$-CF_3$ 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.

CLEVELAND, OHIO RECEIVED MARCH 27, 1935

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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.

ture with other properties such as boiling point, melting point, molecular weight, number of atoms and valences in the molecule, etc.[5]

Furthermore, it was thought that a study of the critical constants of a closely related group of compounds would be advantageous since the above relationships were of necessity developed for gases of widely different composition. Consequently, the gases studied were limited to the fluorides of the elements of group IV and particularly to the fluorochlorosilanes, the synthesis of which was developed during the course of this work.

## Apparatus

**Cailletet Tube.**—Since the temperatures were all above the freezing point of mercury a U-shaped tube (E) (Fig. 1) was used which allowed the complete compression of the sample. The magnetic stirrer (E) was a glass enclosed iron wire with a small glass rod attached, which held the iron in the top part of the tube, permitted clear vision of most of the sample and provided stirring the entire length of the tube. The glass covering permitted the use of rigorous cleaning methods.

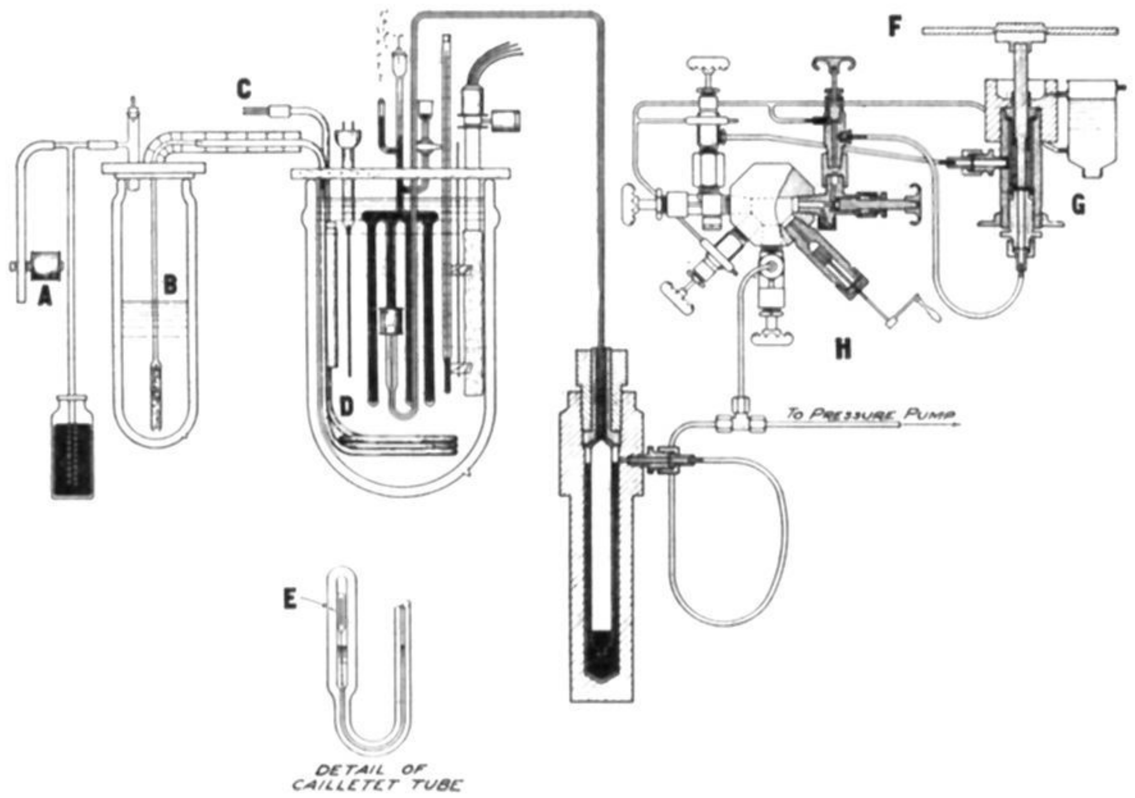

Fig. 1.

**Thermostat and Resistance Thermometer.**—In this work it was extremely important that the thermostat maintain a temperature constant within narrow limits for at least twenty minutes and at the same time retain flexibility in adjustment of the temperature. This thermostat consisted of a 3.7 liter Dewar jar (Fig. 1) having a mercury-filled thermoregulator which actuated the magnetic pinch clamp (A) causing the pressure developed by the boiling in (B) to force the liquid air into the cooling coil (D). The amount added was limited by the constriction (C) in the outlet. In this manner the temperature was maintained constant to ±0.01°. The bath was mechanically stirred and for temperatures above 20° the cooling system was replaced by a Cenco heating element, the metal shield of which had been removed to improve the sensitivity.

The temperature of the thermostat was measured by a shielded platinum resistance thermometer, the windings of which were of the strain-free type, and mounted in a Pyrex glass tube, protected against moisture by a drying tube filled with activated silica gel.

**Dead Weight Manometer.**—The pressure was measured and maintained constant by the dead-weight gage (G) which consisted of a differential piston of a type used widely.[6] This construction permitted the piston to be rigid enough to carry the load without distortion. Also with a suitable arrangement of valves (H) the large area of the piston could be utilized for a low pressure range (below 15 atmospheres) and the buoyancy upon the piston could be maintained constant by appropriate connections to the reservoir. A smooth operating vernier volume control assisted in adjustments.

## Calibration and Manipulation

**Measurement of Temperature and Calibration of the Resistance Thermometer.**—To aid in the setting of the thermoregulator and as a check upon the resistance thermometer, calibrated mercury thermometers reading to 0.1° were used for the range −40 to +100°, and reading to 0.2° for temperatures above 100°. The temperature calculated from the resistance thermometer was taken as the true temperature.

Calibration of the resistance thermometer was made at all of the standard points in the range +100 to −183°.[7] Doubly distilled mercury was used at its freezing point. For the carbon dioxide point, the thermometer was inserted through a stopper into a large tube filled with solid carbon dioxide which was vented to the air through a meter length of small tubing which maintained the partial pressure of the carbon dioxide vapor equal to the atmospheric pressure. The large tube was loosely packed with solid carbon dioxide in a Dewar flask. Calibration at the boiling point of oxygen was made by immersing the thermometer in pure liquid electrolytic oxygen, boiling against atmospheric pressure with an oxygen atmosphere above the surface of the liquid.

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(5) These relations have been recently reviewed: K. M. Watson, *Ind. Eng. Chem.*, **23**, 360 (1931); H. H. Stephenson, *Chem. News*, **143**, 135 (1931).

(6) A. Michels, *Ann. Physik*, **72**, 285 (1923); **73**, 577 (1924); F. G. Keyes and Jane Dewey, Publication from Mass. Inst. Tech., **63**, No. 28; *J. Opt. Soc. Am. and Rev. Sci. Inst.*, **14**, No. 6 (1927); C. H. Meyers and R. S. Jessup, *Bur. Stand. J. Res.*, **6**, 1061 (1931).

(7) "International Critical Tables," McGraw-Hill Book Co., New York, 1926, Vol. I, p. 53.

**Measurement of Piston and Calculation of Pressure.**—The two surfaces of the piston in the dead-weight manometer were shown to be round, concentric and straight to within 0.00002 cm. The diameters at 21° were measured at seven points each, using an optical lever micrometer against standard Johansen thickness gages and found to be 1.59591 and 1.28410 ( ±0.00002) cm. The effective diameters were regarded to be larger by one-half the estimated clearance, but because of the differential construction of the piston this correction was minimized. For comparison

| | Large | Small | Differential |
|---|---|---|---|
| Area effective, sq. cm. | 2.003539 | 1.297609 | 0.705930 |
| Area of piston, sq. cm. | 2.000352 | 1.295054 | .705292 |

The weights used in calibration of the chromium plated machined disks (F) were checked by the Bureau of Standards and weighings were made to 0.01 g.

In calculation of pressures, allowances were made for barometric pressure, temperature, buoyancy upon piston, gravitation and relative mercury and glycerol heights in the apparatus.

Because of the difficulty others have had in balancing the weight upon the gage in connection with this type of apparatus, critical pressure measurements have been rated at ±0.1 atmosphere. However, after the first two gases had been studied it was found that by first observing the movement of the mercury in the capillary of the Cailletet tube, and then for close setting, the relative rise and fall of the two menisci of the *liquefied gas*, as shown in Fig. 1, for at least fifteen minutes, a sensitivity to 0.001 atmosphere was demonstrated. All readings were made thereafter to less than 0.01 atmosphere. In this manner accuracy was obtained without sacrificing the simplicity and flexibility of this apparatus for measurements with small samples.

## Preparation and Purification of Gases

The first three gases studied were obtained pure from other workers in the laboratory and further purified by distillation. The special fractionating column[8] was developed with the second method of preparing silicon tetrafluoride and also used for the fluorochlorosilanes.

**Difluoromonochloromethane**, $CHClF_2$, was obtained from Miss Bixby,[9] who prepared it by the fluorination of chloroform with an antimony trifluoride-antimony pentachloride mixture. At first the gas behaved as if slightly impure, but twelve fractionations gave a sample the critical constants of which were not changed by further fractionations.

**Trifluoromonochloroethylene**, $C_2ClF_3$, which was obtained from McKelvey,[10] was fractionated eleven times for the first sample. Further determinations were not made for the second sample contained air since it was not totally condensable, and no more gas was available.

**Ethyl fluoride**, $C_2H_5F$, was also prepared by McKelvey using the synthesis of Fremy,[11] in which a mixture of potassium bifluoride and diethyl sulfate was heated. The gas was passed through bromine water to remove unsaturates, then over solid potassium hydroxide and barium oxide. The gas obtained was fractionated more than ten times for the first sample, followed by five more for the second.

**Silicon tetrafluoride** was prepared by three methods: (1) Gay-Lussac's reaction of sulfuric acid upon ground calcium fluoride and quartz, (2) the action of sulfuric acid upon sodium fluosilicate and quartz, (3) fluorination of silicon tetrachloride by antimony trifluoride containing 5–10% antimony pentachloride.

(1) Selected crystals of fluorspar and quartz were separately crushed and boiled with acid to remove carbon dioxide and other impurities. The silicon tetrafluoride formed was passed from the generating flask through glass wool and phosphorus pentoxide. The crude gas was contaminated with hydrogen fluoride, a white solid that was carried along in distillation, and sulfur compounds. The rapid attack of the hydrogen fluoride upon the generating flask usually led to its failure and the solid calcium sulfate formed also interfered with complete reaction.

Germann and Booth[3] have shown that silicon tetrafluoride cannot be purified by sublimation. Since one solid phase does not affect the vapor pressure of another, "fractional" sublimation cannot effect a separation of volatile solids. Following the method of Germann and Booth, the gas was liquefied and distilled under 2–4 atmospheres pressure. Because the liquidus range is only 12°, by condensing the gas to a liquid using a solid carbon dioxide–ether mixture slightly cooled by liquid air, rather than freezing with liquid air alone, the time-consuming melting operation was eliminated. After a number of distillations the gas was stored and the apparatus was rebuilt. Fifteen ampoule to ampoule distillations were then made to ensure a pure sample, before filling a Cailletet tube, which had been dried and then rinsed with the pure gas at least ten times to remove residual air. The gas was fractionated two times further before filling each successive Cailletet tube.

(2) The following method developed in this research gave better yields and the gas was more easily purified. Sodium fluosilicate and ground quartz were each freed of carbon dioxide by acid, dried in an oven at 110°, thoroughly mixed and introduced while still warm into the generating flask which was evacuated immediately. When cool, concentrated sulfuric acid was added dropwise, and the temperature gradually brought to about 70°. Upon addition of an excess of sulfuric acid the reacting mass became liquid and the reaction went to completion. This method gave a 95% yield of silicon tetrafluoride. The flask was hardly attacked and was used repeatedly. The product melted to a clear liquid and was apparently free from hydrogen fluoride. About six fractionations as described above and one in the special fractionating column yielded a pure sample. The gas was further fractionated in the column for the second sample.

(3) The silicon tetrafluoride obtained as a by-product in the fluorination of silicon tetrachloride in the preparation of the fluorochlorosilanes[8] was further fractionally distilled, but did not behave as if quite so pure as that prepared by methods (1) and (2). The impurity was probably hydrogen chloride from the hydrolysis of the chloride.

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(8) H. S. Booth and C. F. Swinehart, THIS JOURNAL, **57**, 1333 (1935).

(9) H. S. Booth and E. May Bixby, *Ind. Eng. Chem.*, **24**, 637 (1932).

(10) H. S. Booth, P. E. Burchfield, E. May Bixby, J. B. McKelvey, THIS JOURNAL, **55**, 2231 (1933).

(11) E. Fremy, *Ann.*, **92**, 246 (1854); *Compt. rend.*, **38**, 393 (1854); *Chem. Gazette*, **12**, 138 (1854).

**Trifluoromonochlorosilane,** $SiClF_3$.—The purified gas[8] was further distilled in the column three times before filling the first Cailletet tube and three times more before filling the second.

**Difluorodichlorosilane,** $SiCl_2F_2$.[8] was further purified by fractionally distilling three times in the column for the first sample and twice more for the second sample.

**Monofluorotrichlorosilane,** $SiCl_3F$.[8]—The first sample was obtained by purifying the gas prepared in the first method of reaction, the crude mixture containing almost no other derivatives. The second sample was obtained by distillation of the gas mixture from the third method which yielded all the derivatives.

**Filling of Sample Tube.**—The critical point tube was attached to the apparatus for the purification of gases[8] which was dried by alternately evacuating and filling with carbon dioxide-free dry air about twenty times. After this the tube was rinsed ten times with the pure gas to be studied in order to remove residual air. When filled to a little less than atmospheric pressure, the tube was broken under mercury at (J) (Fig. 1),[8] and transferred with a little cup to the mercury in the pressure well. The inner seal (I)[8] at the bottom of the tube kept bits of broken glass from rising with the mercury and clogging the capillary and also served as a trap for moisture which might travel along the glass–mercury interface. The purity of the gas in the Cailletet tube was judged by several criteria: (a) constant vapor pressure of fractions, (b) fractionating to constant critical temperature and pressure, (c) constancy of the pressure required to hold the sample nearly all vapor or nearly all liquid at the same temperature, (d) retrograde condensation, if observed, would show definitely the presence of more than one component.[12]

## Adjustment to Critical Conditions

The most dependable method of adjusting the pressure, temperature and volume for observation of the critical point was found to be as follows. When the critical point was approached the pressure gage was shut off and the volume of the sample regulated by the threaded plunger until with rising temperature the meniscus disappeared without moving from the center of the tube. The temperature was noted upon the mercury thermometer. Then with the gage connected, the pressure was adjusted at a temperature slightly lower. When these conditions had been maintained for ten to fifteen minutes to assure equilibrium, the temperature was raised slightly and equilibrium was again established. This process was repeated until the highest temperature at which two phases could be seen was found and held constant. If the critical point be approached by this method no opalescence is observed and the flat meniscus will be seen to broaden out at a definite temperature, becoming little more than a striation which completely disappears if the stirrer is moved, and does not reform. This point was taken as the critical point. Although the above process required accurate pressure and thermal control, and was time consuming, it yielded more reproducible results than any of the more rapid methods.[13] The advantage of this improved equilibrium method is that it is unaffected by the thermal lag which is inherent in the heavy-walled construction of the sample tube.

The values of the vapor pressures and critical constants for the various gases studied are represented in Table I. For each gas only those samples are recorded which met the tests for purity, and the values are arranged in order of ascending temperature up to the critical point.

TABLE I

VAPOR PRESSURES AND CRITICAL CONSTANTS

| Sample | t, °C. | P, atm. | Sample | t, °C. | P, atm. |
|---|---|---|---|---|---|
| | | Difluoromonochloromethane | | | |
| A | $22.6^a$ | $9.39^b$ | A | 85.4 | 39.23 |
| A | 31.4 | $11.97^b$ | B | 91.0 | 45.13 |
| B | 31.5 | $12.07^b$ | A | 94.5 | 45.69 |
| B | 40.1 | $14.87^b$ | B | 94.8 | 46.94 |
| A | 41.1 | $15.31^b$ | A | 95.3 | 47.44 |
| A | 50.3 | 19.46 | B | 96.0 | 48.08 |
| A | 60.3 | 24.08 | B | 96.3 | 48.17 |
| B | 64.7 | 25.63 | | Critical point | |
| B | 70.6 | 29.64 | A | 96.4+ | 48.54 |
| A | 71.5 | 30.62 | B | 96.4+ | 48.42 |
| A | 81.1 | 36.13 | Mean | 96.4 | 48.48 |
| B | 81.1 | 35.97 | | ±0.1 | ±0.05 |
| | | Trifluoromonochloroethylene | | | |
| | $21.9^a$ | $5.7^b$ | | 100.8 | 35.1 |
| | 33.8 | $8.0^b$ | | 101.7 | 35.4 |
| | 40.3 | $9.9^b$ | | 104.3 | 37.1 |
| | 60.3 | $15.5^b$ | | Critical point | |
| | 72.3 | 19.1 | | 107.0 closed manometer | |
| | 81.2 | 24.6 | | 107.0 | 39.0 |
| | 91.3 | 28.2 | | ±0.1 | ±0.1 |
| | | Ethyl Fluoride | | | |
| | 25.65 | $9.20^b$ | | 88.22 | 38.36 |
| | 33.45 | $10.86^b$ | | 95.39 | 41.92 |
| | 43.55 | $14.58^b$ | | 100.99 | 48.87 |
| | 51.65 | $17.74^b$ | | 101.79 | 49.48 |
| | 51.65 | 17.80 | | 101.97 | 49.49 |
| | 60.64 | 21.92 | | Critical point | |
| | 69.73 | 26.49 | | 102.16 | 49.62 |
| | 78.58 | 31.79 | | ±0.02 | ±0.05 |
| | | Silicon Tetrafluoride | | | |
| C | −36.16 | $19.02^b$ | A | −14.77 | 35.43 |
| C | −36.19 | 19.04 | A | −14.67 | 36.41 |
| C | −32.92 | 21.01 | B | −14.58 | 36.31 |
| C | −32.22 | 21.14 | C | −14.54 | 36.21 |
| C | −27.21 | 24.98 | C | −14.34 | 36.62 |
| C | −21.16 | 30.02 | A | −14.34 | 36.57 |
| B | −20.07 | 34.72 | C | −14.27 | 36.62 |
| B | −17.42 | 35.50 | | Critical point | |
| A | −16.28 | 34.01 | A | −14.14 | 36.80 |
| A | −15.6 | 34.91 | B | −14.14 | 36.66 |
| C | −15.58 | 35.55 | B | −14.17 | 36.66 |
| B | −15.45 | 35.90 | B | −14.14 | 36.66 |
| B | −15.28 | 36.24 | C | −14.17 | 36.62 |
| B | −15.18 | 36.25 | Mean | −14.15 | 36.66 |
| C | −14.87 | 36.10 | | ±0.02 | ±0.05 |

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[12] Duhem, *J. Phys. Chem.*, **1**, 273 (1897).

[13] S. F. Pickering, Rev. of Lit. relating to Crit. Const., Sci. Papers of Bureau of Stand., No. 541 (1926); Cardoso, *J. chim. phys.*, **10**, 491 (1910).

TABLE I (*Concluded*)

| Sample | t, °C. | P, atm. | Sample | t, °C. | P, atm. |
|---|---|---|---|---|---|
| | | Trifluoromonochlorosilane | | | |
| A | 0.0 | 14.38 | B | 34.34 | 34.08 |
| B | 9.30 | 18.60 | | Critical point | |
| B | 20.24 | 24.44 | A | 34.47 | 34.14 |
| A | 23.40 | 26.33 | A | 34.50 | 34.14 |
| B | 30.96 | 31.32 | B | 34.47 | 34.25 |
| A | 31.03 | 31.44 | B | 34.47 | 34.25 |
| A | 31.47 | 31.72 | Mean | 34.48 | 34.20 |
| A | 31.47 | 31.74 | | ±0.02 | ±0.05 |
| | | Difluorodichlorosilane | | | |
| A | 24.05 | 7.37$^b$ | B | 92.21 | 32.40 |
| A | 34.51 | 9.98$^b$ | A | 93.52 | 33.59 |
| B | 43.25 | 11.21$^b$ | B | 94.48 | 33.58 |
| A | 44.96 | 12.29$^b$ | A | 94.52 | 34.07 |
| A | 55.79 | 15.41$^b$ | B | 95.65 | 34.41 |
| B | 60.57 | 17.33 | B | 95.73 | 34.54 |
| A | 65.34 | 18.89 | | Critical point | |
| A | 72.70 | 21.96 | A | 95.75 | 34.55 |
| A | 80.33 | 25.87 | A | 95.73 | 34.55 |
| B | 81.83 | 26.50 | B | 95.79 | 34.54 |
| B | 86.82 | 29.10 | B | 95.79 | 34.54 |
| A | 89.43 | 30.59 | Mean | 95.77 | 34.54 |
| | | | | ±0.02 | ±0.05 |
| | | Monofluorotrichlorosilane | | | |
| A | 66.45 | 5.41$^b$ | B | 161.41 | 33.34 |
| B | 69.76 | 5.90$^b$ | B | 162.66 | 33.88 |
| A | 89.81 | 9.05$^b$ | A | 163.80 | 34.20 |
| B | 93.64 | 9.94$^b$ | A | 164.11 | 34.40 |
| A | 99.32 | 11.28$^b$ | B | 164.71 | 34.94 |
| A | 115.98 | 15.52$^b$ | B | 164.90 | 35.06 |
| A | 129.23 | 19.34 | | Critical point | |
| A | 145.09 | 25.45 | A | 165.22 | 35.31 |
| B | 147.93 | 25.91 | B | 165.30 | 35.34 |
| A | 157.81 | 31.24 | Mean | 165.26 | 35.33 |
| | | | | ±0.02 | ±0.05 |

[a] For $CHClF_2$ and $C_2ClF_3$ temperatures were measured upon a calibrated PTR mercury thermometer, others by the platinum resistance thermometer. [b] Pressure measured with the large piston. Other measurements made with the differential piston.

For the first two gases, the pressure was adjusted to 0.1 atm., but later, by the method described above, it was found that the pressure could be ascertained to 0.01 atm., giving values of better agreement, thus ±0.05 atm. was chosen arbitrarily as the accuracy of the method.

## Discussion of Results

The disagreement between the critical temperature and pressure of silicon tetrafluoride as given by Moissan and those obtained in this work is quite readily explained by the inadequate purification to which he subjected his gas, as has been stated above. That hydrogen fluoride is the probable impurity giving rise to his high results is shown by two determinations, the data of which are not presented, in which glycerol was accidentally introduced into the sample. Although neither hydrolysis nor etching was evident for a few hours, the gas was liquefied at as high a temperature as +3° by 41 atm. pressure. Further it was found that approximately 0.5% of air introduced into a pure sample lowered the critical temperature 0.6° with but little effect upon the pressure, and made the condensation take place over a range of two atmospheres of pressure.

The behavior of the gases studied under closely controlled equilibrium conditions brought out the following points with regard to the stability of the opalescence at the critical temperature.

1. The critical temperature may be reached and exceeded without observing any opalescence.
2. There is no discontinuity in the time necessary for the two phases to separate between lower temperatures and the critical temperature. This separation of the two phases was observed within 0.05° of the critical temperature only when the most accurate thermal control was obtained.
3. The very slight opalescence that can be induced above the critical temperature by rapid stirring is of short duration when the temperature and pressure are constant.

These observations confirm the opinion of Cardoso[14] and others that the phenomenon of opalescence is due to emulsion of the two phases, owing its stability below the critical temperature to low surface tension and near equality of the densities.

Van Laar[15] has made a very extensive representation of the constants in van der Waals equation, and has directly correlated them with the periodic system and the structure of molecules.

The values of $b_c$ and $\sqrt{a_c}$ were calculated from van Laar's equations from the critical constants measured from silicon tetrafluoride and the fluorochlorosilanes, and compared with those calculated from his tables of additive values. The results are recorded in Table II.

TABLE II

THE VALUES[a] OF $b_c$ AND $\sqrt{a_c}$ FOR SILICON TETRAFLUORIDE AND THE FLUOROCHLOROSILANES

| Gas | $b_c \times 10^5$ Obsd. | $b_c \times 10^5$ Calcd. | $\sqrt{a_c} \times 10^2$ Obsd. | $\sqrt{a_c} \times 10^2$ Calcd. |
|---|---|---|---|---|
| $SiF_4$ | 323.3 | 375 | 10.3 | 11.6 |
| $SiClF_3$ | 411.6 | 435 | 12.6 | 14.1 |
| $SiCl_2F_2$ | 488.8 | 495 | 15.1 | 16.6 |
| $SiCl_3F$ | 567.9 | 555 | 17.7 | 19.1 |

[a] The units are those used by van Laar, vol. 22412 cc $R = 1/273.09$, $P$ in atm.

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(14) Cardoso, *J. chim. phys.*, **10**, 491 (1910).

(15) J. J. van Laar, *ibid.*, **14**, 3 (1916).

The agreements between the observed and calculated $b_c$ and $\sqrt{a_c}$ are reasonably accurate when one considers that the value for chlorine is one of the exceptions to the regularity of the series, and the values for silicon and fluorine are not as well established as some of the others due to the few available determinations of critical values among their compounds.

A further relation among the critical temperatures of the fluorochlorosilane series is as follows

| | $T_c$, °A. obsd. | 1st diff. | 2d diff. | 8d diff. |
|---|---|---|---|---|
| $SiF_4$ | 258.95 | | | |
| | | 48.63 | | |
| $SiF_3Cl$ | 307.58 | | 12.66 | |
| | | | ($3K = 12.6$) | |
| | | 61.29 | | −4.46 |
| | | | | ($K = 4.2$) |
| $SiF_2Cl_2$ | 368.87 | | 8.2 | |
| | | 69.49 | ($2K = 8.4$) | |
| $SiFCl_3$ | 438.36 | | (4.2) | −4.0 |
| | | (73.69) | ($1K = 4.2$) | |
| $SiCl_4$ | (512.05) | | | |
| | 506.7 observed[16] | | | |

Values in parentheses are calculated.

The values of $T_c$ may be low for they observed that continued heating of silicon tetrachloride lowered its critical temperature, probably due to decomposition or reaction with the glass.

It may be pointed out that the value of $n$ in $nK$ in the second difference corresponds to the number of fluorine atoms in the following molecule; and furthermore from the above relation the critical temperature of any one in the series in relation to that of $SiF_4$ is given by the following equations in which $K$ has the same value as before

$$T_{c\,SiF_3Cl} = T_{c\,SiF_4} + 1\,(48.63)$$
$$T_{c\,SiF_2Cl_2} = T_{c\,SiF_4} + 2\,(48.63) + 3K + 0.06$$
$$T_{c\,SiFCl_3} = T_{c\,SiF_4} + 3\,(48.63) + 8K + .11$$
$$T_{c\,SiCl_4}\ (\text{obsd.}) = T_{c\,SiF_4} + 4\,(48.63) + 14K - 5.57$$
$$T_{c\,SiCl_4}\ (\text{calcd.}) = T_{c\,SiF_4} + 4\,(48.63) + 14K - 0.22$$

The fact that the critical temperature of silicon tetrachloride reported in the literature does not agree with the above relations which hold for the observed values of the other gases in this series within the experimental limit, suggests that the value for the critical temperature of $SiCl_4$ is too low. It will be noticed also in these equations that the factor in the second term of the equation is the same as the number of chlorine atoms in the compound.

The above suggests that some fundamental relation between the critical constants exists for the regularities revealed here scarcely seem accidental, though of course they may be fortuitous. It is hoped that the determination of the critical constants of other chlorofluorides now being studied in this Laboratory may reveal the significance of this relation.

## Summary

The critical constants of seven fluoride gases were found to be

| | $CHClF_2$ | $C_2F_3Cl$ | $C_2H_5F$ |
|---|---|---|---|
| $T_c$, °C. | 96.4 ± 0.1 | 107.0 ± 0.1 | 102.16 ± 0.02 |
| $P_c$, atm. | 48.48 ± .05 | 39.0 ± .1 | 49.62 ± .05 |

| | $SiF_4$ | $SiF_3Cl$ |
|---|---|---|
| $T_c$, °C. | −14.15 ± 0.02 | 34.48 ± 0.02 |
| $P_c$, atm. | 36.66 ± .05 | 34.20 ± .05 |

| | $SiF_2Cl_2$ | $SiFCl_3$ |
|---|---|---|
| $T_c$, °C. | 95.77 ± 0.02 | 165.26 ± 0.02 |
| $P_c$, atm. | 34.54 ± .05 | 35.33 ± .05 |

The equilibrium method used for the last five allowed the temperature to be ascertained to 0.02° and the pressure to less than 0.05 atmosphere.

The critical opalescence was shown to be a dispersion of two phases and not stable above the critical temperature.

Van Laar's addition of van der Waals constants was applied to the silicon compounds.

A numerical relationship between the critical temperatures of the fluorochlorosilanes and silicon tetrafluoride, which suggests that the value of the critical temperature of silicon tetrachloride in the literature is too low, has been demonstrated.

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(16) T. W. Parker and P. L. Robinson, *J. Chem. Soc.*, 2977 (1927).