ture range 0 to 70° using a considerably improved experimental procedure. The water transfer potential of the cell was calculated by a direct method eliminating tedious successive approximations.

The activity coefficient of the hydroxide for the concentration range 0.1 to 12 molal was found to be expressed adequately by the equation

$$\log \gamma = -\frac{u\sqrt{m}}{1+\sqrt{2m}} + Bm + Cm^2 + Dm^3 + Em^4$$

where u is the universal constant of the limiting law, m the molality of the hydroxide, B, C, D and E empirical constants varying according to second order equations with the temperature.

At higher concentrations a second order equation was used for the calculation of $\log \gamma$. The curves for $\log \gamma$ do not within the experimental accuracy show any breaks at higher concentrations like those of the apparent partial molal volumes.

Using the formulas for $\log \gamma$ equations have been given for the calculation of the activity and vapor pressure of the solvent, the relative partial molal free energy, heat content, entropy, and heat capacity of both solute and solvent. Other properties that have been discussed are the total heat capacity, specific heat and relative heat content of the solutions, the heat of dilution between two finite concentrations, differential and integral heats of vaporization of the solvent and finally the effect of pressure upon the thermodynamic properties of sodium hydroxide. The computed values of most of the properties treated are given in a series of tables.

NEW HAVEN, CONN. RECEIVED OCTOBER 21, 1939

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

The Fluorination of Thionyl Chloride[1]

BY HAROLD SIMMONS BOOTH AND FRANCIS CARL MERICOLA

In 1896, M. Meslans[2] found that when thionyl chloride was treated with certain metallic fluorides such as zinc fluoride, a gaseous product, thionyl fluoride was formed. He reported this gas as being colorless and boiling in the neighborhood of −30° and added that the gas attacked the respiratory organs vigorously. Later Moissan and Lebeau[3] prepared this gas using free fluorine and also arsenic trifluoride as the fluorinating agents.

In 1905, Ruff and Thiel[4] prepared thionyl fluoride by heating N_4S_4 and hydrogen fluoride in the presence of water and cupric oxide in a sealed glass tube for two hours at 100°.

Since none of the previous investigators found any intermediate fluorination products, it seemed advisable to study the fluorination of thionyl chloride by means of antimony fluoride in the presence of a catalyst. This reaction has been successfully applied to the stepwise fluorination of various non-polar halides in this Laboratory.[5,6]

Experimental

The generator was similar to that described by Booth and Bozarth.[6] The sublimed antimony trifluoride was slowly fed into the refluxing reaction mixture of 80% thionyl chloride and 20% antimony pentachloride (maintained at 50°, and at 200 mm. pressure) at such a rate that the automatic bleed-off valve would be continually in the open position but such that it would not allow the pressure to rise more than a few millimeters above this point. In this way as soon as any thionyl chlorofluoride was formed it was immediately removed from the reaction zone, thus ensuring the maximum yield. Reaction took place immediately.

The distillation analysis revealed the product to consist of 50% thionyl fluoride, 20% thionyl chlorofluoride, 5% sulfur dioxide and about 25% unreacted thionyl chloride. The yields were dependent upon the conditions of the reaction. Higher temperatures and pressures increased the percentage of thionyl fluoride and thus decreased the yield of the chlorofluoride. If the pressure were kept too low, thionyl chloride would distil out of the reaction zone.

The design and operation of the purification system was as already described[7] save that a glass spiral replaced the copper spiral in the fractionating column since copper was attacked. After the first rough separation two distillations in the column were sufficient to obtain pure gases for the determination of properties.

Analysis.—The samples were taken in small bulbs as liquids and absorbed in aqueous sodium hydroxide as usual.[8] Chlorine was determined gravimetrically as silver

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(1) From a portion of a thesis submitted by Francis Carl Mericola in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in Chemistry, to the Graduate School of Western Reserve University, May, 1938.

(2) M. Meslans, *Bull. soc. chim.*, [3] **15**, 391 (1896).

(3) H. Moissan and P. Lebeau, *Compt. rend.*, **130**, 1436 (1900).

(4) O. Ruff and K. Thiel, *Ber.*, **38**, 549 (1905).

(5) H. S. Booth and C. F. Swinehart, THIS JOURNAL, **54**, 4751 (1932).

(6) H. S. Booth and A. R. Bozarth, *ibid.*, **61**, 2927 (1939).

(7) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(8) Booth and Dutton, THIS JOURNAL, **61**, 2937 (1939).

TABLE I

ANALYSES

	Sulfur, % Theory	Sulfur, % Found		Oxygen, % Theory	Oxygen, % Found		Chlorine, % Theory	Chlorine, % Found	
$SOCl_2$	26.74	26.70	26.63				59.97	59.84	59.90
$SOClF$	31.29	31.21	31.15	15.61	15.79	15.43	34.59	34.50	34.51
SOF_2	37.25	37.25	37.40	18.59	18.57	18.69			

chloride and sulfur as barium sulfate. In the latter case the solution was kept strongly acidic to avoid co-precipitation of barium fluoride. The oxygen was established indirectly by titration of the solution, alkaline with sodium bicarbonate, with excess iodine and back titration of the excess with sodium thiosulfate. The presence of fluorine was established qualitatively.

TABLE II[a,b]

VAPOR PRESSURE OF THIONYL FLUORIDE

$\text{Log } P_{\text{mm.}} = 30.333 - 1908.4/T - 8.1053 \log T$

Sample temp., °C.	P obsd. mm. (cor.)	P calcd. mm.	Deviation, mm.
B −91.86	32.5	31.6	−0.9
A −91.62	33.8	32.3	−1.5
B −82.16	71.2	71.0	−0.2
A −81.76	72.6	73.2	+ .6
B −79.86	84.7	84.7	.0
B −76.04	112.5	112.3	− .2
A −71.04	158.3	159.2	+ .9
B −68.46	187.4	188.4	+1.0
A −64.44	244.4	244.2	−0.2
B −61.65	286.8	286.6	−0.2
A −57.60	365.4	366.7	+1.3
B −57.59	366.9	366.9	0.0
B −57.32	372.0	372.6	−0.6
B −52.29	494.0	491.4	−2.6
B −48.23	612.3	610.6	−1.7
A −45.90	682.2	682.4	+0.2
B −45.32	711.8	702.9	+8.9
A −41.05	862.0	862.0	0.0

VAPOR PRESSURE OF THIONYL CHLOROFLUORIDE

$\text{Log } P_{\text{mm.}} = 7.0466 - 1278.2/T + 0.1268 \log T$

Sample temp., °C.	P obsd. mm. (cor.)	P calcd. mm.	Deviation, mm.
A −73.62	8.5	8.4	−0.1
A −69.52	11.5	11.5	.0
B −64.90	15.9	15.9	.0
A −53.44	34.5	33.6	− .9
B −50.46	39.3	40.1	+ .8
B −43.97	57.7	58.4	+ .7
A −34.36	100.5	97.9	−2.6
B −30.06	121.0	122.7	+1.7
A −22.65	174.2	176.2	+2.0
A −13.78	264.0	265.0	+1.0
B − 9.15	323.6	323.6	0.0
A − 5.39	380.2	379.8	−0.4
B − 1.86	436.6	438.4	+1.8
A + 1.30	498.3	498.4	+0.1
B + 3.04	531.1	532.8	+1.7
B + 5.11	577.3	578.0	+0.7
B + 7.98	644.0	645.5	+1.5
A +10.29	703.7	703.6	−0.1
A +11.29	728.1	730.1	+2.0
B +14.19	805.3	811.3	+6.0
A +14.68	822.4	826.2	+3.8

[a] Samples A and B were from different distillations.

[b] The calculated values were determined by use of the equations.

Physical Properties.—The liquid density was determined by means of a special pycnometer.[9] Freezing points, vapor pressures and gas densities were measured according to the standard practice in this Laboratory.[7] With thionyl chloride supercooling of from 10 to 15° occurred, but with thionyl fluoride none was observed. In the case of thionyl chlorofluoride much difficulty was encountered in measuring the freezing point. Upon cooling, the liquefied gas slowly solidified to a viscous transparent glassy solid which upon further cooling crystallized spontaneously with such force that on several occasions it burst the melting point tube. To obviate this difficulty the gas was first crystallized in the melting point tube and then allowed to melt slowly by placing a dewar flask, with a little liquid nitrogen in the bottom, around the jacketed melting point tube and the *melting point* of the thionyl chlorofluoride was obtained in this way.

Critical Constants.—The critical constants of thionyl chloride and thionyl chlorofluoride were not determined due to the fact that mercury reacts with both these compounds. The critical and vapor pressure data of thionyl fluoride at high pressures were obtained. The measurements were made in the apparatus and as described by Booth and Swinehart.[10]

TABLE III

CRITICAL DATA FOR SOF_2

Sample	Temp., °C.		Pressure, atm.	
1	25.1		11.2	
2	34.8		16.4	
1	40.2		19.3	
2	49.6		23.7	
1	52.3		25.3	
2	60.0		30.4	
1	61.4		30.8	
2	65.8		34.3	
1	71.1		37.7	
2	71.7		39.1	
1	81.4		46.3	
2	77.4		43.7	
2	85.1		51.3	
1	88.9	89.0°	55.3	Critical point 55.3 atm.
2	89.1		55.4	
3	89.0		55.3	

Table IV summarizes the physical properties of the three compounds as obtained in this Laboratory.

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(9) Booth and Herrmann, THIS JOURNAL, 58, 63 (1936).

(10) Booth and Swinehart, *ibid.*, 57, 1337 (1935).

TABLE IV

PHYSICAL PROPERTIES OF THIONYL CHLORIDE, THIONYL FLUORIDE AND THIONYL CHLOROFLUORIDE

	$SOCl_2$		$SOClF$	SOF_2
Boiling point,[a] °C.	75.7[b]		12.2 ± 0.10	− 43.8 ± 0.1
Freezing point, °C.	−99.5	−104.5[c]		−129.5 −110.0[d]
Melting point, °C.			−139.5	
Liquid density	1.675	1.676[13]	1.580	
Gas density (detd.)			102.0	86.8
(calcd.)			102.5	86.1
Critical temperature, °C.				89.0
Critical pressure, atm.				55.3
Heat of vaporization, cal.	7682		5937	5202
Trouton's constant	21.4		20.7	22.6

[a] Taken from the graph of the vapor pressure data. [b] K. Arii, *Bull. Inst. Phys. Chem. Res. Tokyo*, **8**, 719 (1929). [c] H. A. Mayes and J. R. Partington, *J. Chem. Soc.*, **128**, 2594 (1926). [d] Ruff and Thiel, *Ber.*, **38**, 549 (1905).

Chemical Properties.—Thionyl fluoride in the absence of moisture was found to be the most stable of the three compounds studied. It was found to be so stable that it would not decompose at red heat in an iron retort although in glass it reacted with the silica forming sulfur dioxide and silicon tetrafluoride. Water reacts with thionyl fluoride giving hydrogen fluoride and sulfur dioxide. It is very inert toward such elements as iron, nickel, copper, mercury, silicon, manganese, boron, magnesium, aluminum, zinc, etc., even at temperatures up to 125°.

An attempt to chlorinate thionyl fluoride by passing chlorine and thionyl fluoride over activated charcoal gave negative results, whereas this chlorination runs smoothly in the case of sulfur dioxide and chlorine, giving sulfuryl chloride.[11]

In contrast to thionyl fluoride, thionyl chloride is quite reactive with metals. Its reactions may be represented by the equations[12]

$$3M + 4SOCl_2 \longrightarrow 3MCl_2 + 2SO_2 + S_2Cl_2$$
$$3M + 2SOCl_2 \longrightarrow 2MCl_2 + MS + SO_2$$

With zinc, cadmium, magnesium, lead, chromium and nickel, no reaction was observed up to 200°.

In the case of metal sulfides, the reaction may be represented by

$$MS + SOCl_2 \longrightarrow MCl_2 + SO_2 + S_2Cl_2$$

These reactions were corroborated in this Laboratory.

Thionyl chlorofluoride reacts with very few metals at temperatures up to 150°. Tests with such metals and metalloids as boron, magnesium, silver, aluminum, silicon, zinc, phosphorus, manganese, arsenic and antimony were negative. With copper and mercury, reaction took place readily at room temperature. With iron reaction took place at about 70°. The products of the reaction were identified as SOF_2, SO_2, MS and MCl_2. In all cases some thionyl chloride was also found. This would indicate that a decomposition probably first occurs and that the speed of this reaction is greater than that of the reaction of the metals with thionyl chloride.

$$2SOClF + (Hg) \longrightarrow SOCl_2 + SOF_2 \text{ (fast)}$$
$$2SOCl_2 + 3Hg \longrightarrow 2HgCl_2 + HgS + SO_2 \text{ (slow)}$$

This is borne out by the fact that thionyl chlorofluoride on standing for some months in the gaseous state at room temperature decomposed to a considerable extent to $SOCl_2$ and SOF_2. In general, thionyl chlorofluoride behaves chemically like thionyl chloride.

An attempt to remove the chlorine by reaction with sodium amalgam in order to produce a condensation product of the formula $(SOF)_2$ was not successful. Instead, the reaction was one of oxidation–reduction. Reactions with Grignard reagents were analogous to those of thionyl chloride. No attempt was made to isolate the reaction products. When pure, all three substances are colorless in all states. They hydrolyze in moist air or water very readily.

Summary

The fluorination of thionyl chloride using antimony fluoride and antimony pentachloride, yields two gaseous products, thionyl fluoride, first described by Meslans, and a new compound, thionyl chlorofluoride. Physical and chemical properties of these two gases have been determined. The freezing point of thionyl chloride has also been redetermined.

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(11) "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., p. 114.

(12) H. B. North, THIS JOURNAL, **32**, 184 (1910); H. B. North and C. B. Conover, *ibid.*, **37**, 2486 (1915); H. B. North and A. M. Hageman, *ibid.*, **34**, 890 (1912).