TABLE II.	PHYSICAL] DIH	UORO- Boiling Point, °C.		
Dibromopropanes	Boiling Poi Predicted			
$CF_1CBr_2CH_3$ $CF_1CH_2CHBr_2$ $CF_1CHBrCH_2Br$	$\begin{array}{r} 88.1\\112\\116.6\end{array}$	111 115.8	CF3CCl2CH3 CF2CH2CHCl2, CF3CHClCH2Cl	$\substack{\textbf{48.1}\\\textbf{72}\\\textbf{76.6}}$

by a preponderance of the monobromide in the reaction product and only small amounts of polybromides.

1,1,1-Trifluoropropane (2.60 moles) was bubbled into liquid bromine at the rate of 0.227 mole per hour, a total of 0.87 mole of bromine being vaporized. The temperature of the bromine was maintained between 35° and 40° C. The mixed vapors were passed through the reactor at a temperature of $450\,^{\circ}\mathrm{C.}$; the contact time was about 20 seconds. Upon rectification the brominated product was found to contain CF₃CHBrCH₃ (0.22 mole), CF₃- CH_2CH_2Br (0.38 mole), and $CF_3CH_2CHBr_2$ (0.20 mole).

Although it was shown that substitutive chlorination of CF₃- CH_2CH_3 occurs almost exclusively on the omega carbon atom(?), considerable bromination occurs also on the middle carbon atom. Identity of the bromofluoropropanes was established by fluorine and bromine analyses, boiling point analogy, and molar refractivity. There are three possible dibromo-1,1,1-trifluoropropanes obtainable by bromination of $CF_3CH_2CH_3$ without rearrangement: CF₃CHBrCH₂Br, CF₃CBr₂CH₃, and CF₃CH₂CHBr₂. As Table II shows, $CF_3CBr_2CH_3$ would boil about 25° C. lower than the dibromotrifluoropropane (111° C.) obtained in this reaction. Consequently it was excluded from further consideration. 2,3-Dibromo-1,1,1-trifluoropropane was prepared by adding bromine to $CF_3CH=CH_2$ obtained by dehydrochlorination of CF_3 -CH₂CH₂Cl. The physical properties of CF₃CHBrCH₂Br obtained thus are different from those of the dibromo compound obtained by thermal bromination of CF₃CH₂CH₃ (Table I). Therefore the dibromo-1,1,1-trifluoropropane was assigned the formula CF₃CH₂CHBr₂.

1-Chloro-1,1-difluoropropane (1.37 moles) was bubbled through liquid bromine at 25° C. over an 11-hour period. The mixed vapors passed through the reactor at 500° C. Rectification of purified products gave CClF₂CHBrCH₃, CClF₂CH₂CH₂Br, and unreacted CClF2CH2CH3. A residue of 17 grams was not identified. The yields of CClF2CHBrCH3 and CClF2CH2CH2Br were 3% and 12%, respectively.

 $\label{eq:constraint} 2\text{-}Bromo\text{-}1\text{-}chloro\text{-}1\text{,}1\text{-}diffuoropropane \ (CClF_2CHBrCH_3) \ was$ also prepared by the fluorination of CBrCl₂CHBrCH₃ with hydrogen fluoride and mercuric oxide. For example, a 750-ml. nickel-lined autoclave was charged with $CBrCl_2CHBrCH_3$ (0.83 mole), hydrogen fluoride (7.5 moles), and mercuric oxide (1.5 moles) in the manner previously reported (δ). The autoclave was then sealed and heated at $88\,^\circ$ C. for 72 hours. Rectification of the products gave a 9.6% yield of $CF_3CHBrCH_5$ and a 5.0% yield of CClF₂CHBrCH₃.

2-Chloro-1,1,1-trifluoropropane (0.34 mole) was bubbled through liquid bromine at 45-50° C. The mixed vapors were passed at a uniform rate through a 120-cm, reactor of 12-mm. Pyrex tubing during a 2-hour period. Products were collected under ice water, separated, and dried. Rectification showed that the product contained 0.045 mole of unreacted CF3CHClCH3 and 0.057 mole of CF₃CBrClCH₃. No CF₃CHClCH₂Br was isolated from the product.

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ABSTRACTED from a doctoral thesis of W. G. Toland, Jr., submitted to the faculty of Purdue University.

Preparation and properties of SULFUR HEXAFLUORIDE

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LTHOUGH the chemical inertness and thermal stability of certain nonmetal fluorides, such as sulfur hexafluoride, carbon tetrafluoride, and nitrogen trifluoride, have been known for many years, practical applications of these substances have been slow in developing. Thus in 1900 the discoverers of sulfur hexafluoride, Moissan and Lebeau (6), described it as a colorless. tasteless, incombustible gas, with an inertness resembling nitrogen, unchanged even at the softening temperature of hard glass and unaffected by water or caustic potash. Some of its physical constants were reported by them and were later somewhat modified by Prideaux (8) and by Schumb and Gamble (9). The excellent properties of this gas, as well as Freon 12 (CCl_2F_2) for high voltage insulation were observed by the General Electric Company some years ago (2), as well as in the high voltage laboratory of this institute, where the gas was employed in tests as an insulating medium for an electrostatic generator with applied potentials as high as 5.6 million volts direct current across the gap $% \left({{{\mathbf{x}}_{i}}} \right)$ between terminal and tank (1).

In order to be able to carry out larger scale tests with larger generators than were employed in these earlier tests, some 1500 pounds of sulfur hexafluoride were prepared for the high voltage project in 1942 by the Hooker Electrochemical Company by the method described below; with a procedure worked out in this laboratory, approximately 150 pounds more of the substance were prepared and stored as liquid in steel cylinders.

PREPARATION OF SULFUR HEXAFLUORIDE

The method employed in the laboratory consisted of burning coarsely crushed roll (lump) sulfur in a current of fluorine gas in a steel box, provided with staggered horizontal shelves, each bearing about 8 pounds of sulfur. The top of the box was securely bolted down and provided with an asbestos gasket to make it gastight. (The method employed at the Hooker Electrochemical Company was to burn molten sulfur, contained in a horizontal steel pipe, in a stream of fluorine.) The fluorine passed in a cir-

	Reference				Referenc
VAPOR PRESSURE Solid: $\log_{10} P_{mm.} = 8.736 - \frac{1224.8}{T}$	(ϑ)	Density Gas Soli	:: 5.106 (air = 1) at : id: 2.51 at m.p. (-50°	20.0° C., 753.5 mm. ' C.)	$(g) \\ (5)$
logie $P_{\rm min.} = 8.7648 - \frac{1231.3}{T}$	(14)	Lio	$2.683 \text{ at} - 195^{\circ} \text{ C}.$ $2.74 \text{ at} - 273^{\circ} \text{ C}.$ (wid: $1.787 \text{ at} - 39^{\circ} \text{ C}$	estd.)	· (8)
Liquid: log. $P_{mm.} = 7.705 - \frac{995.6}{T}$ (over a	(9)	шq	1.819 at -45° C. 1.91 at -50° C.		0.77
small range of temp.) Liquid at 25° C. = 330 lb./sq. in. (total)	Preston	Expansion Co Expansion on	DEFFICIENT IN INTERVAL 8 Melting, 36%	-18.5° to 30° C., 0.027	(8) (5)
Melting Point $-50.8^{\circ} \pm 0.2^{\circ}$ C. -50.8° C. $-50^{\circ} \pm 0.5^{\circ}$ C	$(9) \\ (14) \\ (5)$	HEAT CAPACIT	$\begin{array}{c} Cp, \\ Temp., \\ Cal. \end{array}$	Cp, Temp., Cal/	(3)
SUBLIMATION TEMPERATURE -63.7° C. -63.5° C.	(9) (5) (1)		° K. (Mole)(° K.) 13 2.68	° K, (Mole) (° K. 95 13.63)
CRITICAL TEMPERATURE 54°C. HEAT OF FUSION 1390 cal. 1100 cal.	(14) (8) (14) (5)		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
HEAT OF VAPORIZATION 4500 cal. at b.p. HEAT OF SUBLIMATION 5640 cal. 5570 cal.	(5) (14) (5)		$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccc} 130 & 16.20 \\ 140 & 17.06 \\ 150 & 17.96 \\ 160 & 18.95 \end{array}$	
TROUTON'S CONSTANT 22 FREE ENERGY OF FORMATION (GAS) -235,000 cal. at 25° C	(?) (13)		$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccc} 100 & 20.11 \\ 180 & 21.43 \\ 180 & 21.43 \\ \end{array}$	
HEAT OF FORMATION (GAS) 262,000 cal. at 25° C., constant pressure	(14)		$\begin{array}{cccc} 60 & 12.51 \\ 65 & 12.94 \\ 70 & 13.39 \end{array}$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	
SURFACE LENSION AT B.P. 13.78 dynes/cm.	$\langle i \rangle$		75 13.90	220 44.	
MEAN DIELECTRIC COEFFICIENT AND POLARIZATION $E_{0-1}^{25} E_0^{25} E_0^{-50} P^{25}$ 2049 2026 2018 16.51	(12, 13)		80 14.49 85 15.22 90 16.15 94.3 Transition point	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	
DIELECTRIC DEVIATION Pmm. at 0° C. 708 704 590 457 369 216 13 Dielectric deviation 1.91 1.90 1.58 1.23 0.98 0.37 0.3	(4) 31 34	Entropy at 2 Index of Ref Atomic Dista	98° K. 69.6 cal./ TRACTION $nD = 1.0$ INCE, S-F 1.58 Å.	^{7°} K. 00783 at 0° C., 760 mm.	$(14) \\ (11) \\ (14) \\ (14)$

TABLE I. PROPERTIES OF SULFUR HEXAFLUORIDE

cuitous path over the shelves in succession, entering at the top shelf. The sulfur ignited and produced a crude gas consisting largely of SF_6 but also some hydrogen fluoride (with possibly some oxygen or oxygen fluoride) from the generator, some air, which may not have been completely excluded from the system, and variable quantities of other, lower fluorides of sulfur, such as S₂F₂, SF₄, and S_2F_{10} . Some of these lower fluorides are quite poisonous and corrosive and, until purified, the gas mixture THE remarkable properties of sulfur hexafluoride, SF6, for high voltage insulation has awakened the general interest in the production of this gas, especially since the availability of industrial fluorine, required for its largescale preparation, seems now to be assured. The combustion of sulfur in fluorine gas leads to a mixture containing principally SF6, together with some lower fluorides of sulfur, such as S_2F_2 , SF_4 , and S_2F_{10} ; some air, oxygen, or oxygen fluoride (OF₂), and hydrogen fluoride from the fluorine generator (10). Pyrolysis of S_2F_{10} , thorough washing and alkali scrubbing, drying, and condensation of the gas is followed by transfer to steel cylinders, in which the liquid is stored under about 300-350 pounds gage pressure. Production of over 1600 pounds of SF_6 by this process in 1942 is described. A brief summary of the chief physical properties of this gas is included.

ide on glass wool. The remaining step was the transfer of the gas to steel cylinders in which it could be stored as liquid. (The gage pressure of these cylinders was about 300 to 350 pounds per square inch at ordinary room temperature.) This transfer was accomplished in one of two ways. A steel compressor was used in one case to bring the gas between 100 and 200 pounds pressure, and, following the compressor, a cooler chilled the gas sufficiently to liquefy it; the liquid was run into the steel cylinder, which was

must be secured against leakage into the air.

Purification of the crude gas coming from the sulfur burner was carried out in an all-metal apparatus until it was safe to use glass. The gas mixture was first passed through a Monel or nickel tube heated electrically to about 400° C. in order to pyrolyze the S_2F_{10} into SF_4 and SF_6 . The efficiency of this process had been previously checked by independent experiments. Then the gas passed through copper tubing to the bottom of a packed copper tower (filled with pieces of copper scrap). A spray of water was passed down through the tower and left at the bottom through an S-shaped exit tube. The gas leaving the top of the scrubber passed next to the bottom of a steel column packed with pieces of carbon (or scrap iron or other suitable material), through which a spray of 1 N sodium hydroxide was continuously circulated by means of a small motor-driven, circulatory pump; the latter raised the alkali solution from a supply carboy, situated below the tower, up to the top of the alkali tower. Hydrolyzable fluorides, such as S_2F_2 and SF_4 , together with hydrogen fluoride, were largely removed, leaving SF₆, moisture, and some air to pass on.

The gas next passed through a drying tower containing solid caustic soda (or other suitable material) and then through similar absorbers filled with porous barium oxide or phosphorus pentox-

of a type provided with an inlet and an outlet, so that air or other permanent gases could be vented from the cylinder as the liquid entered. Other portions of the gas were collected in 20-liter glass carboys by displacement of a solution of caustic soda and were later transferred to the steel storage cylinders, as follows: The gas in the carboy was displaced with water, dried thoroughly, and condensed to the solid state by cooling to -78° C. in a roomy Pyrex trap. The trap containing the solid was now connected by a ground joint to a metal system for transferring the gas to steel storage cylinders. This apparatus consisted of a high vacuum line through which the SFs trap, cooled by liquid nitrogen, was pumped down to remove air or other inert gases. The vacuum line was also connected by metal tubing to a metal trap and from that to the storage cylinder, which was also provided with a pressure gage. The metal trap could be shut off from the glass portions of the apparatus by means of a valve. When the vacuum line and the steel cylinder had been well pumped out, the metal trap was cooled with liquid nitrogen, and the SF6 from the glass trap was condensed in it. When the metal trap was then allowed to warm up and the valves properly adjusted, the SF₆ was driven over into the storage cylinder. After the addition of SF_6 in this way had raised the tank pressure to about 300-350 pounds, liquefaction of the gas began within the cylinder, and thereafter a con-

The conversion of fluorine into SF_6 by the above process yielded not less than 87% of the amount theoretically possible.

PROPERTIES OF SULFUR HEXAFLUORIDE

Table I summarizes some of the properties of SF_6 as found in the literature, together with data obtained in this laboratory. The total gage pressure (measured by F. S. Preston) shown by liquid SF6 contained in steel cylinders was 180 pounds at 0° C. and 330 pounds at 25° C.

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Vapor pressure of HYDROFLUORIC ACID SOLUTIONS

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THE partial pressures of hydrogen fluoride and water vapor over solutions of hydrofluoric acid containing 2 to 30% hydrogen fluoride were determined by a dynamic method at 25°, 40°, 60°, and 75° C. The results, which are more consistent than previously published data, are

TUDY of the recovery of fluorine from gases containing small percentages of hydrogen fluoride required data on the partial vapor pressures of hydrogen fluoride and water over solutions of hydrofluoric acid. It was expected that the concentration of the solutions of recovered fluorine would not exceed 20% hydrogen fluoride and that the solutions would not be heated to more than 75° C.

Khaidukov, Linetskaya, and Bognovarov (7) reported measurements of vapor pressures of hydrogen fluoride and water over hydrofluoric acid solutions containing 5 to 39% hydrogen fluoride at several temperatures from 25° to 75° C. Their data do not extend

as far as was desired into the range of dilute solutions, and the large increments in concentration make interpolations uncertain. Moreover, the data are somewhat inconsistent among themselves and are markedly inconsistent with values that Fredenhagen and Wellmann (4) reported for dilute solutions at 25° C. A bulletin recently issued by the General Chemical Company (5) includes a chart of the partial pressure of hydrogen fluoride $over \, hydrofluoric \, acid \, solutions.$ This chart does not extend into the range of low concentrations of acid at room temperature, and the increments in concentration are large. No



expressed by empirical equations that fit the data within the limits of experimental error. The heats of vaporization of hydrogen fluoride and of water from the solutions were calculated, and the results agree with values given in the literature.

data are presented with the chart, nor is a description given of the method by which the plotted values were obtained.

The present paper gives measured partial pressures for the components of hydrofluoric acid solutions containing 2 to 30% hydrogen fluoride at 25°, 40°, 60°, and 75° C. Empirical equations for relating partial pressures to liquid composition are also presented.

MATERIALS AND APPARATUS

Reagent grade hydrofluoric acid was twice distilled over po-tassium fluoride (θ) in a platinum still. The distillate contained about 35% hydrogen fluoride and was shown by colorimetric

methods to be free from silica. The purified acid was diluted with freshly boiled distilled water for use in the vapor pressure measurements.

The apparatus was designed for measurement of the vapor pressures by a dynamic method; an inert carrier gas is saturated with the vapor of the experimental solution and is then analyzed. The errors commonly encountered in the method are due to incomplete saturation of the carrier gas or to entrainment of the solution in the carrier gas. Many investigators attempted to minimize these errors by passing the gas slowly over the surface of the liquid in a long tube. Thistechnique is tedious, however, because of the slowness with which equilibrium is established between the static liquid and the gas.