mined by measuring the volume occupied by the sample in the experimental tube when the meniscus was made to disappear by a slight decrease in pressure on the sample. An average value of the critical density is 0.55 g./ml.

Oak Ridge, Tenn. Received January 24, 1951

[Contribution from the Research Laboratories, K-25 Plant, Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation]

Some Physical Properties of Hexadecafluoroheptane[1a,1b]

By George D. Oliver, S. Blumkin and C. W. Cunningham

The boiling point, melting point, critical constants, density, surface tension, parachor, infrared and Raman spectra are reported for pure hexadecafluoroheptane. Refractive indices for the sodium D, mercury E and G, and hydrogen C and F lines at 20, 25 and 30° are given.

Introduction

The increasing number of applications of fluorocarbons in industry makes it important to have an extensive knowledge of the properties of these substances. A description of the chemical and physical properties of fluorocarbons, in general, has been summarized by Simons.[2] In a previous publication,[3] the vapor pressure, low-temperature thermal properties and other derived data for pure hexadecafluoroheptane were presented. The melting point, boiling point, critical constants, refractive index, density, surface tension, parachor, infrared and Raman spectra of hexadecafluoroheptane are reported here.

In order to show the differences in the properties of fluorocarbons and the respective hydrocarbons, a comparison of some of the physical properties of *n*-heptane and hexadecafluoroheptane at 20° is given in Table I. These differences and the great stability of this compound suggest its possible use as a standard for physico-chemical measurements.

Table I

Comparison of Properties of Hexadecafluoroheptane and *n*-Heptane at 20.0°

Property		n-C_7F_{16}	n-C_7H_{16}
Boiling point, °C.		82.51	98.43
Freezing point, °C.		−51.29	−90.60
Freezing point depression, °C.	K_F	19.2	2.1
Density	d	1.73184	0.68368
Refractive index	n_D	1.26019	1.38764
Specific refraction	$\frac{n^2-1}{n^2+2}\cdot\frac{1}{d}$	0.09464	0.34486
Specific dispersion	$\frac{n_F-n_C}{d}$	0.00136	0.00982
Surface tension	γ	13.19	20.26
Parachor	$\gamma 1/4\cdot\frac{M}{d}$	427.7	310.9

Material.—All samples used in this investigation were taken from material produced by the fluorination of *n*-heptane with cobalt trifluoride. The methods used in the purification of the technical grade material will be described in a subsequent publication.[4] During the process of purification, the impurity was checked at each step by a freezing curve method and by the infrared spectrum. The purity of the final material, 99.92 ± 0.02 mole per cent., was determined calorimetrically by a study of the melting point[3]; the infrared spectrum of this material is given below. Pure hexadecafluoroheptane has a triple point of 221.87 ± 0.05° K.

Boiling Point.—An ebulliometer of the type described by Swietoslawski[5] was used to determine the boiling point, 82.51 ± 0.05° at 760.0 ± 0.1 mm. pressure. The temperature measurements were made with a platinum resistance thermometer certified by the National Bureau of Standards, and the pressure in the system was maintained to ±0.1 mm. Voltage imposed on the pot heater was varied from 20 to 50 volts, and the boiling point was taken at that temperature which did not vary with a large change in voltage input. This boiling point is in very good agreement with that calculated from published vapor pressure data.[3]

Critical Data.—The critical constants were measured with an apparatus similar to that described by Kay[6] which consisted of a heavy-walled capillary tube with the sample confined over mercury, and the necessary apparatus for applying and measuring pressure. Double copper-constantan thermocouples and a K-2 potentiometer were used to measure the temperature of the vapor-bath surrounding the capillary tube. A Gaertner cathetometer was employed in the volume measurements. Pressure measurements were corrected to standard millimeters of mercury. Unreported measurements on benzene and *n*-heptane indicate experimental uncertainties of ±0.05° and ±0.02 atmosphere.

Fowler, *et al.*,[7] had measured the critical temperature by heating a sample in a sealed tube until the meniscus disappeared and obtained a value 0.8° lower than the present value of 201.7°. The pres-

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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. (b) For detailed tables supplementary to this article order Document 3261 from American Documentation Institute, 1719 N Street, N.W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

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ent critical pressure, 16.0 atm., and critical density, 0.584 g./ml., are slightly lower than their calculated values.

Density.—A density balance similar to the one described by Forziati[8] was used to determine the density at 20.00, 25.00, and 30.00°. The National Bureau of Standards refinement of a balance beam calibrated to read density directly was not incorporated in this balance. Instead, the weight of the plummet in air and in the sample was determined to ± 0.00001 g. and density values calculated therefrom. Sample temperatures were standardized in terms of bath temperatures to $\pm 0.01°$ by measurements with a platinum resistance thermometer. Volume of the Pyrex glass plummet at 25.00° was calibrated with a fluorocarbon sample, the density of which had been determined accurately by a pycnometer method. Plummet volumes at 20.00 and 30.00° were calculated from the volume at 25.00°, using the coefficient of expansion of Pyrex glass.

Each value given in Table II is an average of three or more determinations. The equation $d_t = 1.78714 - 0.002765t$ adequately represents the data.

Refractive Index.—A low-range (n_D of 1.20 to 1.51) Bausch and Lomb Precision refractometer, having a precision of $\pm 3 \times 10^{-5}$, was used to determine the refractive indices of hexadecafluoroheptane at 20, 25, and 30° for the sodium D (589 mμ), mercury E (546 mμ) and G (435 mμ), and hydrogen C (656 mμ) and F (486 mμ) lines. The spectral line sources consisted of a sodium vapor-lamp, a high pressure mercury arc lamp with Wratten filter No. 74 for the green line and Corning filters Nos. 3389 and 5113 for the blue line, and a low-pressure commercial hydrogen-discharge tube with no filter for the red line and Wratten No. 57A for the green line. The desired sample temperatures were obtained by pumping water from a large-volume bath whose temperature was controlled to within $\pm 0.01°$ by a sensitive thermo-regulator. The calibration of the instrument was checked and the sample temperature standardized by determinations on standard samples of 2,2,4-trimethylpentane and toluene obtained from the National Bureau of Standards. The hydrogen source was weaker than either the sodium or mercury with the consequence that the precision of n_C and n_F measurements was less than that for the n_D, n_E and n_G.

The experimental values obtained at 20.0, 25.0 and 30.0 for each of the noted wave lengths, are given in Table II. The average over-all precision of the measurements is estimated to be ± 0.00004. Treatment of the refractive index dispersion data by the reciprocal plotting method[9] yields well-defined straight lines.

The atomic refraction of fluorine in hexadecafluoroheptane as calculated by difference from the observed molar refraction, and the accepted atomic refraction of carbon yields a value of 1.238 which checks the 1.23 previously reported[10] for fluorine in completely fluorinated compounds.

TABLE II

DENSITY, SURFACE TENSION AND REFRACTIVE INDEX OF HEXADECAFLUOROHEPTANE

Temperature, °C. →	20.0	25.0	30.0
d (g./ml.)	1.73184	1.71802	1.70419
γ (dynes/cm.)	13.19	12.78	12.37
n_C	1.25947	1.25736	1.25532
n_D	1.26020	1.25818	1.25610
n_E	1.26080	1.25879	1.25669
n_F	1.26188	1.25976	1.25761
n_G	1.26314	1.26109	1.25904

Surface Tension and Parachor.[11]—Seven measurements of the surface tension were made at each temperature, using the maximum bubble pressure method.[12] The bubbler was calibrated before and after measurement using pure heptane and octane as reference materials whose surface tension had been determined repeatedly upon National Bureau of Standards samples. Experimental values at 20, 25 and 30° are listed in Table II and the calculated values of the molecular parachor at the same temperatures are 427.7, 427.9 and 427.9, respectively. Empirically derived vapor densities, used in the calculation, have values of 0.00175, 0.00209 and 0.00247 g./ml. at 20, 25 and 30, respectively. The parachor is considered to be accurate to within 0.1%.

Infrared Spectrum.[13]—The infrared absorption spectrum has been observed by previous investigators[14] with less pure samples and only from 2 to 22 μ. The spectrum of the 99.92% hexadecafluoroheptane has been obtained from 2 to 38 μ. There is no trace in this spectrum of any of the impurities observed in the crude material or concentrated in the waste material during purification.

The absorption spectrum was obtained with Perkin–Elmer spectrometers. A double-beam model 21, with a prism of sodium chloride was used from 2 to 15 μ. For the remainder of the spectrum a model 12-C, equipped with a 7-cycle detection system, was used with a potassium bromide prism from 15 to 22 μ and a KRS-5 prism from 21 to 38 μ. The potassium bromide and KRS-5 prisms were calibrated with water and other well known molecules and the accuracy in these regions should be similar to the model 21 which is 0.02 μ. The windows of the cells were of the same material as the prism with which they were used.

Liquid samples were used throughout the spectrum. Cell thicknesses were 0.02, 0.14, 0.26 and 3.9 mm. as marked on the curves in Fig. 1. In addition, two gas samples were required in the region of strongest absorption from 7 to 20 μ, particularly in the C–F stretching region around 8 μ. The gaseous samples were in a 10-cm. cell at pressures of 0.5 and 4.6 mm. as marked on the curves. A table giving

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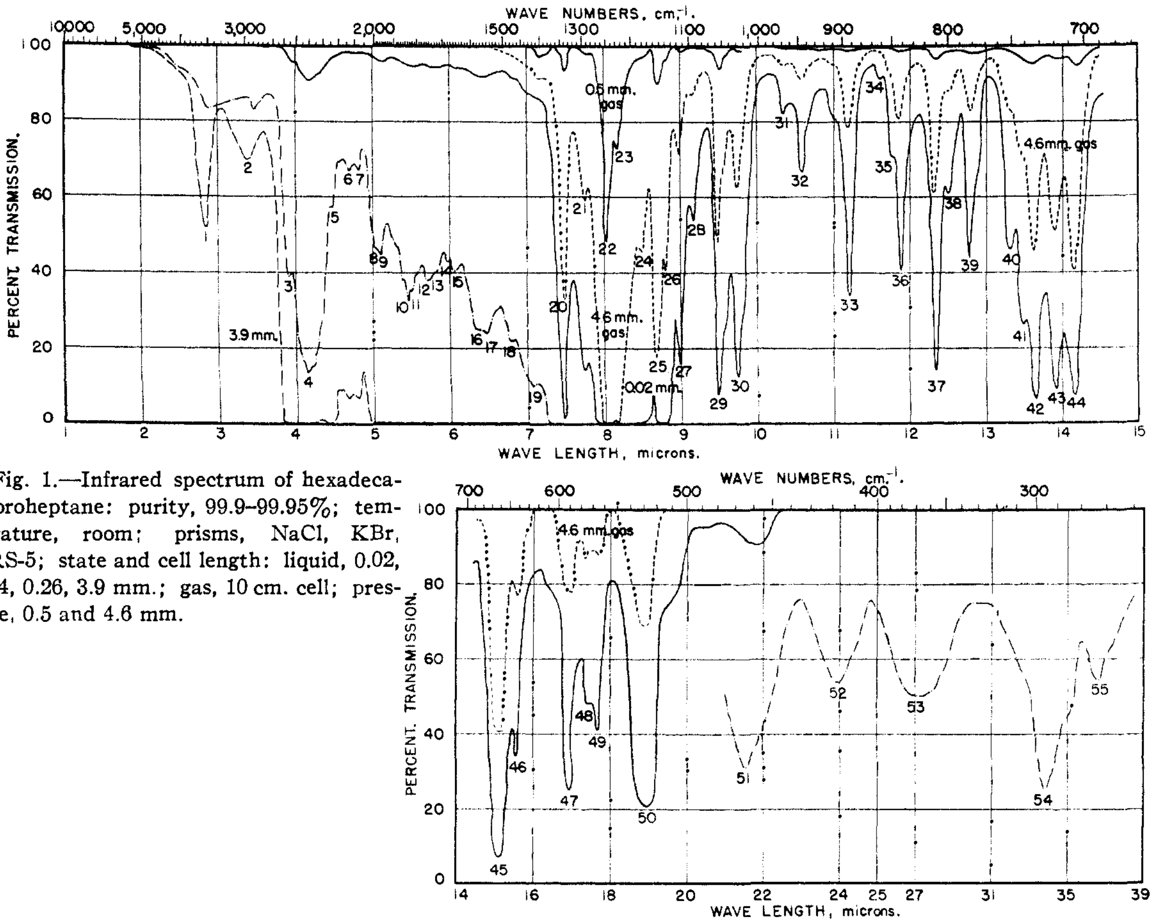

Fig. 1.—Infrared spectrum of hexadecafluoroheptane: purity, 99.9–99.95%; temperature, room; prisms, NaCl, KBr, KRS-5; state and cell length: liquid, 0.02, 0.14, 0.26, 3.9 mm.; gas, 10 cm. cell; pressure, 0.5 and 4.6 mm.

the position and relative intensities of the bands are available on microfilm.[1b]

Raman Spectrum.[15]—The Raman spectrum of hexadecafluoroheptane has been reported by previous investigators[14c] using less pure samples. The spectrum of 99.92% material has been studied in the liquid phase by means of a Lane–Wells spectrometer utilizing the standard Lane–Wells mercury arc irradiation unit. The mercury 4358 Å. line was used as the parent. A filter solution of 0.01 g. DuPont Rhodamine 5GDN Extra and 13 g. of p-nitrotoluene per 100 ml. of ethyl alcohol was employed to clean out the mercury spectrum in the region of the observed Raman lines.

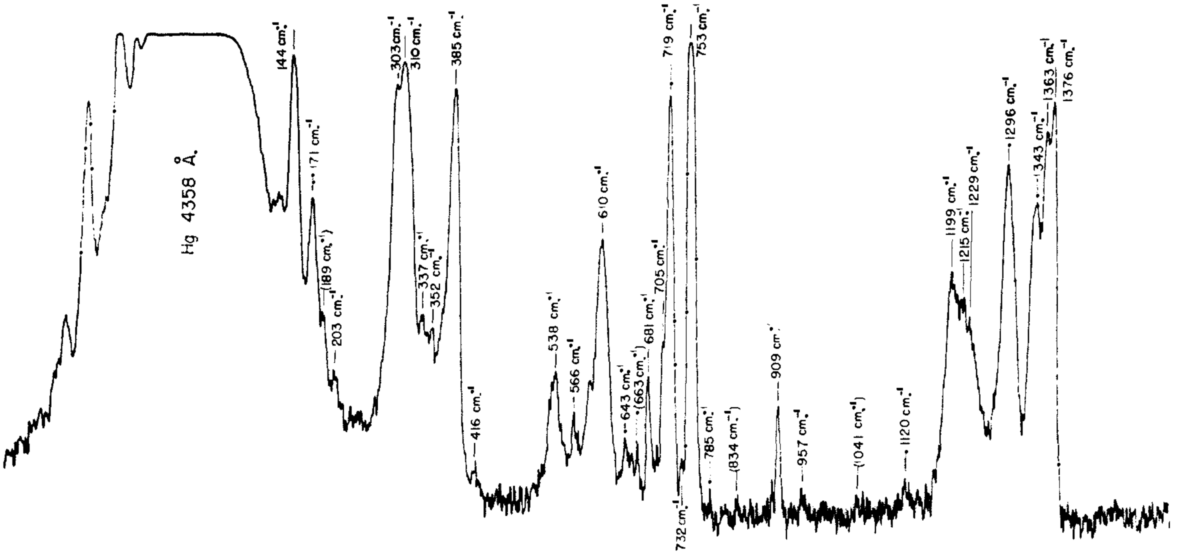

Fig. 2.—Raman spectrum of hexadecafluoroheptane.

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(15) This work was performed by Mr. T. O. Burke and Mr. T. V. Blosser of the Physics Department.

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.

OAK RIDGE, TENN. RECEIVED MARCH 19, 1951

[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.

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