[Contribution from the Morley Chemical Laboratory of Western Reserve University]

The Fluorochlorosilanes[1]

By Harold Simmons Booth and Carl F. Swinehart

For some time past this Laboratory has been engaged in studying the fluorochlorides of carbon and had several times confirmed the rule of Swarts[2] that among the fluorochlorides of carbon there is an almost exact additivity of boiling point differences with the substitution of fluorine for chlorine.[3] It was thought that this rule should hold for other gaseous fluorochlorides. The fact that no fluorochlorides of silicon analogous to those of carbon had been reported in the literature suggested at once the possibility of their preparation by the reaction of silicon tetrachloride with antimony trifluoride and a catalyst similar to the preparation of the carbon fluorochlorides by Swarts.[4] Furthermore, no reference was found showing that any inorganic halides had been partially and progressively fluorinated by this reaction despite the lapse of forty years since the discovery of the reaction by Swarts.[4] Investigations in this Laboratory have now shown that this is a general reaction of nonpolar halides.[5] When the study of the fluorochlorosilanes was practically completed Schumb and Gamble[6] announced the preparation of trifluoromonochlorosilane and difluorodichlorosilane by the explosion of hexafluorodisilane (Si_2F_6) in chlorine. However, because of the small and uncertain yields and the difficulty of obtaining their starting material, Si_2F_6, our method of preparation has many advantages.

Preparation and Purification of Gases

The apparatus for preparing and purifying the gases was of all glass construction, and was changed during the course of the work to meet the requirements of the various gases. Since silicon tetrafluoride was a product of the reaction, some distillations were carried out under pressures of 2 to 4 atmospheres using pressure manometers similar to those employed by Germann and Booth.[7]

For the separation of these complex gas mixtures an efficient and easily constructed distilling column A (Fig. 1) was devised in which pressures up to 8 atmospheres could be used. This consisted of a vertical tube in which was a close-fitting spiral of No. 18 copper wire wound about a glass core. The tube was thermally insulated by a vacuum jacket made from an all-glass Pyrex condenser, silvered with the exception of a clear strip for observing the rate of reflux in the column. The lagged container (B) held a refrigerant such as carbon dioxide–ether mixture, melting chloroform, melting carbon tetrachloride or ice, which condensed the gas in the vertical tube, causing it to descend the spiral, wetting the entire surface, and restricting the rising gas to a spiral path. The liquid from the bottom of the column was returned directly to the boiling liquid by the dripper (C). Since the temperature was maintained constant by the refrigerant, the purity of the gas leaving the column was indicated by the constancy of the pressure.

Since it was found that most of the gases studied hardened the rubber in ordinary stopcock grease, there was developed a special lubricant which consisted of lanolin, beeswax, and white vaseline melted together and treated with silicon tetrachloride. The volatile components were then removed by heating *in vacuo*. This lubricant was used successfully throughout the apparatus for the preparation and purification of gases, except in the analysis tubes where chlorides were avoided.

Methods of Preparation

The silicon tetrachloride was purified by fractional distillation to a constant boiling point (±0.05°) and the antimony trifluoride was sublimed. The reaction between these in the presence of antimony pentachloride yielded the fluorochlorosilanes in varying amounts. Antimony trifluoride and silicon tetrachloride did not react unless some pentavalent antimony was present as a catalyst.

Three modifications of the method of preparation were investigated. (Method I.) Silicon tetrachloride (50 cc.) was added dropwise to a warmed mixture of antimony trifluoride (200 g.) and antimony pentachloride (50 cc.). The reaction product was one-third silicon tetrafluoride containing some hydrogen chloride and the remainder chiefly monofluorotrichlorosilane. (Method II.) Pressure reactions carried out in a manner similar to that described by Booth, Mong and Burchfield[3a] yielded principally silicon tetrafluoride. (Method III.) The best method consisted of mixing the antimony trifluoride with an *excess* of silicon tetrachloride and then adding the catalyst slowly. To accomplish this, 600 g. of distilled silicon tetrachloride and 200 g. of sublimed antimony trifluoride were placed in a three-necked flask equipped with a stirrer and a safety manometer. Through a second opening the catalyst was slowly added. From the third neck the gas produced in the reaction passed up through two reflux condensers, the first cooled by an ice and salt mixture, and the second by liquid ammonia. The gas was condensed in two spiral

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[1] From a portion of a thesis submitted by Carl F. Swinehart in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry, Western Reserve University, June, 1933.

[2] F. Swarts, *Bull. soc. chim.*, **35**, 1557 (1924).

[3] (a) Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932); (b) Booth and Bixby, *ibid.*, **24**, 637 (1932); (c) Booth, Burchfield, Bixby and McKelvey, This Journal, **55**, 2231 (1933).

[4] F. Swarts, *Acad. Roy. de Belgique*, **24**, 309 and 474 (1892).

[5] (a) Booth and Swinehart, This Journal, **54**, 4750, 4751 (1932); (b) Booth and Bozarth, *ibid.*, **55**, 3890 (1933); (c) Booth and Stillwell, *ibid.*, **56**, 1531 (1934).

[6] W. C. Schumb and E. L. Gamble, *ibid.*, **54**, 3943 (1932).

[7] Germann and Booth, *J. Phys. Chem.*, **21**, 92 (1917).

traps in a solid carbon dioxide–ether mixture, followed by two traps in liquid air. In this reaction vigorous stirring was essential for without it the product was chiefly silicon tetrafluoride since the antimony trifluoride remained at the bottom of the flask, giving little chance for the product to escape before it was completely fluorinated. Stirring slowed the reaction, allowed the escape of the partially fluorinated compounds and prevented local over-heating. Although chlorine gas, when added as a catalyst, gave better control of the reaction, it was carried along with the gases evolved and was not completely removed from them after repeatedly passing through mercury, sodium amalgam or titanium trichloride. On the other hand, with antimony pentachloride as the catalyst, a very clear product was obtained which did not smut the mercury.

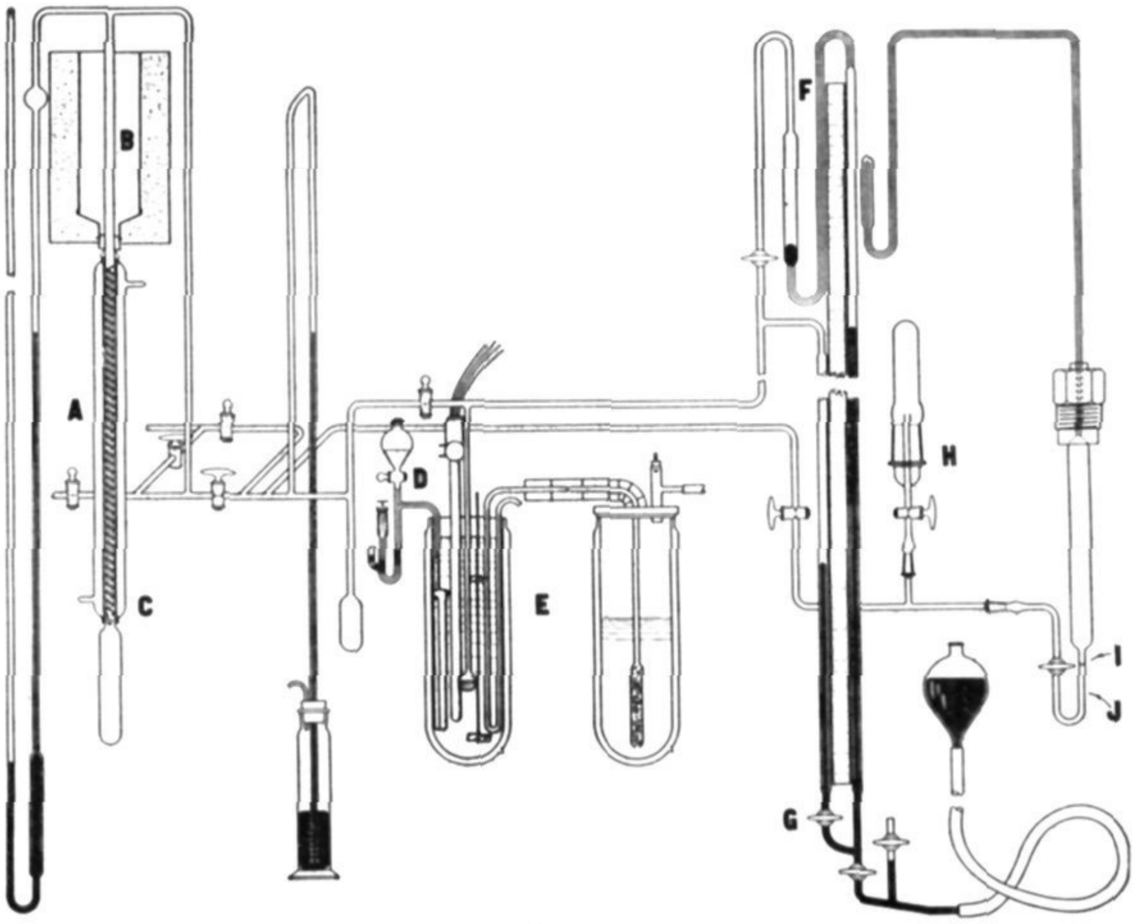

Fig. 1.

If uncontrolled, the rate of gas evolution periodically increased to a maximum, and then almost stopped. However, this rate was controlled by cooling the reaction flask, resulting in a greater yield of the chlorofluorides.

An unexpected phenomenon was observed with these reaction products. If the crude product was completely liquefied under pressure, cooled with solid carbon dioxide–ether mixture and allowed to settle, five immiscible liquid layers were seen. Fortunately, upon warming slightly the liquids became miscible, so that at the temperatures at which the distillations were carried out, the sample was homogeneous and could be separated.

Successive fractionations were carried out in the column until four fractions were obtained which distilled without change in pressure when the temperature was maintained constant in the condenser (B) (Fig. 1) by a refrigerant. The four gaseous products corresponded to (1) silicon tetrafluoride (with some impurity, possibly hydrogen chloride), (2) trifluoromonochlorosilane, (3) difluorodichlorosilane, and (4) monofluorotrichlorosilane. These gases are readily hydrolyzed in moist air, yielding products which are nauseating and very irritating to the respiratory tract. In this investigation about six kilos of silicon tetrachloride was used, and it is estimated that this yielded in all the different preparations 75 liters of (2), 100 liters of (3) and 200 liters of (4).

In order to ensure pure samples for determining the physical constants, each of these compounds was further purified by repeated fractional distillation in the column after the apparatus had been cleaned and rebuilt.

Analysis and Identification of Gases

Fractionation of the products of the reaction yielded four pure gases, as shown by the constancy of their melting points, vapor pressures and critical temperatures. One fraction was identified as silicon tetrafluoride by its physical constants. The other gases each gave qualitative tests for fluorine, chlorine and silicon, and their boiling points agreed with those predicted from the boiling points of silicon tetrachloride and silicon tetrafluoride. The physical constants of two of these, as will be shown later, correspond with those given by Schumb and Gamble[6] for trifluoromonochlorosilane and difluorodichlorosilane.

Molecular weight determinations and analyses showed the intermediate compounds to be trifluoromonochlorosilane, difluorodichlorosilane, and monofluorotrichlorosilane (this last has not been previously described).

The molecular weights were calculated from the observed gas density and the critical constants[8] using Berthelot's equation.

The densities of the first two gases were determined at 0° and that of the third at 24.8°, as this one boiled at 12.2°.

TABLE I

WEIGHT OF NORMAL LITER AND MOLECULAR WEIGHTS

Gas	Wt. of 1 liter at N. T. P.	Mol. wt. (Berthelot)	Mol. wt. (Theoretical)
SiF_3Cl	5.4550	120.38	120.52
	5.4547	120.37	
SiF_2Cl_2	6.2784	136.95	136.97
	6.2728	136.91	
$SiFCl_3$	6.4923 (24.8°)	153.34	153.43
	6.5190 (24.8°)	153.97	
	6.5025 (24.8°)	153.58	

The analysis of these gases was accomplished by decomposing the sample by either of two methods. (1) The

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(8) Booth and Swinehart, THIS JOURNAL, **57**, 1337 (1935).

gas was weighed in a tared tube (H) (Fig. 1) condensed to a solid in the bottom and alcoholic potassium hydroxide admitted. After warming slowly and shaking to effect solution of the sample, ether was added in order to extract gas dissolved in the lubricant in the stopcock and conical joint. (2) The monofluorotrichlorosilane was weighed in a small tube and absorbed in standard alkali using an apparatus similar to that described by Booth and Stillwell.[5c]

Chlorine was determined by the Volhard method using sufficient ferric iron to exceed that required to form the colorless complex ferric fluoride and taking the faintest permanent coloration as the end-point. These modifications were closely checked in the standardization of the silver nitrate solution. The percentage of chlorine found in the gases is shown in Table II.

TABLE II

ANALYSIS OF GASES

Gas	Method of decomposition	Wt. of sample	% Chlorine	Theoretical % Cl
$SiClF_3$	1	0.4268	29.62	29.42
	1	.4011	29.47	
$SiCl_2F_2$	1	.4925	51.57	51.77
	1	.4283	51.58	
	1	.5303	51.55	
$SiCl_3F$	1	.2822	69.22	69.33
	1	.3068	69.35	
	2	$^1/_5$(.9526)	69.15	
	2	$^1/_5$(.9950)	68.92	

Silicon was determined by the hydrolysis in boiling water of potassium fluosilicate which was prepared by acidifying with hydrofluoric acid and rendering insoluble by adding alcohol. For $SiCl_3F$, the average of four determinations was 18.31% (theoretical 18.29).

Physical Properties

Melting Points (triple points).—The melting points of the fluorochlorosilanes under their own vapor pressures were determined from cooling curves recorded on a special high speed Leeds and Northrup recording potentiometer. The temperature was measured by a three-junction thermocouple in a slender thin-walled glass tube placed in the sample. The sample was automatically stirred while being slowly cooled. The first formation of crystals was simultaneous with a sharp break in the cooling curve.

The melting points observed were:

	t, °C.
$SiFCl_3$	-120.8 ± 0.1
SiF_2Cl_2	-139.7 ± 0.1
SiF_3Cl	-142.0 ± 0.1

Boiling Points from Vapor Pressure Measurements.—The static method of measuring vapor pressures was used throughout this work. The apparatus consisted of a thermostat (E), Fig. 1, controlled by a thermoregulator which was filled with petroleum ether, the amount of which could be varied. This regulator operated an electromagnetic valve[9] which governed the flow of liquid air into the cooling coil. Temperatures were measured by a platinum resistance thermometer. The pressure was shown by a special U manometer having a vacuum on one side, which was established by a trap (F) after the manner of the Germann barometer.[10]

One of the criticisms of the static method has been failure to establish equilibrium. However, in this work the attainment of equilibrium was shown when upon closing and later reopening stopcock (G), the mercury levels remained the same. Also by closing (G) the mercury level could be fixed for accurate measurement. That the sample was air-free and pure was confirmed when a portion of the gas was removed without a resulting change of vapor pressure at constant temperature.

The vapor pressures and boiling points of the fluorochlorosilanes are shown in Table III.

TABLE III

VAPOR PRESSURES

Press., mm.	t, °C.	Press., mm.	t, °C.	Press., mm.	t, °C.
Trifluoromonochlorosilane		Difluorodichlorosilane		Monofluorotrichlorosilane	
324	−85.3	280.4	−53.23	116	−30.5
449	−79.5	253.1	−55.14	164	−23.5
577	−75.0	479.1	−42.6	309	−10.0
739	−70.5	746	−32.45	474.1	0.0
(760)	(−70.0)	746	−32.45[b]	474.1	0.0[a]
825	−68.4	(760)	(−32.2)	606.1	6.6
956	−65.7	780.9	−31.35	622.5	7.4
955	−65.6[a]	974.1	−26.22	699.2	10.4
				736.6	11.2
				760	12.2
				765.5	12.4
				769.4	13.0
				838.7	15.3

[a] One-half of sample removed by distillation.

[b] Three-fourths of sample removed by distillation.

Discussion of Results

The application of the Swarts reaction to nonpolar inorganic halides has made possible the direct preparation of many new mixed halides containing fluorine, as in the case of the fluorochlorosilanes. The generalization of this reaction, which in the past has only been used for carbon halides, leads to some indications as to its mechanism.

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(9) For details of this device, see Booth and Swinehart, THIS JOURNAL, **57**, 1337 (1935).

(10) A. F. O. Germann, *ibid.*, **36**, 2456 (1914).

TABLE IV

SUMMARY OF PHYSICAL DATA

Compound	M. p., °C.	B. p., °C.	Diff. in b. p.	Vapor pressure eqn., log P mm. =
SiF_4[a]	−90 (1318 mm.)	−95.7 (760)		
SiF_3Cl	−142 ± 0.1	−70.0 ± 0.1	25.7	7.4563 − 929.3/T
(S. and G.) (5)	(−144 ± 2)	(−70.0 ± .2)		(7.6440 − 967.16/T)
SiF_2Cl_2	−139.7 ± 0.1	−32.2 ± .1	37.8	7.4247 − 1095/T
(S. and G.) (5)	(−138 ± 2)	(−31.7 ± .2)		(7.4832 − 1111.1/T)
$SiFCl_3$	−120.8 ± 0.1	12.2 ± .1	44.4	7.3530 − 1278/T
$SiCl_4$	−70	57.57	45.4	

[a] W. I. Patnode and J. Papish, *J. Phys. Chem.*, **34**, 1494 (1930); O. Ruff and E. Ascher, *Z. anorg. allgem. Chem.*, **196**, 413 (1931).

Under comparable fluorinating conditions the reactions of SbF_3, in the presence of pentavalent antimony, upon various non-polar halides now appear to fall into three distinct classes:

Class I. Non-polar halides which are covalently unsaturated.

Examples: $SiCl_4$, $SiHCl_3$, $GeCl_4$, PCl_3, $SOCl_2$, etc.

Class II. Non-polar halides which are covalently saturated.

Examples: CCl_4, $CHCl_3$, C_2Cl_6 and most poly-halogenated chemically saturated carbon compounds, and SO_2Cl_2.

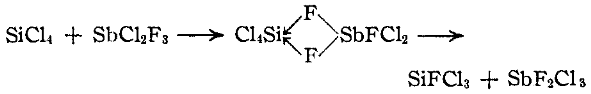
Class III. Non-polar halides not exhibiting reaction with SbF_3 in presence of pentavalent antimony halide.

Examples: CH_3Cl, C_2H_5Cl, etc., C_2Cl_4, C_2H_3Cl, etc., C_6H_5Cl, etc., *i. e.*, organic compounds with only one halogen per carbon atom, and unsaturated halides.

The Swarts reaction with halides of Class I proceeds readily at room temperatures, and the completely fluorinated product is all too readily formed, while with halides of Class II the reaction is slower, proceeds at higher temperature, and the fluorination is incomplete. Even the next to last substitution is difficult or impossible. Apparently, the less the covalent saturation the greater the tendency toward completeness of fluorination.

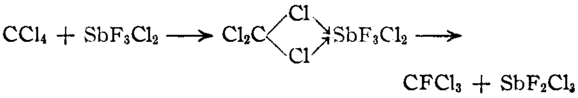
This correlation between covalency and extent of fluorination suggests that the reaction proceeds by the formation of intermediate compounds of two types.

Type A Intermediate Compound.—The halides of Class I may coördinate the fluorine of the antimony compound with an increase of covalency and thus act as acceptors. For example

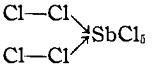


With the substitution of fluorine for chlorine upon the silicon, these coördination compounds should be more easily formed, thus favoring complete fluorination.

Type B Intermediate Compound.—The antimony compound may coördinate two halogens of a compound of Class II with an increase of covalency and thus the antimony compound acts as the acceptor. For example



That this is probable is shown by the quite analogous compound, $SbCl_5{\cdot}2Cl_2$,[11] which can hardly be written in any way save



As the fluorination progresses there is accumulated on the antimony more and more chlorine in direct combination which would undoubtedly make this pentavalent antimony halide react more and more reluctantly to form an intermediate compound of type B, as evidenced by the instability of the corresponding $SbCl_5{\cdot}2Cl_2$.

That this is the mechanism is further substantiated by the fact that in some cases, when fluorination of an organic halide stops, it may be carried further by isolation of the pure chlorofluoride and reaction of it with fresh SbF_3Cl_2.[12]

Furthermore, in a number of cases, it has been found in this Laboratory that an excess of $SbCl_5$ catalyst is detrimental to the progress of the reaction.

The coördination of single chlorine atoms from separate organic molecules is less probable. This may explain the difficulty of forming the group

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(11) Biltz and Jeep, *Z. anorg. Chem.*, **162**, 32 (1927).

(12) From the paper by A. L. Henne, Fluorine Symposium, Cleveland Convention, A. C. S., September 14, 1934.

$-CF_3$ except in the few cases where the chlorine is made reactive by other groups on the carbon.

The compounds of Class III probably do not react (a) because in the case of monochloro compounds they cannot "donate" two chlorine atoms to the SbF_3Cl_2 so as to take the first step toward reaction, *i. e.*, the formation of an intermediate coördination compound, or (b) because in the case of Cl attached to a double-bonded carbon atom (olefins, aryl compounds) the bond strength is so great between the C and the Cl as to preclude the organic halide acting as donor.

As a result of the general application of the Swarts reaction, the large group of new mixed halides which can now be made should be especially suited for the correlation of physical constants and structure. The regularities that may be expected are indicated by the differences in boiling points among the carbon chlorofluorides of a given series (40° for methane derivatives).

For the first two substitution products, the fluorochlorosilanes herein described exhibit a constant difference in boiling point. The deviation for the third and fourth is unexplained, but may be associated with the sublimation of SiF_4 or the peculiar immiscibility at low temperatures. Table IV shows these differences and compares the physical constants determined upon large samples with those obtained by Schumb and Gamble for trifluoromonochlorosilane and difluorodichlorosilane which were prepared in small amounts by the explosive reaction of chlorine and Si_2F_6.

Summary

The fluorination of $SiCl_4$ using sublimed SbF_3 (with $SbCl_5$ as a catalyst) yields $SiFCl_3$, SiF_2Cl_2, SiF_3Cl and some SiF_4. ($SiFCl_3$ has not been previously described.)

A special distillation column which is efficient and easily made was used for the separation and purification of the gases.

Physical properties were accurately measured, and those for SiF_3Cl and SiF_2Cl_2 agreed with the ones reported by Schumb and Gamble.

Two mechanisms for the Swarts reaction were postulated in order to explain the two types of reaction recognized: (I) with those halides which are covalently unsaturated, (II) with those halides which are covalently saturated, and an explanation suggested for a third type which does not react.

It has been shown that the rule of Swarts holds for the first two differences in the boiling points of the fluorochlorosilanes, but not for the last two.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

The Critical Constants and Vapor Pressures at High Pressure of Some Gaseous Fluorides of Group IV[1]

BY HAROLD SIMMONS BOOTH AND CARL F. SWINEHART

The critical constants of only a few of the large number of gaseous fluorides have been determined and only the more recent of these may be considered reliable. In this investigation it was proposed to carry out these measurements on some of the fluoride gases which for some time have been of interest in this Laboratory.

The critical constants of silicon tetrafluoride given by Moissan[2] were thought to be incorrect considering the value of the molecular weight calculated from the gas density with their aid together with the improved purification obtained by Germann and Booth.[3] An investigation of the literature showed that van Laar[4] had also criticized Moissan's value. He pointed out from the additivity of the atomic values of van der Waals b and $\sqrt{a}$ that the value for the critical temperature (−1.5°) was too high and that the pressure should have been about 33 atmospheres instead of 50 atmospheres.

This discrepancy is also noted in the case of some of the other empirical relations that have been suggested to correlate the critical tempera-

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(1) From a portion of a thesis submitted by Carl F. Swinehart in partial fulfilment of the requirements for the Degree of Doctor of Philosophy in Chemistry, to the Graduate School of Western Reserve University, 1933.

(2) H. Moissan, *Compt. rend.*, **139**, 711 (1904); *Ann. chim. phys.*, [8] **8**, 84 (1906).

(3) A. F. O. Germann and H. S. Booth, *J. Phys. Chem.*, **21**, 81 (1917).

(4) J. J. van Laar, "Zustandsgleichung von Gasen und Flüssigkeiten," Leopold Voss, Leipzig, 1924.