidence limits[12] on the temperatures. These limits were calculated for a straight line, log P *vs.* $1/(c + t)$, where c was treated as a known. From −2 to 70° the limits were ±0.03° which increased to ±0.06° at the higher temperatures.

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[7] D. R. Douslin and H. M. Huffman, THIS JOURNAL, **68**, 1704 (1948).

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

[9] (a) S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947); (b) L. Gutman and K. S. Pitzer, *ibid.*, **67**, 324 (1945).

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

[11] R. D. Fowler, *et al.*, *Ind. Eng. Chem.*, **39**, 375 (1947).

[12] Calculations were made by P. B. Wood of the Engineering Development Division using the methods outlined in W. E. Deming, "Statistical Adjustment of Data," John Wiley & Sons, Inc., New York, N. Y., 1943.

The observed temperature and pressure data listed in Table IV were fitted to the Antoine equation by a method of least squares.[8] The equation obtained is

$$\log_{10} P_{\text{mm.}} = 6.96493 - \frac{1196.067}{t + 210.36}$$

The deviations of the data from this equation are given in columns 3 and 6 of Table IV.

TABLE IV

VAPOR PRESSURE

$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$
−1.89	16.88	0.00	58.99	334.70	0.27
1.57	20.94	− .02	64.03	403.91	.32
6.93	29.09	.22	68.96	482.15	.29
13.54	41.72	− .25	74.27	579.51	.37
19.19	56.64	− .18	79.71	694.49	− .16
23.95	72.52	.01	85.27	830.09	.00
30.49	99.68	− .06	90.08	963.72	− .02
35.91	128.39	.09	95.03	1118.0	.21
41.80	166.62	.03	99.93	1288.7	− .43
46.86	206.57	.05	104.54	1467.0	1.12
52.56	260.63	.16	106.03	1528.8	0.93

Values for the heat of vaporization at 25° and the boiling point were calculated from the vapor pressure data by means of the exact Clapeyron equation. Critical constants, measured in this Laboratory by the Kay method,[13] were used in the Berthelot equation to calculate the vapor volume, and the gas imperfection correction for entropy. Experimental critical constants are the following: critical temperature, 201.7 ± 0.1°; critical pressure, 16.0 ± 0.1 atmosphere; and critical density, 0.584 g./ml. The calculated heat of vaporization is 8686 cal./mole at 25° and 7543 cal./mole at the boiling point, 82.50 ± 0.05°.

The above experimental data were used to calculate the entropy in the liquid and ideal gas states at 298.16°K. The results of these calculations are summarized in Table V. The calculation of the entropy at 18°K. was based on Debye's T^3 relationship of heat capacity and temperature. The large molal entropy value of 4.13 e.u. at 18°K. results from the fact that the heat capacity at this temperature is also large. It was realized that the use of this method to determine the entropy of a molecule of this size might be open to question. Nevertheless, a reasonably constant theta value was obtained by assuming 12 degrees of freedom and using Debye's tables of C_V values based on 3 degrees of freedom, and the molal heat capacity data below 30°K.

TABLE V

SUMMARY OF MOLAL ENTROPY DATA

	Cal./deg.
$S_{18°}$ (Debye, 12° freedom, $\theta = 88.67$)	4.13
$\Delta S_{18-180.46°\text{K.}}$ Solid, graphical	70.126
$\Delta S_{180.46°}$ Transition, 1594.4/180.46°	8.837
$\Delta S_{180.46-221.870°}$ Solid, graphical	15.725
$\Delta S_{221.87°}$ Fusion, 1660.5/221.87°	7.484
$\Delta S_{221.87-298.16°}$ Liquid, graphical	27.975
$S_{298.16°}$ of liquid	134.28 ± 0.27
$\Delta S_{298.16°}$ Vaporization, 8686/298.16	29.13
$\Delta S_{298.16}$ Compression, $R \ln P/760$	−4.57
$\Delta S_{298.16}$ Gas imperfection	0.04
Entropy in the ideal gas state at 1 atm. and 298.16°K.	158.88

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(13) W. B. Kay, THIS JOURNAL, **69**, 1273 (1947).