need not agree precisely with that indicated by the 354 mμ peak.

The two absorption peaks found for protonated mesitylene in HF at $\sim$ 260 and $\sim$ 360 mμ may correspond to those predicted by Muller, Pickett and Mulliken[18] for the benzenium ion (at 320 and 400 mμ), but the calculations are certainly too approximate to permit a clear distinction between the bonding suggested by the authors (a localized bonding stabilized by hyperconjugation) and the generalized π-bonding suggested by Dewar.[19]

The data for hexamethylbenzene are more difficult to interpret. The conductivity observations of ref. 5 would imply that hexamethylbenzene is completely ionized in anhydrous hydrogen fluoride. This would yield an absorption maximum at 395 mμ for singly protonated hexamethylbenzene of about 7400 and on the basis of the observed absorption in 17.5 *M* H_2SO_4 (H_0 = −8.7) the pK_a^1 for hexamethylbenzene as a proton acceptor indicator would be −8.3. However, the optical absorption found in strong sulfuric acid corresponds to some additional process, either a rapid rearrangement followed by sulfonation or perhaps a second protonation. It is not immediately obvious why the latter should take place more readily in sulfuric than in hydrofluoric acid solutions showing comparable acid strength when measured with trinitroaniline. However, as was noted above, lack of exact correspondence in acidities in using two different types of indicators is unfortunately encountered in a number of similar situations.

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[19] M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE]

Some Physical Properties of Perfluoro-*n*-hexane

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A sample of perfluoro-*n*-hexane was refined by fractional crystallization and found to be 99.98 mole % pure by analysis of the freezing curves. The freezing point, heat of fusion, vapor pressures, densities of air saturated and degassed liquid between 15 and 45°, vapor densities at 30°, and critical temperature were determined.

Introduction

Although the characterization of fluorocarbons has been the object of intensive research since their discovery,[1] very little work has been done on highly purified samples. Impurities introduced during synthesis by existing methods are not easily removed by fractional distillation because a large number of substances, *e.g.*, fluorocarbons containing hydrogen,[2,3] nitrogen[3] or oxygen,[3] and even structural isomers[2,4,5] can boil at nearly the same temperature.

A sample of perfluoro-*n*-hexane, prepared by the Simons electrochemical process,[6] was obtained through the courtesy of the Minnesota Mining and Manufacturing Company. Purification methods investigated were fractional distillation, silica gel adsorption, treatment with cobalt trifluoride and fractional crystallization. Of these only the last was found to be capable of removing the impurities. A sample determined to be 99.98 mole % pure by analysis of the freezing curve was obtained.

Stiles and Cady[4] prepared a sample of perfluoro-*n*-hexane by fluorination of the pure hydrocarbon with cobalt trifluoride, treated it with alkaline permanganate and after fractional distillation obtained a product which they estimated to be 96.5 mole % pure. Their fluorocarbon boiled at 57.23°, 0.08° higher than ours. Our vapor pressures are approximately 1 mm. higher than theirs at 30° and 2 mm. higher at 60°. Although the liquid density of blended fractions from our distillation plateau was only slightly less than 1.6845 at 25° reported by the above workers, fractional crystallization produced a sample having considerably lower density. The density of our purified sample saturated with air at 25° is 1.66970 g./cm.^{3}. The freezing point is −82.26°, 0.21° lower than the highest value obtained by Stiles and Cady.[5] The heat of fusion, calculated from the freezing point lowering produced by small amounts of perfluorotri-*n*-butylamine is 1580 ± 90 cal./mole. Stiles and Cady[5] report a value of 4300 cal./mole for this property.

The infrared spectrum of the refined sample is identical with that shown by Weiblen.[7] The only perceptible change in the infrared spectrum during purification was the removal of an absorption band at 830 cm.$^{-1}$.

Experimental

Purification.—The crude fluorocarbon was distilled in a fractionating column which when tested with hydrocarbons was found to have 90 theoretical plates. From 2.2 kg. of

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[1] J. H. Simons and L. P. Block, THIS JOURNAL, **61**, 2962 (1939).

[2] A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).

[3] W. H. Pearlson, "Fluorocarbon Derivatives" in "Fluorine Chemistry," Vol. I, Edited by J. H. Simons, Academic Press, Inc., New York, N. Y., 1950.

[4] L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1951).

[5] V. E. Stiles and G. H. Cady, *ibid.*, **74**, 3771 (1952).

[6] J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949).

[7] D. G. Weiblen, "The Infrared Spectra of Fluorocarbons and Related Compounds" in "Fluorine Chemistry," Vol. II, Edited by J. H. Simons, Academic Press, Inc., New York, N. Y., 1954.

fluorocarbon, 1.3 kg. had a boiling range from 56.9 to 57.6°. The densities of successive fractions boiling in this range increased from 1.6787 to 1.6835 at 25°. The molecular weights of these fractions were the same, within our precision for determining this property. The average value obtained by the method of limiting gas density was 335.0 ± 0.3 g./mole. The theoretical value is 338.06.

One of the fractions from the above mentioned distillation plateau was passed through a 200 cm. × 1 cm. adsorption column packed with Davison Chemical Corp. 28–200 mesh silica gel. The liquid densities of successive fractions of eluted material increased by only 0.0002 g./cm.^{3}. There was no perceptible change in the gas density.

In a further attempt to remove the impurities, presumably compounds containing hydrogen, or unsaturated material, 167 g. was passed through a cast iron pipe packed with about 400 g. of cobalt trifluoride at 330°. No appreciable change in the gas and liquid densities was achieved.

Fractional crystallization[8] was carried out in a relatively simple glass apparatus consisting of a glass bulb 4.8 × 22 cm., narrowed at the top to a tube 2 cm. in dia. A small 8 mm. well was attached to the bottom to aid in the removal of liquid from the crystals. The flask was supported in the center of a 1 liter silvered Dewar vessel by a large rubber stopper which contained a tube for pumping on Dry Ice packed in the annular space. Controlled temperatures down to −120° were easily obtained by regulating the pressure. It was usually necessary to cool the liquid to −120° to initiate crystallization. The temperature was then raised and held constant at some higher temperature. When equilibrium between solid and liquid was obtained, the liquid was forced out through a tube extending to the bottom of the 8 mm. well by applying pressure on the surface. Liquid residues from various crystallizations were combined systematically and recrystallized. After 21 crystallizations, 325 g. from the 1.3 kg. of starting material was obtained and had a molecular weight of 337.9 ± 0.3. Another crystallization gave 160 g. found to be 99.98 mole % pure and 165 g. found to have a purity of 97.8 mole %. These portions are referred to hereinafter as sample A and sample B, respectively.

Temperature Measurement.—Temperatures were determined with copper–constantan thermocouples calibrated at the Dry Ice point by the method of Scott,[9] at the mercury and sodium sulfate hydrate points, against a standard thermometer between 0 and 50°, and the vapor pressure of *n*-hexane[10] above 50°. The vapor pressures of *n*-hexane determined on our temperature scale between 30 and 50° were in agreement with those cited. The largest discrepancy was 0.16 mm. corresponding to less than 0.005°.

The thermocouple potentials were measured with a Leeds and Northrup type K-2 potentiometer and Type E galvanometer. An auxiliary circuit was designed to compensate for potentials due to thermal gradients in the potentiometer. This arrangement gave a sensitivity of 0.2 microvolt or ±0.006°. The calibration was expressed in the form $E = at + bt^2$. The constants were determined by least squares and in no case did the temperatures calculated from the equation and those determined experimentally differ by more than 0.01°.

Freezing Point and Freezing Point Lowering.—Freezing points were determined in the presence of air at atmospheric pressure on 50 g. samples in a 3 × 15 cm. Pyrex tube containing a thermocouple and a stirring device. The tube was surrounded by a dead air space and placed in a Dewar flask containing Dry Ice. Any desired temperature could be achieved by pumping on the Dry Ice at a regulated pressure. The cooling curves of sample A gave horizontal sections at −86.26° which were reproducible to ±0.01° and were independent of the Dry Ice temperature or the degree of supercooling. An estimate of the degree of purity was obtained by the method of Mair, Glasgow and Rossini.[11] The slope of the cooling curve was zero within the precision of our measurements. The slope used in calculating the purity was that imposed by the error in the temperature measurement. Assuming solid-insoluble impurities, this method gave a value of 99.98 mole %. No solid transition was obtained above −120°.

Cooling curves for sample B were not flat. The true freezing point after correcting for supercooling by the method of Taylor and Rossini[12] was −87.56°. Analysis of the slope of the cooling curve by the method of White[13] gave 2.2 mole % of impurities.

The freezing point of a solution containing 0.008479 mole of perfluorotri-*n*-butylamine (mol. wt. 671) and 0.1683 mole of sample B was found to be −89.60°. The heat of fusion calculated from the freezing point depression of 2.04° was 1580 ± 90 cal./mole.

Vapor Pressure.—The vapor pressures of sample A were determined in an isothermal equilibrium still. The apparatus will be described in a subsequent publication.[14] It was a static method where the liquid was contained in a copper bulb connected to a manometer. The bulb was immersed in a water-bath which was regulated at any desired temperature to ±0.01°. The water-bath and manometer were surrounded by an air-bath kept a few degrees warmer than the water-bath to prevent condensation of vapor in the lines. The manometer, 1.3 cm. in dia., was read with a Gaertner M-908 cathetometer in conjunction with a meter scale graduated in millimeters and calibrated by the National Bureau of Standards. Corrections for the capillary depression of the meniscus, and the thermal coefficients of expansion of mercury and the meter scale were made. The pressure is reported in standard millimeters of mercury.

It was necessary to degas the liquid by fractional distillation in the vacuum system. The usual methods of pumping on the frozen solid, or a series of one plate distillations in the vacuum system proved inadequate.

Liquid Density.—The densities were determined in sealed dilatometers of approximately 5-ml. capacity with precision bore 2 mm. capillary stems 20 cm. long containing an etched scale divided into millimeters. They were calibrated with mercury at approximately each centimeter at 10° intervals between 15 and 55°. Weighings against a tare of the same surface area were reproducible to 0.03 mg. The position of the meniscus in the capillary was determined to ±0.03 mm. by interpolating between the divisions on the stem with a bench cathetometer.

The densities of air-saturated liquid were obtained at 15, 25, 35 and 45 ± 0.01° in the following manner. The dilatometer was filled with dry air, weighed and then cooled to 0°. A drying tube was attached during cooling. An appropriate quantity of liquid was then introduced through a length of hypodermic needle tubing; the drying tube was replaced, and the tip sealed with a hand torch. Corrections were made for the weight of air displaced by the liquid and vapor, the weight of material in the vapor phase, the volume in the meniscus, air buoyancy of the weights, and the compressibility of the fluorocarbon. The last was estimated from the relationship

$$\left(\frac{\partial E}{\partial V}\right)_T = n\,\frac{\Delta E_v}{V} \cong T\,\frac{\alpha}{\beta}$$

where ΔE_v is the energy of vaporization, V is the molal volume and α is the thermal coefficient of expansion. The value for n was assumed to be the same as that calculated from the data of Alder, Haycock, Hildebrand and Watts[15] for perfluoro-*n*-heptane. The average deviation of the densities determined in three different dilatometers was ±0.02 mg./cm.^{3}.

The following modifications were introduced for determining the densities of the degassed liquid. The dilatometer was attached to the vacuum system through a ground glass joint and after the appropriate quantity of liquid was condensed into it at Dry Ice temperature, the joint was separated in the flame of a hand torch. Cooling the dilatometer to Dry Ice temperature had no measurable lasting effect on

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(8) Complete details of the procedure are reported by C. J. Murphy, M.S. Thesis, University of Maine, 1954.

(9) R. B. Scott, "The Calibration of Thermocouples at Low Temperatures" in "Temperature, Its Measurement and Control in Science and Industry," Reinhold Publ. Corp., New York, N. Y., 1941.

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(11) B. J. Mair, A. R. Glasgow and F. D. Rossini, *ibid.*, **26**, 2343 (1941).

(12) W. J. Taylor and F. D. Rossini, *ibid.*, **32**, 197 (1944).

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(14) R. D. Dunlap, R. G. Bedford, J. C. Woodbrey and S. D. Furrow, "Liquid-Vapor Equilibria for the System Perfluoro-*n*-hexane–*n*-Hexane (to be published).

(15) B. J. Alder, E. W. Haycock, J. H. Hildebrand and H. Watts, *J. Chem. Phys.*, **22**, 1060 (1954).

its calibration. Corrections were made for the weight of air in the dilatometer before introducing the sample, the displacement of air by the weights, the weight of the vapor, and the volume in the meniscus. The densities are reported at the equilibrium vapor pressure. The average deviation of the densities determined in 5 different dilatometers was ±0.2 mg./cm.^{3}.

Vapor Density.—The vapor densities of perfluoro-*n*-hexane between 50 and 175 mm. at 30° were determined in a gas density balance. It was similar to the one described by Simons, Scheirer and Ritter,[16] but without the automatic features. The buoyant force was determined by measuring the current through Helmholtz coils located above and below a permanent magnet sealed in the balance beam at the fulcrum. The null point was determined by observing through a telescope the image of the fine wire pointer as projected on coördinate paper 15 feet from the balance. With the electrical and optical arrangement used, the balance was capable of determining a change in density smaller than 1×10^{-7} g./ml. This corresponds to a pressure of 0.05 mm. of oxygen or 0.005 mm. of perfluoro-*n*-hexane at 30°. The accuracy and precision was therefore limited by the pressure measurement, which was 0.1% for gases at 100 mm. pressure. The balance was calibrated with extra dry oxygen from the Matheson Chemical Company.

Critical Temperature.—The critical temperature was determined by heating samples enclosed in heavy walled capillary tubes and noting the temperatures at which the meniscus disappeared and reappeared.

Results

Perfluoro-*n*-hexane freezes at −82.26 ± 0.01°. The heat of fusion is 1580 ± 90 cal./mole. It forms coarse transparent needle-like crystals.

Constants for the Antoine vapor pressure equation were determined from the data by the least square method described by Willingham, Taylor, Pignocco and Rossini.[10] The experimental data and equation are shown in Table I. The goodness of fit is ± 0.2 mm. or 0.02°. The normal boiling point calculated from the equation is 57.15 ± 0.02°. The heat of vaporization at the boiling point was calculated by means of the exact Clapeyron equation. A vapor volume of 24.854 liters was calculated from the second virial coefficient. Its value at the boiling point was calculated from the measured value at 30°, by estimating its rate of change with temperature from the Berthelot equation. The calculated heat of vaporization at the boiling point is 6754 cal./mole. The corresponding entropy of vaporization is 20.4 e.u.

TABLE I

VAPOR PRESSURE OF PERFLUORO-*n*-HEXANE

(Standard mm. of Hg)

Temp., °C.	Vapor pressure	$P_{\text{obsd.}} - P_{\text{calcd.}}$
30.06	273.48	0.0
34.89	332.70	.1
39.90	405.99	− .5
44.85	490.61	− .1
47.43	539.81	.0
49.76	587.18	.0
52.31	642.75	− .2
54.28	688.47	− .3
57.40	766.30	− .3

$$\log_{10} P_{\text{mm}} = 6.89190 - \frac{1090.52}{214.73 + t}$$

The densities of air saturated and degassed perfluoro-*n*-hexane are shown in Table II, together with the constants for the equation

$$d_0 = a + bt + ct^2 + dt^3$$

obtained from the data by the method of least squares. The densities of degassed perfluoro-*n*-hexane are 0.0020 g./cm.^{3} higher than those of the air saturated liquid. The effect of dissolved air on the density was not unexpected, as gases are known to be more soluble[17] and have larger partial molal volumes[18] when dissoved in solvents of low internal pressure. If the solubility and partial molal volume of air in perfluoro-*n*-hexane are approximated from the values given by Gjalbaek and Hildebrand[17,18] for nitrogen in perfluoro-*n*-heptane, the estimated effect of dissolved air on the density is in agreement with that observed.

TABLE II

DENSITIES OF PERFLUORO-*n*-HEXANE

Temp., °C.	Air satd. at 1 atm., g./cm.^{3}	Degassed at the equilibrium vapor pressure, g./cm.^{3}
15	1.69943	1.7016
25	1.66970	1.6717
35	1.63901	1.6414
45	1.60752	1.6102

$$d = d_0 + at + bt^2 + ct^3$$

	d_0	$a \times 10^3$	$b \times 10^6$	$c \times 10^8$
(Air satd. 1 atm.)	1.74181	−2.7271	−7.041	2.944
(Degassed at equilibrium v.p.	1.7450	−2.847	−3.324	

A low pressure equation of state for the gas of the form

$$PV = RT(1 + \beta P)$$

describes the behavior of the vapor at 30° between 50 and 175 mm. $\beta_{30°}$ was calculated from the vapor densities and found to be −0.093 ± 0.009 atm.$^{-1}$. The critical temperature is 174.5°. The critical pressure obtained by extrapolating the vapor pressure equation is 16 atm. When these critical constants are used in the Berthelot equation to calculate the gas imperfection

$$\beta_{30°} = 9T_c/128P_cT\left[1 - 6\left(\frac{T_c}{T}\right)^2\right] = -0.077 \text{ atm.}^{-1}$$

For comparison the low pressure gas densities of *n*-hexane were determined in the gas density balance. For this substance, $\beta_{30°} = -0.057 \pm 0.008$ atm.$^{-1}$ The corresponding value from the Berthelot equation for *n*-hexane is −0.062 atm.$^{-1}$.

NOTE ADDED IN PROOF.—Recently Dr. Colin Booth, in Professor Robert L. Scott's laboratory at the University of California at Los Angeles, determined the second virial coefficient for perfluoro-*n*-hexane with a simple Boyle apparatus. His value of −2264 ± 60 cm.^{3}/mole at 30° confirms the large deviation from the ideal gas law (−2313 cm.^{3}/mole) reported above.

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