anate and dichloracetate complexes are formed in solution from iron(III) ion.

A decrease in moment takes place when acetate, monochloracetate, hydrogen-phosphate, pyrophosphate, lactate, tartrate, citrate and aminoacetate

complexes are formed. In these cases the apparent moment varies with the concentration of excess anion, or with the acidity, or both, indicating the presence of more than one compound.

DURHAM, N. C.　　　　RECEIVED AUGUST 28, 1943

Systems with Boron Trifluoride. III[1]

BY HAROLD SIMMONS BOOTH AND JOHN HARPER WALKUP[2]

This paper presents the results of further[3] studies by thermal analysis on coördination of boron trifluoride and seven fluoride gases.

Sources of Gases.—Commercial boron trifluoride, supplied by the kindness of the Harshaw Chemical Co., was purified further as previously described. The dichlorodifluoromethane was kindly supplied by Kinetic Chemicals, Inc. The monochlorotrifluoromethane was from a stock made by Dr. Ralph McNabney of this Laboratory by the arc decomposition of CF_2Cl_2. The tetrafluoromethane was generously supplied by Professor Lucius A. Bigelow of Duke University. The phosphorus trifluoride,[4] the phosphoryl fluoride,[5] the thiophosphoryl fluoride,[6] and the thionyl fluoride[7] were made by fluorination of the corresponding chloride by means of antimony fluoride.

Method.—The method of thermal analysis used is the improved procedure described by Booth and Martin.[3c] Before use the gases were purified by fractional distillation in columns as previously described in papers from this Laboratory.

1. The System Dichlorodifluoromethane–Boron Trifluoride

It has been found that fluorine is a member of that small group of elements that are capable in some compounds of donating electrons to boron of boron trifluoride to form "addition" compounds. For this reason the system of dichlorodifluoromethane–boron trifluoride was investigated.

It was found upon mixing the first mole fraction that the two liquids were practically completely immiscible. Fourteen mixtures between 0 and 1.0 mole fraction of BF_3 were tried with the same results.

2. The System Monochlorotrifluoromethane–Boron Trifluoride

After it had been found that dichlorodifluoromethane and boron trifluoride were immiscible, the question arose as to what effect an increase in the fluorine content of the molecule would have upon the mutual solubility of the two liquids. For that reason the system monochlorotrifluoromethane–boron trifluoride was studied.

It was found that the increase of the fluorine content and the consequent reduction of the chlorine content of the compound increased the miscibility of the two liquids. Boron trifluoride was soluble in monochlorotrifluoromethane up to 20.0

TABLE I

DATA FOR SYSTEM MONOCHLOROTRIFLUOROMETHANE–BORON TRIFLUORIDE

Mole fraction BF_3	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF_3	Freezing point, °C.
0.0000	−181.6		0.0000	−181.6
.0381	−140.3	−183.2	.0663	−137.8
.0836	−136.0	−183.2	.1193	−134.1
.1165	−134.5		.1605	−133.1
.1568	−132.1		.1968	−131.1
.2069	−130.5		.2281	−130.5
.2526	−130.6		.2811	−130.5
.3030	−130.6		.3190	−130.5
.3483	−130.6		.3797	−130.5
.4001	−130.5		.4155	−130.5
.4559	−130.5		.4772	−130.5
.5032	−130.6		.5296	−130.5
.5538	−130.4		.6580	−130.5
.5961	−130.6		.7261	−130.5
.6499	−130.6		.7760	−130.4
.6989	−130.6		.8282	−130.4
.7467	−130.5		.8613	−130.4
.7975	−130.6		.9310	−128.6
.8331	−130.5		1.0000	−127.6
.8633	−130.5			
.9020	−129.5			
.9289	−128.8			
.9652	−128.1			
1.0000	−127.6			

(1) Presented at the Detroit meeting of the American Chemical Society, April 12, 1943.

(2) From a thesis submitted by John Harper Walkup in partial fulfillment of the requirements of the degree of Doctor of Philosophy in Chemistry to the Graduate School of Western Reserve University, February, 1943.

(3a) A. F. O. Germann and H. S. Booth, *J. Phys. Chem.*, **30**, 369 (1926).

(3b) H. S. Booth and K. S. Willson, THIS JOURNAL. **57**, 2273 (1935).

(3c) H. S. Booth and D. R. Martin, *ibid.*, **64**, 2198 (1942).

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

(5) H. S. Booth and Fred Dutton, *ibid.*, **61**, 2937 (1939).

(6) H. S. Booth and Catherine Cassidy, *ibid.*, **62**, 2369 (1940).

(7) H. S. Booth and Francis Mericola, *ibid.*, **62**, 640 (1940).

mole per cent. boron trifluoride, at a temperature of $-130.5 \pm 0.5°$. Monochlorotrifluoromethane was soluble in boron trifluoride to 10.0 mole per cent. at a temperature of $-130.5 \pm 0.5°$.

It was also found that on raising the temperature, the two liquids became miscible in each other even at a mole per cent. of 50.0, and that they could then be separated by distillation.

The freezing point of monochlorotrifluoromethane was found to be $-181.6 \pm 0.5°$. Table I represents two separate samples of the gas mixtures. The data are plotted in Fig. 1.
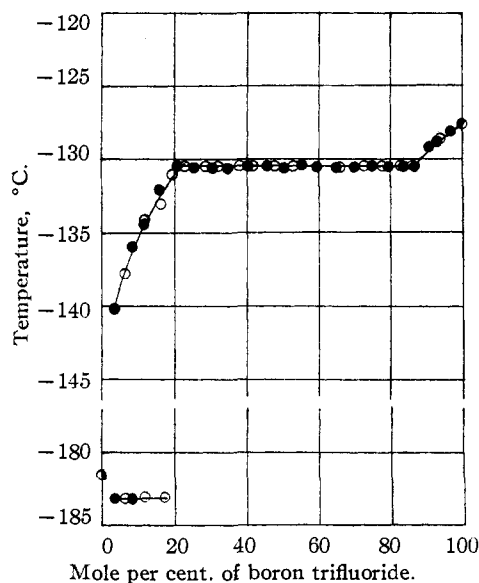

Fig. 1.—Monochlorotrifluoromethane–boron trifluoride ●, data from Table I-A; ○, data from Table I-B.

3. The System Tetrafluoromethane–Boron Trifluoride

Since an increase in the number of fluorine atoms and the reduction of the number of chlorine atoms attached to a single carbon atom increased the solubility of the compound in boron trifluoride, it was thought that with no chlorine atoms present in the molecule, as in tetrafluoromethane, the molecule would be soluble and the fluorine atoms would be capable of donating electrons to the boron atom of boron trifluoride to form an "addition" compound. For this reason the system tetrafluoromethane–boron trifluoride was studied.

It was found that the increase in fluorine on the carbon atom did not increase the solubility enough to make the two liquids miscible in all proportions. There was never noticed any turbidity in the mixtures, but the constant freezing points shown indicate that the liquids were immiscible at some point above the freezing points. This constancy of freezing points occurs in the range 25.0 mole per cent. boron trifluoride to 85.0 mole per cent. boron trifluoride. This shows that boron trifluoride will dissolve in tetrafluoromethane to a

mole per cent. of 25.0 and tetrafluoromethane in boron trifluoride to 15.0 mole per cent. The constant temperature was found to be $-131.4 \pm 0.5°$. The freezing point found for tetrafluoromethane was $-180.1 \pm 0.5°$.

It was found that on raising the temperature of tetrafluoromethane to the boiling point, the two liquids were miscible and could be separated by distillation.

TABLE II

DATA FOR SYSTEM TETRAFLUOROMETHANE–BORON TRIFLUORIDE

Mole fraction BF₃	Freezing point, °C.	Mole fraction BF₃	Freezing point, °C.
0.0000	−180.1	0.0000	−180.1
.0357	−144.1	.1319	−133.1
.0940	−135.1	.1797	−132.4
.1470	−132.9	.2595	−131.4
.1864	−132.0	.2720	−131.4
.2194	−131.6	.3282	−131.4
.3022	−131.2	.3705	−131.4
.3499	−131.2	.4252	−131.4
.4031	−131.2	.4755	−131.4
.4506	−131.2	.5268	−131.2
.5024	−131.4	.5742	−131.4
.5499	−131.4	.5640	−131.2
.5985	−131.4	.6228	−131.4
.6435	−131.2	.6693	−131.2
.6997	−131.2	.7231	−131.4
.7470	−131.2	.7650	−131.3
.8060	−131.4	.8926	−129.8
.8400	−131.2	.9200	−129.0
.8763	−130.9	.9558	−128.4
.9638	−128.5	1.0000	−127.8
1.0000	−127.8		

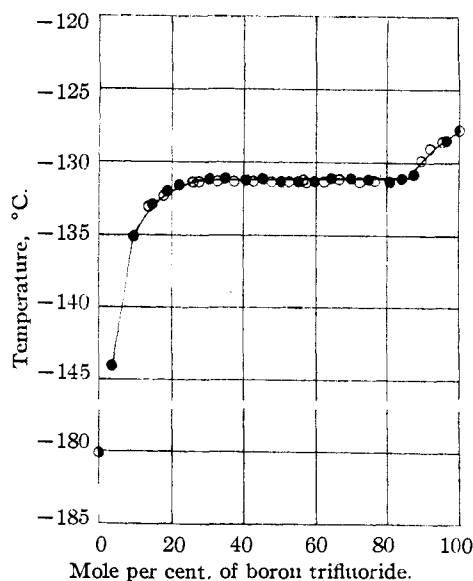The data for this system for different samples of the gases are given in Table II and plotted in Fig. 2.

Fig. 2.—Tetrafluoromethane–boron trifluoride: ●, data from Table II-A; ○, data from Table II-B.

4. The System Phosphorus Trifluoride–Boron Trifluoride

Phosphorus is one of the elements that donates electrons to the boron atom of boron trifluoride to form "addition" compounds. Besson[8] first reported the compound $PH_3 \cdot 2BF_3$; however, the work was repeated by Wiberg and Heubaum,[9] and they reported that no compound of the above composition was formed but that $PH_3 \cdot BF_3$ was formed. In view of the structure of PH_3 one would be more inclined to believe the latter to be the correct composition.

The compound $BCl_3 \cdot PCl_3$ was reported by A. Stieber.[10] It was a white crystalline solid which could be sublimed without decomposition. Wiberg and Schuster[11] have reported the formation of a 1:1 compound between PCl_3 and BBr_3. The compound melts at 42° when freshly prepared, but on standing is said to change into a liquid.

From the above facts it seemed likely that the phosphorus atom of phosphorus trifluoride would donate electrons to the boron atom of boron trifluoride.

Table III presents data for two separate samples of the gases, which are plotted in Fig. 3.
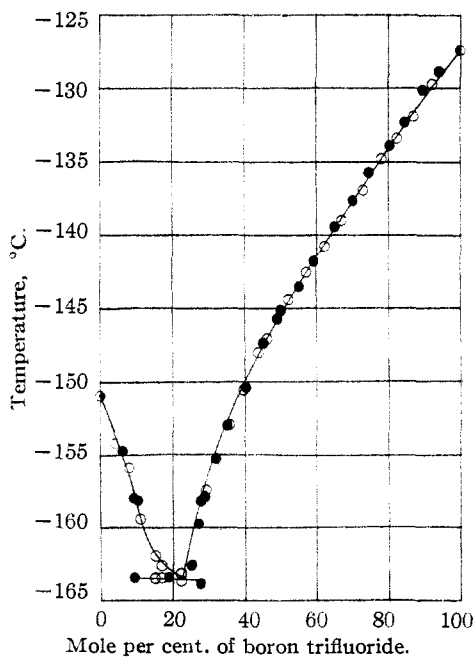

Fig. 3.—Phosphorus trifluoride–boron trifluoride: ●, data from Table III-A; O, data from Table III-B.

The freezing point of pure phosphorus trifluoride checked the values found by Booth and Bozarth[4] and was found to be −151.1 ± 0.5°. The freezing point diagram was a smooth curve with a

(8) A. Besson, *Compt. rend.*, **110**, 80 (1890).

(9) E. Wiberg and U. Heubaum, *Z. anorg. allgem. chem.*, **225**, 270 (1935).

(10) A. Stieber, *Compt. rend.*, **195**, 610 (1932).

(11) E. Wiberg and K. Schuster, *Z. anorg. allgem. Chem.*, **213**, 94 (1933).

TABLE III
DATA FOR SYSTEM PHOSPHORUS TRIFLUORIDE–BORON TRIFLUORIDE

Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.
0.0000	−151.1		0.0000	−151.2	
.0650	−154.9		.0485	−154.5	
.1083	−158.2		.0838	−156.0	
.0922	−158.0	−162.4	.1118	−159.5	
.1938		−162.4	.1522	−162.0	−163.5
.2563	−162.7		.1720	−162.7	−163.5
.2745	−159.9		.2014	−163.2	−163.5
.2931	−158.0		.2286	−163.7	−163.7
.2802	−158.2	−163.0	.2792	−159.5	
.3228	−155.3		.2949	−157.5	
.3548	−153.1		.3608	−153.1	
.4042	−150.4		.4004	−150.7	
.4564	−147.4		.4405	−148.1	
.5048	−145.2		.4674	−147.2	
.4958	−145.8		.5254	−144.4	
.5528	−143.6		.5498	−143.7	
.5975	−141.8		.5749	−142.6	
.6511	−139.5		.6272	−140.8	
.7010	−137.7		.6725	−139.1	
.7482	−135.8		.7342	−137.0	
.8052	−134.0		.7825	−134.9	
.8493	−132.4		.8252	−133.5	
.8967	−130.2		.8710	−132.0	
.9426	−128.9		.9255	−129.8	
1.0000	−127.5		1.0000	−127.5	

eutectic occurring at 21.5 mole per cent. boron trifluoride at a temperature of −163.5 ± 0.5°.

Although other phosphorus compounds of similar structure form "addition" compounds, the thermal analysis curve shows only a simple eutectic with no evidence of any compound between phosphorus trifluoride and boron trifluoride.

5. The System Phosphoryl Fluoride–Boron Trifluoride

The oxygen atom is one of the elements that is frequently capable of donating electrons to the boron atom of boron trifluoride to form "addition" compounds. Baumgarten and Henning[12] have prepared compounds with boron trifluoride where the oxygen is joined to a phosphorus atom; for example, $K_3PO_4 \cdot BF_3$. Therefore, the system phosphoryl fluoride–boron trifluoride was investigated.

With this system it is impossible to mix mole fractions and get freezing points for a complete curve; due to the great difference between the freezing point of phosphoryl fluoride and the boiling point of boron trifluoride, the pressure that built up when trying to melt the mixtures containing more than 45% BF_3 was so great that the freezing point cell was shattered. The boron trifluoride side could not be obtained because on melting the first mixture, the phosphoryl fluoride would distil out and freeze on the

(12) P. Baumgarten and H. Henning, *Ber.*, **72B**, 1743 (1939).

thermocouple well. For this reason the freezing point curve was determined only up to a mole per cent. of 42.73 boron trifluoride.

The freezing point of pure phosphoryl fluoride was found to be $-39.6 \pm 0.5°$. A eutectic was found at a mole per cent. of 16.5 boron trifluoride at a temperature of $-47.5 \pm 0.5°$. The freezing point curve then rises until at a mole per cent. of 43.73 of boron trifluoride, the freezing point of the mixture is $-23.8 \pm 0.5°$. From this it is obvious that a maximum would appear somewhere along the curve. By extrapolation of the curve, and assuming that the compound will be F_3POBF_3, the freezing point would be about $-20°$.

Table IV contains data for three different samples of the gases, all plotted in Fig. 4.

TABLE IV

DATA FOR SYSTEM PHOSPHORYL FLUORIDE–BORON TRI-FLUORIDE

Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.
0.0000	−39.6		0.0000	−39.6	
.0441	−41.4		.0573	−41.0	
.1256	−45.6		.1069	−44.4	−48.0
.1858	−43.5	−47.5	.1536	−47.0	−47.5
.2036	−40.5	−47.7	.2433	−37.0	−47.7
.2295	−37.5		1.0000	−127.8	
.2812	−33.8		0.0000	−39.6	
.3498	−29.0		.0490	−42.1	
.3896	−25.6		.0857	−43.8	
.4273	−23.8		.1013	−44.8	
1.0000	−127.8		.1528	−46.9	−47.5
			.1963	−41.2	
			1.0000	−127.7	

From the behavior of the pressure it is believed that the molecules combined in the liquid state and perhaps even in the gaseous state. When a new mole fraction of boron trifluoride was taken into the freezing cell, it would first melt and build up a pressure; however, when the excess phosphoryl fluoride would start to melt, the pressure would fall as if a cooling agent had been applied to the freezing point cell. Every time this failed to happen the freezing point tube would burst.

6. The System Thiophosphoryl Fluoride–Boron Trifluoride

Since phosphoryl fluoride formed a compound with BF_3 that would melt at a higher temperature than either of the components, it was thought that the analogous thiophosphoryl fluoride would form a compound with boron trifluoride. Also, since the thiophosphoryl fluoride has a longer liquidus range than phosphoryl fluoride, this system could be investigated for all mole fractions. The sulfur atom has already been shown by Germann and Booth[13] to donate electrons to the boron atom of boron trifluoride, in the case of hydrogen sulfide. With the above facts in mind

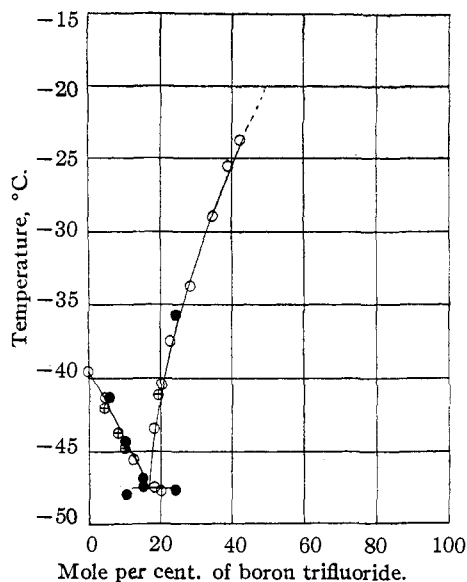(13) A. F. O. Germann and H. S. Booth, J. Phys. Chem., 30, 369 (1926).

Fig. 4.—Phosphoryl fluoride–boron trifluoride: ○, data from Table IV-A; ●, data from Table IV-B; ⊕, data from Table IV-C. The freezing point of boron trifluoride was found to be $-127.8°$.

the system thiophosphoryl fluoride–boron trifluoride was studied.

Table V gives the data for separate runs with two different samples of the gases, which are plotted in Fig. 5.

TABLE V

DATA FOR SYSTEM THIOPHOSPHORYL FLUORIDE–BORON TRIFLUORIDE

Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.
0.0000	−148.8		0.0000	−148.8	
.0624	−149.8		.0407	−149.5	
.0943	−150.6		.1233	−151.1	
.1761	−152.0	−152.2	.1510		−152.1
.2038	−148.4	−152.1	.1750	−150.6	−152.1
.2467	−145.0		.2080	−148.2	−152.1
.3049	−141.5		.2429	−145.4	
.3475	−140.4		.2882	−142.6	
.3838	−138.9		.3191	−141.2	
.4490	−137.4		.3671	−139.8	
.5046	−135.7		.4190	−138.0	
.5415	−134.9		.4776	−136.1	
.5986	−133.9		.5120	−135.5	
.6514	−133.3		.5868	−134.2	
.6973	−132.7		.6922	−132.8	
.7500	−132.0		.7183	−132.2	
.7974	−131.2		.7705	−131.8	
.8466	−130.6		.8104	−131.2	
.8999	−129.2		.8725	−130.0	
.9458	−128.3		.9265	−128.8	
1.0000	−127.4		.9589	−128.2	
			1.0000	−127.4	

The freezing point of pure thiophosphoryl fluoride was found to be $-148.8 \pm 0.5°$. A eu-
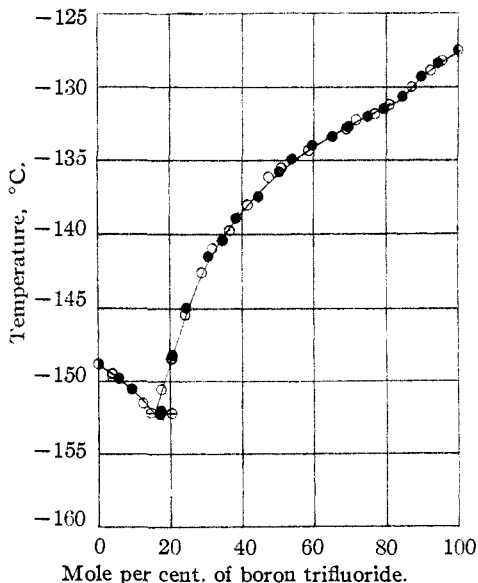
Fig. 5.—Thiophosphoryl fluoride–boron trifluoride: ●, data from Table V-A; ○, data from Table V-B.

TABLE VI

DATA FOR SYSTEM THIONYL FLUORIDE–BORON TRI-FLUORIDE

Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.
0.0000	−129.0		0.0000	−129.0	
.0508	−130.5		.0832	−131.7	
.1243	−133.0		.1924	−136.9	
.1714	−135.5		.2164	−140.0	
.2354	−139.2		.2541	−140.8	
.3185		−145.9	.2762	−141.9	−145.8
.3787	−143.5	−145.9	.3033	−143.5	−145.8
.4040	−142.5		.3914	−142.9	−145.8
.4517	−140.8		.4303	−141.2	
.5015	−140.4		.4851	−140.4	
.5605	−141.2		.5169	−140.6	
.5438	−140.8		.5651	−141.2	
.5989	−142.1		.6221	−142.6	
.6508	−143.9		.6555	−144.1	
.6974	−144.1	−145.4	.7135	−141.7	−145.3
.7455	−139.2		.7705	−137.6	−145.4
.8024	−135.3		.8186	−134.5	
.8527	−132.9		.8782	−131.8	
.8995	−131.3		.9434	−129.2	
.9407	−129.5		1.0000	−127.4	
1.0000	−127.4				

Table VI gives the data for two separate runs with different samples of the gases, which are plotted in Fig. 6.

tectic was found at 16.00 mole per cent. boron trifluoride at a temperature of −152.1 ± 0.5°. The curve is not a V-type of freezing point curve; however there is no maximum shown. There is a change in slope at 82.5 mole per cent. boron trifluoride at a temperature of −130.8 ± 0.5°. This temperature compares with that for the transition point for boron trifluoride noticed by Eucken and Schroder[14] and found to be −131.01°.

Since this is a transition point of boron trifluoride, one cannot say that this inflection shows that a compound has been formed. However, it can be said that above this point on the curve the liquid is in equilibrium with the alpha form of boron trifluoride, below the point it is in equilibrium with the beta form of boron trifluoride. At this point both forms can exist in equilibrium with the liquid, and the point would be invariant, by the phase rule for condensed systems.

7. The System Thionyl Fluoride–Boron Trifluoride

Booth and Martin[3c] have shown that the oxygen atom attached to a sulfur atom in sulfur dioxide is capable of donating electrons to the boron atom of boron trifluoride. It has also been shown by Baumgarten and Henning[12] that the oxygen atom attached to a sulfur atom, in the case of the sulfate radical, is capable of donating electrons to the boron atom of boron trifluoride to form stable complexes of this nature, $K_2SO_4 \cdot BF_3$. It seemed of interest to study the system thionyl fluoride–boron trifluoride to see if the oxygen atom here could also donate electrons to the boron atom of boron trifluoride when the other atoms on the sulfur were not oxygen but fluorine, which is more electronegative.

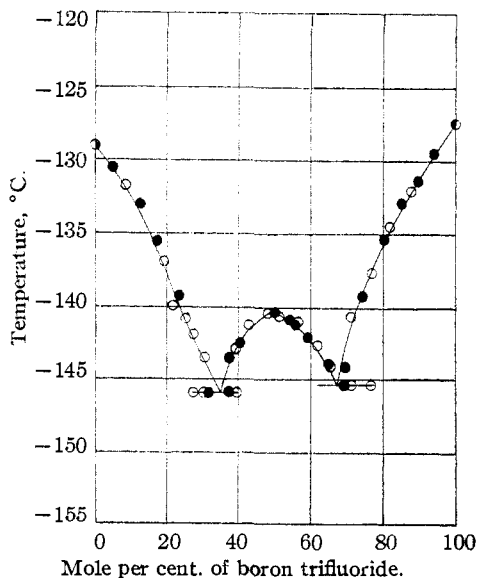(14) A. Eucken and E. Schroder, Z. physik. Chem., **B41**, 307 (1938).

Fig. 6.—Thionyl fluoride–boron trifluoride: ●, data from Table VI-A; ○, data from Table VI-B.

The freezing point of pure thionyl fluoride was found to be −129.0 ± 0.5°. A maximum was found at a mole per cent. of 50.0 boron trifluoride, indicating a compound of the ratio of 1:1 boron trifluoride to thionyl fluoride. The freezing point of this compound was found to be −140.8 ± 0.5°. Two eutectics were found. The first was found

at 34.0 mole per cent. boron trifluoride and at a temperature of $-145.9 \pm 0.5°$; the second at 68.5 mole per cent. boron trifluoride and at a temperature of $-145.4 \pm 0.5°$.

Discussion of Results of Systems Studied

In the chlorofluoromethane systems with boron trifluoride, all of the components showed limited miscibility.

In the system phosphorus trifluoride–boron trifluoride, the question arises as to why the phosphorus atom of phosphine will donate electrons to the boron atom of boron trifluoride to give a compound while the phosphorus atom of phosphorus trifluoride will not. Here the number of atoms attached to the phosphorus is the same. Thus, there are two electrons in the outer orbit unshared.

Since there has not been a large increase in the size of the attached atoms one would not expect the steric factor to play an important part.

If we examine the direction of the dipole moments of the two compounds, a possible answer may be seen: $P^+ - F^-$ and $H^+ - P^-$. As shown, in phosphine the dipole moments tend to increase the negative charge on the phosphorus atom, while in the phosphorus trifluoride the dipole tends to decrease the negative charge on the phosphorus. The moments of the P–H bonds and the P–F bonds are in opposite directions. The electrons on the phosphorus atom in phosphine would be more loosely bound than the electrons of the phosphorus atom in phosphorus trifluoride. The charge on the phosphorus atom of phosphine would be great enough to induce an additional positive charge on the boron atom of boron trifluoride permitting it to take the tetrahedral structure. With this charge on the boron, then the phosphine and boron trifluoride would be drawn together to form a compound.

The resonance effect would not appear in phosphine for hydrogen can have no double bond character[15]; while in the phosphorus trifluoride there would be a small resonance effect, since there is some double bond character in the P–F bond as shown by electron diffraction studies of Brock-

way and Wall.[16] They found that the P–F distance was 1.56 ± 0.02 Å., while the sum of the covalent radii was 1.74 Å. This double bond character would tend to use the two electrons that are in the outer orbit so that they would not be available for donation to the boron atom of boron trifluoride.

In the system phosphoryl fluoride–boron trifluoride, there was a compound indicated. The steric factor would not come into play here for the atoms are still small.

In the system thiophosphoryl fluoride–boron trifluoride one would think that it, too, would form a compound as was found in its oxygen analog phosphoryl fluoride.

The fact that no maximum was found can scarcely be due to the increase in size of the sulfur atom over the oxygen atom for there has only been an increase of ten electrons. Hence the steric factor would not be of great importance here.

Part of the inability of thiophosphoryl fluoride to form a compound with boron trifluoride must lie in the fact that the negative charge on the sulfur is not great enough to induce a dipole on the boron atom of boron trifluoride to cause an attraction of the two molecules.

In the system thionyl fluoride–boron trifluoride, the steric factor would not be much greater than that found for sulfur dioxide. The compound found here would be expected to be less stable than the one formed with sulfur dioxide[3c] due to the lower bond moment.

Summary

1.　Thermal analysis of BF_3 and chlorofluoromethanes and tetrafluoromethane showed limited miscibility, such that compound formation could not be established.

2.　While phosphoryl fluoride forms a compound with BF_3, the sulfur analog PSF_3 gave on evidence of compound formation nor did PF_3.

3.　Thionyl fluoride reacts with BF_3 to give a 1:1 compound melting at $-140.8 \pm 0.5°$.

CLEVELAND, OHIO　　　　　RECEIVED JULY 23, 1943

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