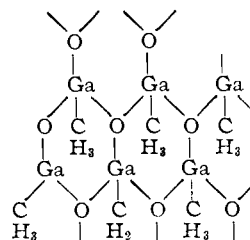


formed by the reaction of methyl groups with adjacent hydrogens in the hydroxyl groups. This however appears to be ruled out by the non-volatile, inert and glassy nature of the residue. Instead, the decomposition may well involve intermolecular condensation, with the splitting out of methane and the production of highly cross-linked chains in the glass or of an endless gallium-oxygen puckered sheet framework with one methyl group attached to each gallium.

Construction of a model of such a high polymeric sheet molecule indicates that the methyl groups would be attached alternately on either side of the



sheet to produce two hydrocarbon surfaces sandwiching the puckered gallium-oxygen framework.

As a result of this investigation it is seen that dimethylgallium hydroxide behaves quite differently from the organo monohydroxy compounds of boron and silicon which condense very readily with the splitting out of water. Cyclic boron-oxygen and silicon-oxygen frameworks are obtained by the intermolecular splitting out of water from diol molecules.

ITHACA, N. Y.

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Dielectric Constants of Liquid Chlorine Trifluoride and Iodine Pentafluoride¹

BY MAX T. ROGERS, H. BRADFORD THOMPSON AND JOHN L. SPEIRS

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The dielectric constants of chlorine trifluoride and iodine pentafluoride have been measured in the range 0 to 42° at several frequencies and may be expressed by the equations $\epsilon_t = 4.754 - 0.018t$, for chlorine trifluoride, and $\epsilon_t = 41.09 - 0.198t$, for iodine pentafluoride. The results indicate that these substances are associated in the liquid state.

Introduction

Considerable interest has arisen concerning the solvent properties of halogen fluorides, and it has been proposed that some of them may be associated liquids.^{2,3} In the present study the dielectric constants of chlorine trifluoride and iodine pentafluoride have been determined and the results have been considered with respect to liquid structure.

Experimental

Electrical Apparatus.—Determination of dielectric constants was carried out using a General Radio Twin-T impedance bridge with a stable signal generator and a communications receiver. Due to the high specific conductance (approximately 2×10^{-6} ohm⁻¹ cm.⁻¹) of iodine pentafluoride, it was necessary to extend the conductance range of the instrument to achieve a balance. This was accomplished by addition of a 400 μ mf. variable capacitor in parallel with the conductance balance capacitor. As the dielectric constant is obtained from the susceptance, rather than the conductance, of the sample, the readings of this capacitor were not used in the calculations described below. Frequencies were measured using a calibrated BC 221-O frequency meter.

Cells.—Two different cells were used, both of which were arranged to plug directly into the sockets of the Twin-T bridge, thus minimizing the distributed capacitance and inductance of the leads. Internally the cells were of nickel construction and the electrical insulation of the central electrode, as well as the vacuum sealing of the lead, were accomplished by a Teflon bearing and packing gland.

The larger cell, used for chlorine trifluoride, was arranged to permit use of a variety of central electrodes to obtain various replaceable capacitances reproducibly. The outer electrode was a hollow cylinder with removable end plates ground to seal against the vertical portion of the cylinder. The upper end of the central nickel electrode was centered in the Teflon bearing and the lower end was provided with a shaft which was carried through the Teflon stuffing box. The whole assembly was held together by a three piece outer aluminum jacket which was provided with ducts for circulation of water from a constant temperature bath. The smaller cell, used for iodine pentafluoride, was of particularly simple construction (Fig. 1). Both cells differ from conventional cell construction practice in that the outer grounded cylinder is also the container for the liquid; this reduces the volume of liquid required for a measurement and simplifies temperature regulation.

The cells were calibrated using benzene, chlorobenzene, nitrobenzene and water as standards. The larger cell had a replaceable capacitance of 143.5 μ mf. and a series inductance of 0.045 μ henries, while these constants for the smaller cell were 10.32 μ mf. and 0.02 μ henries, respectively.

Materials.—Chlorine trifluoride was purified by taking the center cuts of two successive simple distillations at room temperature. The cell was then evacuated and filled with the liquid, and a pressure of approximately two atmospheres (inert gas) was applied to cause the liquid chlorine trifluoride to fill all voids. Measurements were carried out on three different samples, with results agreeing within the limits reported. The low specific conductance of the chlorine trifluoride used, $<6 \times 10^{-9}$ ohm⁻¹ cm.⁻¹, indicated the absence of conducting impurities, such as hydrogen fluoride, which might cause sizable errors due to its high molecular dipole moment.

The purification of iodine pentafluoride is described elsewhere.¹ Analysis of the freezing curve of the material used indicated that the total molal concentration of impurities was approximately 0.0025.

Treatment of Experimental Data.—An equivalent circuit for the experimental cell is represented by the combination

(1) Physical Properties of the Halogen Fluorides. II. For preceding paper see M. T. Rogers, J. L. Speirs, H. B. Thompson, and M. B. Panish, *THIS JOURNAL*, **76**, 4843 (1954).

(2) K. Schafer and E. Wicke, *Z. Elektrochem.*, **52**, 205 (1948).

(3) E. A. Jones, T. F. Parkinson and R. B. Murray, *J. Chem. Phys.*, **17**, 501 (1949).

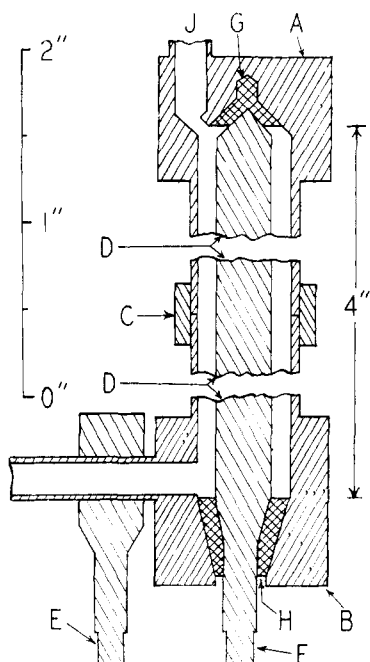


Fig. 1.—Section view of small cell: A, B, outer nickel cylinder; C, sleeve soldered while compressing Teflon; D, inner nickel cylinder; E, F, plugs to bridge; G, H, Teflon insulating spacers; I, J, inlet and outlet tubes (valves not shown).

of an inductance L_u , in series with the parallel arrangement of a cell capacitance C_u , and cell conductance G_u . The latter are associated, respectively, with the dielectric constant and specific conductance of the cell contents, while L_u represents a series inductance associated with the cell proper and with the leads to the bridge. The susceptive portion B_x of the admittance of this system at frequency ω is

$$B_x = \omega C_x = \frac{\omega C_u - \omega^3 L_u C_u^2 - \omega L_u G_u^2}{(1 - \omega^2 L_u C_u)^2 + \omega^2 L_u^2 G_u^2}$$

Thus the apparent capacitance C_x of the cell, as measured on the bridge, is a complex function of G_u and L_u as well as C_u . Fortunately, in the present investigation the specific conductances of the liquids employed were quite low, and terms containing this quantity were in all cases less than one one-thousandth the size of the associated terms in the equation above. Thus this equation could be reduced to

$$\frac{1}{C_x} \cong \frac{1}{C_u} - \omega^2 L_u$$

By determining C_x at two or more frequencies and plotting its reciprocal against ω^2 , a straight line with slope $-L_u$ and intercept $1/C_u$ is obtained.

Results

Chlorine trifluoride was studied at 1 and 10 megacycles in the temperature range 0 to 25°; the results were found to fit the expression

$$\epsilon_t = 4.754 - 0.0187t$$

to within ± 0.02 where t is the temperature in °C.

Iodine pentafluoride was studied at 3, 5, 10, 15, 20 and 25 megacycles in the temperature range 12 to 42°; the results fit the expression

$$\epsilon_t = 41.09 - 0.198t$$

to within ± 0.1 .

For many non-associated liquids, the electric dipole moment may be calculated from the dielectric

constant ϵ , the refractive index n , and the density d , by the Onsager equation⁴

$$\mu^2 = \frac{M}{d} \times \frac{9kT}{4\pi N} \frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2}$$

The deviation of the moment calculated from this equation from that obtained in the vapor state may provide information as to the complexity of molecular species in the liquid.⁵

As experimental refractive indices for iodine pentafluoride and chlorine trifluoride for use in the Onsager equation were not available, these data were estimated from the atomic refractions of the constituent elements. The atomic refraction of fluorine in molecules of this type was calculated from refractive indices of bromine trifluoride and bromine pentafluoride.⁶

TABLE I

CALCULATION OF APPARENT DIPOLE MOMENTS IN LIQUID CHLORINE TRIFLUORIDE AND IODINE PENTAFLUORIDE

Compound	t , °C.	n^2	ϵ	d , g. ml. ⁻¹	μ (Onsager)
ClF ₃	0.0	1.77	4.75	1.897 ⁸	1.00
	25.0	1.76	4.29	1.81	1.03
IF ₅	12.0	2.20	38.7	3.24 ⁹	3.69
	25.0	2.20	36.2	3.19	3.67
	40.0	2.21	33.2	3.13	3.62

The dipole moment of chlorine trifluoride calculated from the dielectric constant of the liquid using the Onsager equation (Table I) is almost twice the vapor-state moment found by Magnuson,¹⁰ 0.554 D . While moments obtained from Onsager's equation may be in error for a number of reasons, discrepancies as large as that for chlorine trifluoride are generally found only for associated liquids such as water or alcohols. Thus association of chlorine trifluoride in the liquid phase seems indicated.

No experimental dipole moment is available for comparison with the calculated moment for iodine pentafluoride. However, the moment of a single I-F bond should be approximately 1.5 D , since the difference between Pauling's electronegativities¹¹ for these two elements is 1.5. For an octahedral structure with one corner unoccupied and the iodine at the body center, the moment would thus be approximately 1.5, while for a tetragonal pyramidal structure a smaller moment would be expected. For the once-proposed trigonal bipyramid configuration, a zero moment would, of course, be expected. Thus it appears that the dipole moment from the Onsager equation (Table I) is much larger than the moment expected for any molecular structure thus far proposed for iodine pentafluoride.

(4) C. F. J. Böttcher, "Theory of Electric Polarisation," Elsevier Publishing Co., Amsterdam, 1952.

(5) J. N. Wilson, *Chem. Revs.*, **25**, 377 (1939).

(6) L. Stein and R. C. Vogel, ANL-4941, Argonne National Laboratories, Chicago, 1953; *Nuc. Sci. Abstracts*, **7**, 238 (1953).

(7) O. Ruff and H. Krug, *Z. anorg. allgem. Chem.*, **190**, 270 (1930).

(8) "Fluorine Chemistry," J. H. Simons, Ed., Academic Press, Inc., New York, N. Y., 1950, p. 192.

(9) O. Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **214**, 91 (1933).

(10) D. W. Magnuson, *J. Chem. Phys.*, **20**, 229 (1952).

(11) L. Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940.

Iodine pentafluoride is therefore probably an associated liquid.¹²

(12) NOTE ADDED IN PROOF.—The electric moment of iodine pentafluoride in the vapor phase has been determined in this laboratory and the value 2.24 ± 0.1 debye found: M. T. Rogers, R. D. Pruet and J. L. Speirs, unpublished results. The refractive indices and molar refractions of chlorine trifluoride and iodine pentafluoride have been measured in the vapor phase in this laboratory: M. T. Rogers, J. G. Malik and J. L. Speirs, unpublished results. From the known liquid

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densities, the squares of the refractive indices n^2 are then estimated to be 1.761 and 2.126 for liquid chlorine trifluoride and iodine pentafluoride, respectively. These observations do not alter the argument presented in this article.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Iodine Pentafluoride, Freezing and Boiling Point, Heat of Vaporization and Vapor Pressure-Temperature Relations¹

BY MAX T. ROGERS, JOHN L. SPEIRS, H. BRADFORD THOMPSON AND MORTON B. PANISH

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The freezing point of pure iodine pentafluoride is $9.43 \pm 0.01^\circ$ and the vapor pressure is given as a function of temperature by the equation $\log p(\text{mm.}) = 8.6591 - 2159.0/T$. The calculated boiling point is 100.5° and the heat of vaporization is 9.88 kcal./mole.

Introduction

As a part of an investigation of the physical properties of several halogen fluorides, we have redetermined the freezing point and the vapor pressure-temperature relations of purified iodine pentafluoride. No reports of these properties have appeared since the original paper of Ruff and Braidia.² Their pioneering work was handicapped by the lack of suitably resistant materials for the construction of apparatus. The availability of fluorinated plastics now permits the preparation and preservation of material of higher purity. Apparatus used in the present work was therefore specially constructed, largely from Fluorothene and Teflon.³

The earlier value of the freezing point of iodine pentafluoride, 9.6° , given by Ruff and Braidia, was obtained on material having an implied purity between 99.2 and 99.9%. The method and limits of error were not stated. In Table I our freezing point results are given for a number of samples of varying degrees of purity as determined from their freezing curves by the method of White.⁴ These samples were prepared and measured using several different techniques over an extended period of time. Based on the samples of higher purity, we report $9.43 \pm 0.01^\circ$ as our most reliable value for the freezing point of pure iodine pentafluoride.

The values given by Ruff and Braidia for the vapor pressure of iodine pentafluoride as a function of temperature are essentially confirmed by our results, although the latter show considerably better internal consistency over the measured range of approximately 30 to 140 mm. pressure. The Ruff and Braidia data for the range from 15 to 70 mm. pressure may be expressed in the form (recalculated)

$$\log p(\text{mm.}) = 8.82 - 2205/T$$

with an approximate uncertainty of ± 2 mm. A

(1) Physical Properties of the Halogen Fluorides. I.

(2) O. Ruff and A. Braidia, *Z. anorg. allgem. Chem.*, **220**, 43 (1933).

(3) Trademark of E. I. du Pont de Nemours and Co., Inc.

(4) W. P. White, *J. Phys. Chem.*, **24**, 393 (1920); C. R. Witschonke, *Anal. Chem.*, **24**, 350 (1952).

calculated value of the boiling point from this expression would be 97.8° rather than the value of $98.5 \pm 1.5^\circ$ given by Ruff and Braidia. Their calculated value of the heat of vaporization is 9.02 kcal./mole. Our result, in equation form, for the vapor pressure-temperature relationship of pure iodine pentafluoride in the range from 30 to 150 mm. pressure is

$$\log p(\text{mm. at } 0^\circ) = 8.6591 - 2159.0/T$$

The equation is based on measurements at thirteen different pressures and the r.m.s. deviation of calculated from experimental values was 0.15 mm. Our calculated value of the heat of vaporization is 9.88 kcal./mole. The calculated boiling point is 100.5° , an extrapolated value which is suggested as a more accurate substitute for the original Ruff and Braidia value.

TABLE I

Sample	$t_f, ^\circ\text{C.}$	$t_x, ^\circ\text{C.}$	m_i	$t_0, ^\circ\text{C.}$
A	9.398	9.376	0.0025	9.420
B	9.408	9.386	.0025	9.430
C	9.336	9.245	.0086	9.427

^a t_f , extrapolated freezing point of original sample; t_x , temperature of half-frozen sample; m_i , the molal concentration of impurity in the original sample; t_0 , freezing point of pure solvent calculated by method of Witschonke.⁴

Experimental

Purification of Material.—Commercially available iodine pentafluoride (General Chemical Co.) was pretreated at room temperature to remove dissolved iodine by agitating with a mixture of dry air and chlorine trifluoride (Harshaw Chemical Co.) in a Fluorothene beaker using a magnetic stirrer. The mixture, containing a considerable quantity of chlorine trifluoride and some non-volatile impurities, was transferred to the pot of the fractionating column and the more volatile impurities were pumped off as the pressure fell below 40 mm. Considerable chlorine trifluoride was evolved as the pot and jacket were heated to raise the pressure to 40 mm. Even after flooding the column and operating under total reflux for as long as two hours it was found advisable to discard at least the first 10% of the product as it still contained demonstrable traces of chlorine trifluoride.

The distilled product was colorless indicating the absence of colored metallic salts. The presence of iodine in even small traces is apparent as a distinct coloration, passing