in qualitative agreement with Fontell's subsequent observation[21] that the calorimetrically determined enthalpy of a 50 mole per cent. solution prepared by crystallization from water is 222 cal. per mole compared with a value of 232 cal. for the fused preparation.

TABLE II

HEATS OF FORMATION OF KBr-KCl SOLID SOLUTIONS

Mole fraction KBr	ΔH_f(cal.-mole^{-1} solid solution)				
	This study eq. 2	Fontell[a]	Durham and Hawkins	Hovi	Wallace
0.17	112	141	130	145	
.34	179	217	196	207	
.50	199	232	208	219	450
.66	179	201	179	201	
.83	112	121	107	134	

[a] Calculated from the equation fitted to Fontell's data by Wallace and Fineman, *Soc. Sci. Fennica Commentationes Phys.-Math.*, 14, No. 6, 1 (1948).

The lower enthalpy values obtained in this investigation are also in agreement with the calculations of Durham and Hawkins[22] who suggested that in the stable state the ions of the alkali halide solid solutions are displaced from their normal lattice sites to positions of minimum potential energy with respect to each other. The heats of formation obtained by them from calculated lattice energies are also listed in Table II, where they are seen to be lower than the calorimetric values though slightly higher than the values calculated from Fig. 3. These latter values, though subject to the previously mentioned assumptions, do indicate that the solid solutions obtained in this investigation are more nearly in a state of thermodynamic equilibrium at room temperature than those used by Fontell.[20] Presumably the ions of this solid solution can readily assume the positions of minimum potential energy characteristic of room temperature only if the lattice is built up isothermally by crystallization from a suitable solvent, and they persist in a structure of higher energy if cooled from the molten state to room temperature.

Independently of Durham and Hawkins, Wasastjerna and Hovi[23-25] have suggested that the solid solution lattice is characterized not only by the geometrical displacements of the ions but by a certain degree of local order. Hovi's calculated enthalpies[25] are also listed in Table II. Calculations by Wallace,[26] based upon the Born-Mayer model, but assuming no ionic displacements, lead to enthalpies considerably higher than the calorimetric data.

Acknowledgment.—The authors gratefully acknowledge the support given to this investigation by the Rutgers University Research Council.

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[21] N. Fontell, V. Hovi and A. Mikkola, *Ann. Acad. Sci. Fennica, Math.-Phys. Ser. A*, **54**, 1 (1949).

[22] G. S. Durham and J. A. Hawkins, *J. Chem. Phys.*, **19**, 149 (1951).

[23] J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **13**, No. 5, 1 (1946).

[24] J. A. Wasastjerna, *ibid.*, **15**, No. 3, 1 (1949).

[25] V. Hovi, *ibid.*, **15**, No. 12, 1 (1950).

[26] W. E. Wallace, *J. Chem. Phys.*, **17**, 1095 (1949).

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

Thermodynamic Properties and *P-V-T* Relations of Chlorotrifluoroethylene[1]

BY GEORGE D. OLIVER, J. W. GRISARD AND C. W. CUNNINGHAM

Thermal measurements made on chlorotrifluoroethylene include heat capacity from 16°K. to the boiling point, 244.80°K., and a heat of fusion, 1327.1 ± 1.3 cal./mole, at the triple point, 115.00 ± 0.05°K. Vapor pressure measurements which covered the temperature range of −67 to −11° and pressure range up to two atmospheres are represented by $\log_{10} P_{\text{mm}} = 6.90199 - 850.649/(t + 239.91)$. Bubble point pressures from 25° to the t_c are represented by $\log_{10} P_{\text{mm}} \times 7.75412 - 1392.82/(t + 319.70)$. The calculated heat of vaporization is 4965 cal./mole at the boiling point, −28.36 ± 0.05°. Entropy values calculated for the liquid and and ideal gas state at the boiling point are 52.74 ± 0.10 and 73.18 cal./deg. mole, respectively. Pressure-volume-temperature relations were measured at five isotherms between 25° and the critical point. The experimental critical constants are: t_c 105.8°; p_c 40.1 atm.; d_c 0.55 g./ml.

Introduction

Chlorotrifluoroethylene may be polymerized to form liquid polymers and a plastic known as Fluorothene.[2] The work of Gabbard and co-workers on the physical properties of the liquid polymers has been summarized and published.[3] Fluorothene has the usual properties attributed to plastics as well as the additional advantage of resisting attack by acids and other corrosive materials. In order to better understand the starting material for these plastics, some of the thermodynamic properties of the pure monomer have been investigated.

Experimental

Material.—The samples investigated were taken from a ten pound cylinder of material prepared at the K-25 Plant by dechlorinating Freon-113 with zinc in alcohol solution. In order to reduce the rate of polymerization, it has been refrigerated at −75° since preparation. In an attempt to obtain the best sample, the cylinder was placed in a Dry Ice-bath before and during transfer of the sample to apparatus, and the top vapors were pumped off each time before a vapor sample was taken. The material used for low temperature studies had a purity of 99.84 mole %, and since identical procedures were followed to obtain the other samples it is reasonable to assume a similar value for their purity.

Apparatus.—Since the vapor pressure of chlorotrifluoroethylene is about 5000 mm. at room temperature, a stronger calorimeter was needed. Therefore, a copper calorimeter of the previously described design,[4] except a wall thickness

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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] J. D. Gibson, *et al.*, *Ind. Eng. Chem.*, **42**, 2314 (1950).

[3] W. H. Reysen and J. D. Gibson, *ibid.*, **42**, 2468 (1950).

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

of 0.4 mm. and convex end plates of 0.8 mm. thickness, was constructed. The low temperature adiabatic cryostat has been fully described elsewhere,[4] consequently only a brief description of apparatus and procedure follows. About 0.55 mole of the material was sealed in the calorimeter and set up in the calorimetric system. 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 temperature with a platinum resistance thermometer which had been certified by the National Bureau of Standards. 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 five 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 the National Bureau of Standards served as a potential reference. Time measurements were made with an electric stop-clock which was frequently checked against a calibrated stop-watch. 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% are the same as previously reported.[4]

The vapor pressure measurements below two atmospheres were made on a single sample with the boiling point apparatus described in another publication.[5]

Measurements were not made below −67° because equilibrium temperatures were not attainable with the present cooling system.

Pressure–volume–temperature measurements were made with an apparatus and procedure similar to those described by Kay.[6] Briefly, the chief components of the apparatus consisted of a heavy-walled capillary tube in which the sample was confined over mercury, an injector for applying pressure to the mercury, a dead weight piston gage for pressure measurements, a glass column used as a vapor bath in which the capillary and contents were held at a constant temperature, and an appropriate pressure regulating system for the vapor-bath. The vapor-bath temperatures were measured with a calibrated double copper–constantan thermocouple through a type K-2 potentiometer. A Gaertner M 1908 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. It was necessary to use five different chlorotrifluoroethylene samples for these measurements because of its ability to polymerize under experimental conditions.

Results and Discussion

Thermal Data.—The melting point was determined by the usual method of melting various fractions of the sample and measuring their equilibrium temperatures.[4] These equilibrium temperatures together with the respective percentages melted are given in Table I. On the assumption that Raoult's law is obeyed, the experimental data of Table I were used in the expression,[7] $N_X = K\Delta T$, to calculate a mole per cent. impurity of 0.16 ± 0.03 for the sample.

Table I

Melting Point Summary

0°C. = 273.16°K.

Melted, %	29.9	47.4	64.9	94.8
$T_{\text{obsd.}}$, °K.	114.882	114.928	114.950	114.962

Triple point. 115.00 ± 0.05°K. $N_X = 0.0505\Delta T$

Impurity = 0.16 ± 0.03 mole per cent.

Heat capacity measurements were made on chlorotrifluoroethylene from 16°K. to the boiling point, 244.80°K. For sake of space economy, only the data at integral temperatures, read from a smooth curve through the experimental points are listed in Table II. The temperature rise, ΔT, for an individual run varied from 2 at 16°K. to 10° at the higher temperatures. Heat capacity data over most of the temperature range of the liquid state were corrected for vapor saturation by using the calculated heat of vaporization, and the liquid density data of Miller.[8] The experimental values for the three heat of fusion measurements were 1326.4, 1327.0 and 1327.9, giving a mean value ΔH_f = 1327.1 ± 1.3 cal./mole.

Table II

Molal Heat Capacity Values at Integral Temperatures

Molecular weight 116.477, 0°C. = 273.16°K.

T, °K.	$C_{\text{satd.}}$, cal./deg.	T, °K.	$C_{\text{satd.}}$, cal./deg.
Crystals		95	15.45
16	3.09	100	15.95[a]
18	3.76	110	16.97[a]
20	4.38	115.00	17.48[b]
25	5.84	Liquid	
30	7.11	115.00	27.15[b]
35	8.18	120	27.11
40	9.10	130	27.03
45	9.88	140	26.97
50	10.57	150	26.98
55	11.23	160	27.09
60	11.83	170	27.23
65	12.38	180	27.39
70	12.89	190	27.61
75	13.41	200	27.87
80	13.92	220	28.47
85	14.43	240	29.11
90	14.94	244.80	29.26[b]

[a] Corrected for premelting. [b] Extrapolated.

Vapor Pressure.—The vapor pressure of chlorotrifluoroethylene was measured from −67 to −11° by the boiling point method. Observed temperature and pressure data, listed in Table III, were fitted to an Antoine equation by a method of least squares[9] to obtain equation (1).

Table III

Vapor Pressure

$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$	$t_{\text{obsd.}}$, °C.	$P_{\text{obsd.}}$, mm.	$P_{\text{obsd.}} - P_{\text{calcd.}}$
−66.82	97.24	0.03	−28.36	760.62	0.44
−52.46	231.17	− .11	−26.47	825.21	− .17
−44.57	352.35	− .33	−23.05	953.71	− .07
−40.74	427.87	.27	−19.00	1126.4	.50
−36.97	513.42	.08	−15.61	1287.3	.30
−33.12	614.50	.0	−10.87	1540.7	−1.4
−30.29	698.40	.12			

$$\log_{10} P_{\text{mm}} = 6.90199 - 850.649/(t + 239.91) \quad (1)$$

A statistical treatment[4] of the experimental data

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[5] G. D. Oliver and J. W. Grisard, This Journal, **73**, 5722 (1951).

[6] W. B. Kay, *ibid.*, **69**, 1273 (1947).

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

[8] W. T. Miller, "The Use of Perfluoro and Chloroperfluoroolefins in the Synthesis of Fluorocarbon Materials," Columbia University, SAM Laboratories, Manhattan Project Report No. M-3113, (MDDC-1177), 1946.

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

gave 95% confidence limits on the temperature that ranged from ±0.02 to ±0.04°. Deviations of the data from equation (1) are given in columns 3 and 6 of Table III. Vapor pressure data measured on this compound by Booth and Swinehart[10] over a limited temperature range varied from the present data by 1 to 2%. Also, their boiling point was 0.5° higher which indicated higher impurity content.

A value for the heat of vaporization at the boiling point was calculated from the above vapor pressure data, vapor volume, and liquid density[8] by means of the exact Clapeyron equation. The critical constants, given below, were used in Berthelot's equation to calculate the vapor volume. The calculated heat of vaporization is 4965 cal./mole at the boiling point, 244.80 ± 0.05°K.

Bubble point pressures taken from $P-V-T$ measurements of Table V represent the vapor pressure over the temperature range 25° to the critical point 105.8°. These data were treated statistically the same as the above vapor pressure data and are represented by the Antoine equation

$$\log_{10} P_{\text{mm}} = 7.75412 - 1392.82/(t + 319.70) \quad (2)$$

Ninety-five per cent. confidence limits on the temperature range from ±0.1 to ±0.2°, and experimental pressure measurements deviate from equation 2 by an average of ±0.3% and a maximum of 0.6% of the pressure.

Entropy.—The calculation of the entropy by the usual method of graphical integration is summarized in Table IV.

TABLE IV

SUMMARY OF MOLAL ENTROPY DATA

	Cal./deg.
$S_{16°}$ (Debye, 5° freedom, θ = 88.30)	1.29
$\Delta S_{16-115°}$ solid, graphical	19.050
$\Delta S_{115°}$ fusion, 1327.1/115.00	11.540
$\Delta S_{115-244.80°}$ liquid, graphical	20.853
Entropy of liquid at 244.80°K.	52.74 ± 0.10
$\Delta S_{244.80°}$ vaporization, 4965/244.80°	20.28
$\Delta S_{244.80°}$ gas imperfection	0.16
Entropy of ideal gas at normal b.p.	73.18

The Berthelot equation

$$S_{\text{ideal}} = S_{\text{exp.}} + \frac{27}{32} \cdot \frac{RT_c{}^3}{P_cT^3}$$

was utilized in correcting for gas imperfection and calculating the entropy of the ideal gas at the boiling point.

Pressure-Volume-Temperature Relations.—The results of volumetric measurements for five isotherms between 25° and the critical point are listed in Table V. A plot of these data, Fig. 1, shows more clearly the relation between the bubble point and dew point pressures with increasing temperature. In determining the isotherms at 75° and lower, the volumes were diminished then expanded and the corresponding pressures were measured.

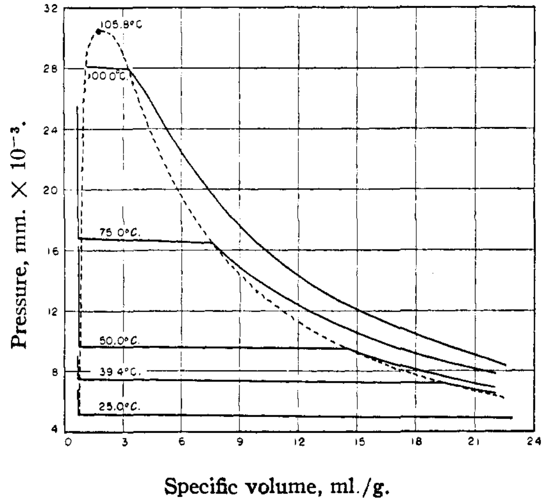

Fig. 1.—Pressure-volume-temperature relation of chlorotrifluoroethylene.

The data at 100° were obtained by expanding a fresh sample (d) from the bubble point. Pressure drop between the bubble and dew points increased with time and was more pronounced for isotherms at 75° and above than for the lower ones. Because the thermal history of each sample influenced its measurements considerably the quality of these data does not meet the usual standards, but does indicate that any measurements made at room temperature or higher will be similarly affected by polymerization of the compound.

The critical measurements on sample (e) in Table V are considered to be the best as this sample was introduced into the tube and the critical measurements only were made as quickly as possible. Critical temperature and pressure values obtained on the other samples are listed in Table V for comparison. These values may be compared with a p_c of 39.0 atm. and t_c of 107.0° determined by Booth and Swinehart.[10] The critical density was deter-

TABLE V

PRESSURE-VOLUME-TEMPERATURE RELATION OF CHLOROTRIFLUOROETHYLENE

Upper figure is pressure in standard mm., the lower figure is specific volume in ml./g.; a, b, c, d and e indicate the sample used for the measurements.

25.0°	35939b	24520b	13863b	5148c	5165b	5142c	5084c	5022b	5022c	4989b	4988c	4960c	4931c	
	0.767	0.769	0.771	0.781	0.788	0.815	3.723	4.993	8.330	9.526	12.179	17.970	21.788	
39.4°	7516c	7507c	7351c	7313c	7235c	7080c	7036c	6890c	6826c	6777c	6726c	6640c	6627c	6602c
	0.810	0.844	7.490	12.413	17.294	19.725	19.972	20.591	20.835	21.029	21.226	21.573	21.624	21.721
50.0°	35945b	9737c	9676b	9625c	9525b	9503b	9524c	9434c	9456c	9440c	9245c	8113c	7635c	7076c
	0.822	0.850	0.853	4.273	5.102	9.444	10.217	13.662	14.640	14.646	15.136	18.041	19.487	21.441
75.0°	36409b	24528b	16828b	16873c	16769c	16606b	16521b	16425c	16402c	14456b	13826c	11601c	9692c	7998c
	0.909	0.933	0.959	0.962	2.075	4.306	7.457	7.744	7.770	9.348	10.309	13.187	16.616	21.452
100.0°	28161d	28132d	28066d	28048d	27983d	27256d	14291d	9054d	6558d	5054d				
	1.227	1.288	1.943	2.883	3.348	3.812	12.034	21.078	29.966	38.812				
Pc	30451a	30613b	30757c	30456d	30451e									
tc	106.63	106.78	106.27	106.56	105.83									

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[10] H. S. Booth and C. F. Swinehart, THIS JOURNAL, 57, 1337 (1935).

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.

(2) J. H. Simons, *Chem. Eng.*, **57**, 129 (1950).

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

(4) S. Blumkin, N. C. Orrick, J. W. Grisard and J. D. Gibson, "Purification of Hexadecafluoroheptane," presented at A.C.S. Meeting, Chicago, Illinois, September, 1950; to be published.

(5) W. Swietoslawski, "Ebulliometric Measurements," Reinhold Publishing Corp., New York, N. Y., 1945.

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

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