TABLE III

COMPARISON OF OBSERVED AND CALCULATED PV'S

Gas	Pressure range.[a] atm.	Reduced temp., T_r	PV van der Waals % Max. dev.	% Av. dev.	PV this paper % Max. dev.	% Av. dev.
Methane	30–300	1.694	7.67	3.66	2.14	0.96
Ethane	38.64–311.09	1.631	− 8.43	4.81	−3.10	1.12
Propane	41.23–303.03	1.481	14.05	6.07	−1.90	0.79
Ethylene	50–300	1.667	− 6.44	4.10	−1.57	0.61
Carbon monoxide	25–200	1.663	− 7.16	4.54	−2.57	0.90
Carbon dioxide	75–500	1.548	11.33	6.26	−3.64	2.17

[a] Above the upper limits of pressure indicated the van der Waals equation gives deviations which are 15% or higher, and which reach 200–300% at pressures approaching 1000 atmospheres.

From the equations given in this paper it is readily possible to derive a generalized equation for the compressibility coefficients of gases obeying the principle of corresponding states. If the values of the α's given by equations (8) to (11) be substituted into equation (1), and Z solved for, the result is

$$Z = 1 + \left[\frac{\beta_1}{T_r} + \frac{\beta_2}{T_r^2} + \frac{\beta_3}{T_r^4}\right]\frac{P_r}{R} + \left[\frac{\beta_4}{T_r^3} + \frac{\beta_5}{T_r^5} + \frac{\beta_6}{T_r^7}\right]\frac{P_r^2}{R} + \left[\frac{\beta_7}{T_r^3} + \frac{\beta_8}{T_r^5} + \frac{\beta_9}{T_r^7}\right]\frac{P_r^3}{R} + \left[\frac{\beta_{10}}{T_r^3} + \frac{\beta_{11}}{T_r^5} + \frac{\beta_{12}}{T_r^7}\right]\frac{P_r^4}{R} \quad (12)$$

This equation should reproduce the generalized compressibility coefficient curves deduced empirically by various authors within the ranges specified. That it will do so is evidenced by the comparisons of calculated and observed volumes given in this paper.

Summary

1. Employing the principle of corresponding states, an equation of state for gases is deduced requiring only the critical temperature and pressure of a gas.

2. The equation is shown to be applicable to pressures as high as 1000 atmospheres and reduced temperatures of $T_r = 1.55$ and above.

3. Below $T_r = 1.55$ the equation proposed is applicable down to $T_r = 1.30$ provided the pressure interval covered is reduced to 100 atmospheres at the lower temperature.

4. A comparison of the proposed equation with several other common equations of state shows the present equation to be superior to these.

5. A generalized equation for compressibility coefficients of gases is deduced.

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

Systems with Boron Trifluoride[1]

BY HAROLD SIMMONS BOOTH AND DONALD RAY MARTIN

The boron atom of boron trifluoride has been found to be an acceptor to form a large number of coördinate compounds. The number of donor atoms has been found so far to be quite small, being confined to the seven elements carbon, nitrogen, oxygen, fluorine, phosphorus, sulfur and argon.

One of the best procedures for the identification of these coördinate compounds is thermal analysis, particularly as applied to liquefied gases. The object of the present investigation was to extend our knowledge of the coördinate compounds of boron

trifluoride and various gases by means of therma analysis.

Apparatus and Procedure

The apparatus shown in Fig. 1 is similar in principle and operation to that described in detail by Germann and Booth,[2] save for the following features.

1. Boron trifluoride[3] from the cylinder B was purified by fractional distillation in the fractionating column[4] LH and stored in ampoule T_2 separated by the mercury cut-off MC to prevent contamination from stopcock grease or from leakage.

(1) From a part of a thesis submitted by Donald Ray Martin to the Graduate Faculty of Western Reserve University, May, 1941, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Germann and Booth, J. Phys. Chem., 30, 369 (1926).

(3) Obtained through the kindness of the Harshaw Chemical Company.

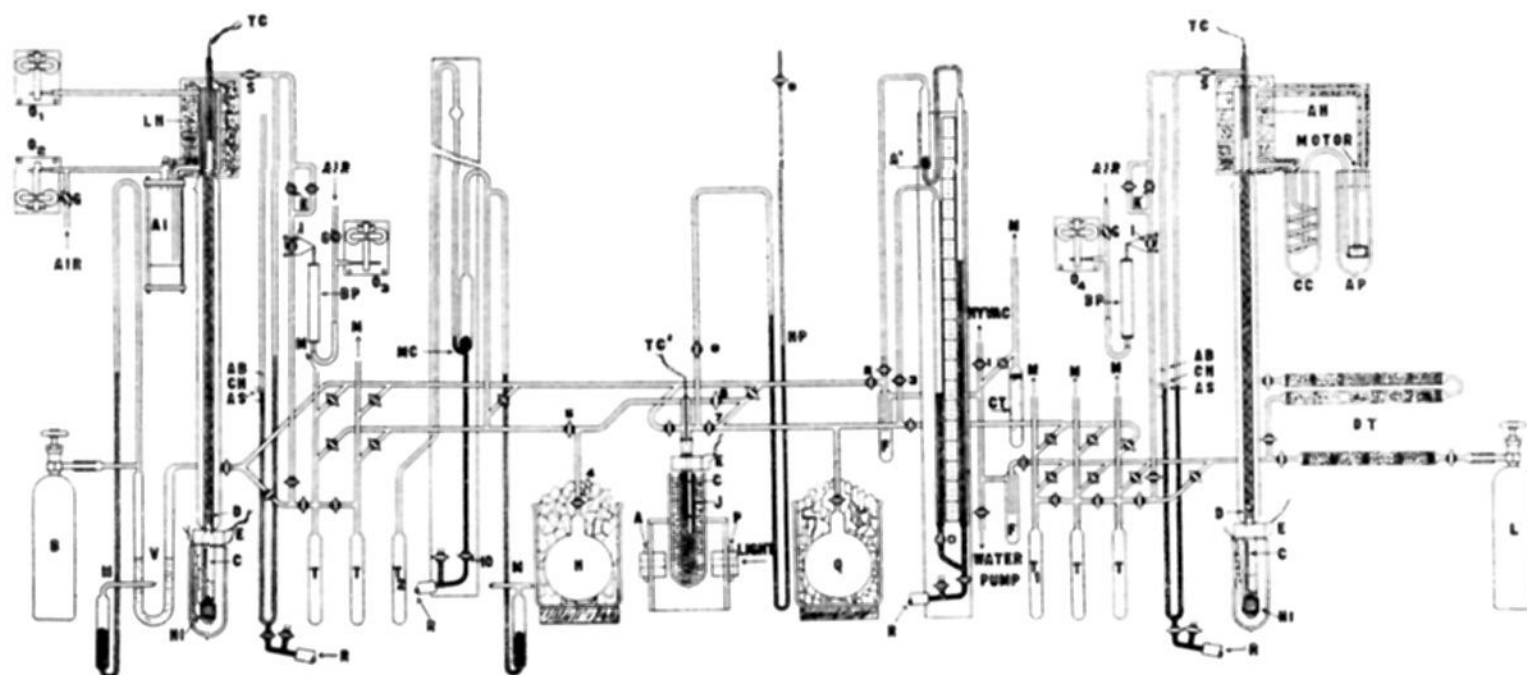(4) Booth and Bozarth, Ind. Eng. Chem., 29, 470 (1937).

Fig. 1.—Apparatus.

2. In a corresponding fashion the right side of the apparatus contained the fractionating column AH for purifying the gases whose systems with boron trifluoride were to be studied.

3. The freezing points of the liquefied gas mixtures were determined by a triple junction copper–constantan thermocouple TC in a thin-walled glass well (3 mm. in diameter) immersed in the freezing point cell J and recorded on a special Leeds and Northrup Micromax recording potentiometer yielding freezing point determinations accurate to ± 0.25 degree (see Fig. 2).

4. The first appearance of crystals on cooling was established in two ways: by the appearance of points of light in the field when the cell was placed between crossed nicols A, P, mounted in a light-proof box, and by the inflection in the cooling curves recorded on the potentiometer.[5]

In the early part of this investigation, on the system methyl chloride–boron trifluoride, we enjoyed the coöperation of Professor W. C. Fernelius of Ohio State University. In applying the procedure as described by Germann and Booth[2] to this system, difficulties in obtaining reproducible results were encountered which led us to undertake a study of the various sources of error in this method.

The following points presented themselves as factors which might in some way affect the accuracy of the determination of freezing points; (1) rate of cooling, (2) chart rate in the recording potentiometer, (3) diameter of freezing point cell, (4) immersion depth of thermocouple, and (5)

(5) Booth and Willson, THIS JOURNAL, **57**, 2273 (1935).

closeness of the thermocouple to the bottom of the freezing point cell.

Rate of Cooling.—By the use of a partially exhausted Dewar type container for the freezing point cell, it was possible to maintain a cooling rate of three to three and one-half degrees per minute. The moment when crystal formation started was detected by means of polarized light, using polarized disks as shown in Fig. 2.
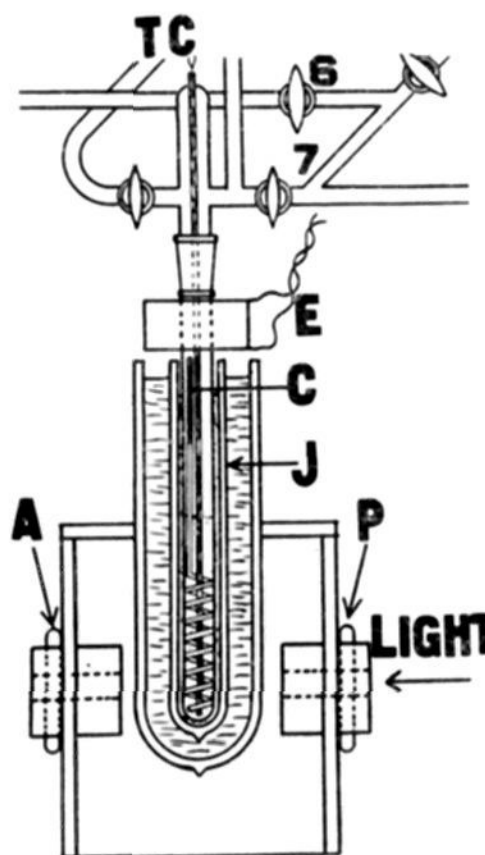

Fig. 2.

Chart Rate in Recording Potentiometer.—The recording potentiometer was found to give

optimum results at a chart rate of eight inches per hour corresponding to 4° min.$^{-1}$.

Diameter of Freezing Point Cell.—In this Laboratory it has been customary to build the freezing point cell of as small a diameter as possible, being just large enough to enable a glass spiral stirrer to operate smoothly between the inner wall of the freezing point cell and the outer wall of the glass thermocouple well. The small diameter freezing point cell was advantageous because it required less gas to give reliable freezing point data.

A study was made with two freezing point cells, one being 14 mm. outside diameter while the other was 19 mm. Provided the thermocouple was sufficiently immersed, reliable freezing point data could be obtained with either freezing point cell.

Immersion Depth of Thermocouple.—It has been reported that a sample depth of 7 cm. above the uppermost thermocouple junction is necessary to obtain reliable freezing point data.[4] With the 14-mm. freezing point cell, an immersion depth of 3.2 cm. above the uppermost thermocouple junction was necessary while the 19-mm. cell required an immersion depth of 3.8 cm. (see Fig. 3). We have found it a safe rule that the uppermost junction of the thermocouple using number thirty-two gage copper and constantan wire, should be immersed at least 4 cm. when the cell is to be used at temperatures around −100°.
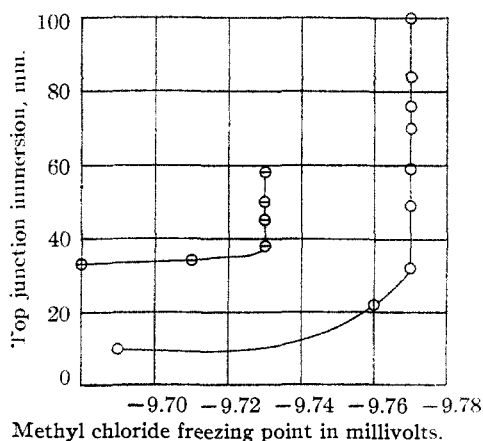

Methyl chloride freezing point in millivolts.

Fig. 3.—Effect of depth of thermocouple immersion on the freezing point: O, 14-mm. cell; ⊖, 19-mm. cell.

Closeness of Thermocouple to the Bottom of the Freezing Point Cell.—It was found that the distance of the thermocouple from the bottom of the freezing point cell had no effect upon the recorded temperature of the freezing point up to a

distance of 2 cm. The effect for more than 2 cm. was not studied.

The System Methyl Chloride–Boron Trifluoride

Since fluorine in its compounds is the only member of Group VII of the Periodic Table which has been found capable of donating to the boron atom of boron trifluoride, and since members of the third period of Groups V and VI were found also to donate, it was of interest to determine the behavior of chlorine in methyl chloride.

Second, acetyl chloride has been found to coordinate with boron trifluoride but there is a question as to whether it is the carbonyl oxygen[6] or the chlorine[7] which is donating to the boron atom of boron trifluoride.

Third, earlier work upon this system left some uncertainty as to whether or not a compound was formed. Germann and Cleaveland[8] working in this Laboratory in 1921 studied this system and reported that they obtained a maximum at 15 and 33 mole per cent. of boron trifluoride and an "angular point" at 50 mole per cent. Since they made their own methyl chloride from concentrated sulfuric acid, methyl alcohol and sodium chloride, they postulated that these maxima might be due to methyl ether which might have been present as an impurity. Since methyl ether and methyl chloride boil within 0.3° of each other, they are difficult to separate by distillation.

They continued the work later using some methyl chloride which had been made by chlorinating gas and after five distillations the system was reinvestigated. A simple curve with no maxima and with a eutectic point at 70 mole per cent. boron trifluoride was found.[9] An uncalibrated propane thermometer was used in their study for the determination of the freezing points and as a result all of the values were high.

The methyl chloride used in this investigation was obtained from the Ohio Chemical Company, dried over barium oxide, and fractionally distilled. The freezing points for various mixtures of boron trifluoride and methyl chloride are given in Table I and are plotted in the phase rule diagram, Fig. 4.

The methyl chloride was condensed and stored as a liquid using dry-ice as the refrigerant because when it was solidified, it made a crackling noise

(6) Brown, Schlesinger and Burg, THIS JOURNAL, **61**, 673 (1939).

(7) Meerwein and Maier-Hüser, J. prakt. Chem., **134**, 51 (1932).

(8) Germann and Cleaveland, Sci., **53**, 582 (1921).

(9) Marion Cleaveland, unpublished laboratory notes, Western Reserve University, Cleveland, Ohio, 1921.

Mole fraction[a] BF₃	Freezing point, °C.	Mole fraction[a] BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction[a] BF₃	Freezing point, °C.	Eutectic temp., °C.
0.000	− 96.7	0.348	−112.5		0.630	−140.5	
.000	96.6	.354	112.8		.638	144.4	
.036	98.2	.360	113.3		.651	144.1	
.067	99.3	.392	115.6		.666	144.1	
.094	100.2	.412	116.8		.688	143.1	
.117	101.1	.431	117.8		.702	142.4	
.128	101.3	.449	120.2		.725	141.0	
.160	102.7	.464	120.4		.751	138.9	−144.8
.194	104.0	.476	121.5		.776	137.2	
.225	105.4	.483	121.3		.807	135.6	
.253	107.0	.486	121.6		.833	134.0	
.279	108.3	.498	122.6		.845	133.3	
.302	109.6	.511	122.6		.845	133.0	
.308	109.9	.526	124.3		.858	132.2	
.318	110.6	.526	126.0		.873	132.4	
.323	111.0	.541	125.8		.885	131.4	
.327	111.5	.562	129.4		.905	130.7	
.331	111.6	.569	130.4		.925	130.0	
.335	111.7	.593	133.6		.948	129.2	
.339	111.8	.616	136.0		.973	128.1	
.342	112.2	.618	136.3	−144.7	1.000	126.8	
					1.000	126.6	

[a] Mole fractions were established according to the equation used by Germann and Booth.[2] This equation becomes $X_{BF_3} = cP_{BF_3}/(P_h + cP_{BF_3})$ where X_{BF_3} is the mole fraction of BF_3, c is the ratio of the volumes of the calibrated flasks $= 1.18910$, P_{BF_3} is the pressure exerted by the number of moles of BF_3 introduced into the freezing point cell, and P_h is the pressure exerted by the number of moles of other gaseous component introduced.

and occasionally broke the glass vessel into which it was being condensed.

The freezing point of the pure methyl chloride was found to be −96.65° and that of the pure boron trifluoride to be −126.7 ± 0.25°. A eutectic point was found at 65.5 mole per cent. boron trifluoride and −144.8 ± 0.25°. The curve is of the same type as found by Cleaveland.[9]

The results of the investigation of this system show that the chlorine atom of methyl chloride does not donate to the boron atom of boron trifluoride to form an addition compound at a pressure of one atmosphere.

Since it is the carbonyl oxygen of aldehydes and ketones which donates to the boron atom of boron trifluoride to form addition compounds, and since the chlorine atom has not been found to donate in methyl chloride, it seems logical to expect that it is the carbonyl oxygen of acetyl chloride which is donating to the boron atom of boron trifluoride to form that addition compound.

The System Hydrogen Chloride–Boron Trifluoride
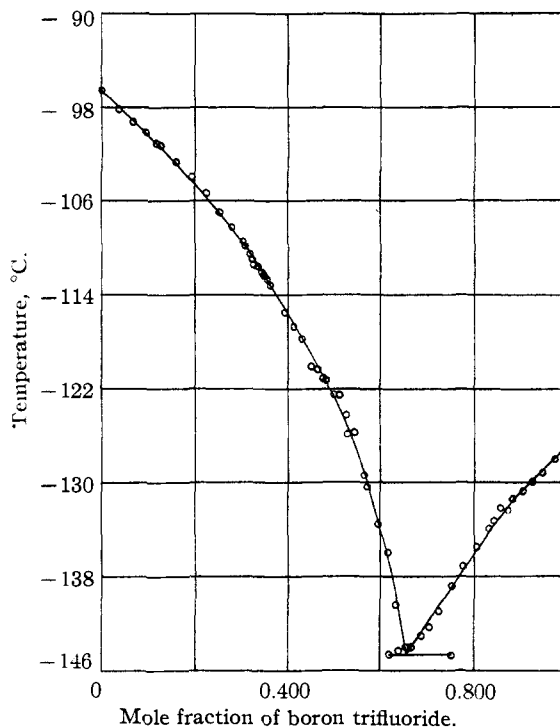
Hydrogen fluoride has been found to form three

Fig. 4.—The system methyl chloride–boron trifluoride.

addition compounds with boron trifluoride.[10] In each case, however, water was present so that it was the fluoride ion which was donating to the boron atom. It was of interest to see whether anhydrous hydrogen chloride would combine with boron trifluoride. Also, it was of interest to find out if the replacement of the methyl group of methyl chloride by hydrogen in the form of hydrogen chloride would affect the coördinating power of the chlorine atom. For these reasons the system hydrogen chloride–boron trifluoride was investigated.

The hydrogen chloride used in this investigation was prepared from hydrochloric acid and sulfuric acid, dried over phosphorus pentoxide, and fractionally distilled. Care had to be exercised in condensing the hydrogen chloride in the usual manner with liquid air as the condensing agent because when it solidified it broke the glass vessels. It was possible to avoid breakage of the freezing point cell by preventing the temperature of the pure hydrogen chloride from dropping more than 20° below its freezing point. This practice had to be followed until a mole fraction of about two-tenths boron trifluoride was reached.

Pure hydrogen chloride was found to freeze at

(10) Berzelius, Pogg. Ann., 2, 113 (1824); Landolph, Compt. rend., 86, 601 (1878); Hantzsch, Ber., 63, 1789 (1930).

TABLE II
DATA FOR SYSTEM HYDROGEN CHLORIDE–BORON TRIFLUORIDE

Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.
0.000	−113.0		0.500	−129.2	−134.2
.000	113.2		.500	129.4	134.2
.047	116.9		.525	129.4	134.1
.075	118.6		.551	130.1	134.2
.098	120.2		.569	130.3	134.1
.126	121.2		.600	131.2	134.2
.148	122.2		.622	131.4	134.1
.179	123.1		.647	132.2	134.2
.203	124.1		.675	133.3	134.1
.223	124.1		.698	133.7	134.2
.251	125.0		.723	134.1	
.285	125.5		.749	133.9	
.301	125.8		.778	133.2	133.7
.324	126.2		.795	133.3	
.350	126.8		.832	131.9	
.378	126.9		.850	131.6	
.403	127.8	−134.1	.897	130.5	
.425	127.8		.917	129.8	
.454	128.4	134.1	.953	128.7	
.485	128.5	133.3	1.000	127.0	
			1.000	127.0	

−113.1° and pure boron trifluoride at −127.0 ± 0.25°. A phase rule diagram was obtained with a eutectic point at 72.3 mole per cent. boron trifluoride and at a temperature of −134.15 ± 0.25°. The data are given in Table II and shown in Fig. 5.
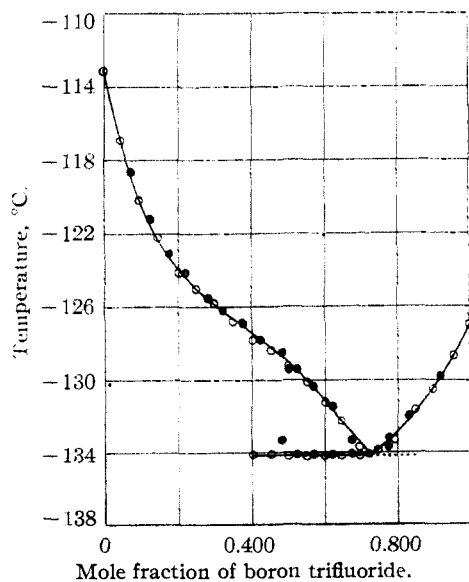

Fig. 5.—The system hydrogen chloride–boron trifluoride: O, first analysis; ●, second analysis.

In most systems where only one eutectic is found, the curve drops slowly with relation to the temperature in the vicinity of the pure components, and then drops rapidly in the vicinity of the eutectic point. The curve obtained with hydrogen chloride and boron trifluoride did just the opposite. This curve dropped rapidly in temperature in the vicinity of the pure components and more slowly in the vicinity of the eutectic point. A similar curve was found by Graff[11] for the system hydrogen chloride–boron trichloride.

As no addition compound was found, it appears that ionization may be the explanation of the difference between the action of hydrogen fluoride with boron trifluoride on the one hand, and of hydrogen chloride and boron trichloride, and of hydrogen chloride and boron trifluoride on the other hand. Also, Wiberg and Sütterlin[12] tried the reaction between hydrogen fluoride and boron trichloride and obtained as reaction products hydrogen chloride on the one hand and boron trifluoride on the other. An additional fraction having a vapor pressure between that of boron trifluoride and that of hydrogen chloride was obtained which had a molecular weight corresponding to the addition compound BF₃·3HCl analogous to BF₃·3HF. They postulated that the reaction between hydrogen fluoride and boron trichloride took place because the fluorine atom of the hydrogen fluoride, through its residual valence, reacted with the boron trichloride, probably forming as a first product in the liquid state BF₃·3HCl. If such a compound exists in the liquid state, it should have given a maximum in the phase rule diagram at 25 mole per cent. boron trifluoride. No maximum was found and we believe that they were mistaken in their conclusion.

It has been shown that the chlorine atom in both methyl chloride and in hydrogen chloride does not coördinate with the boron atom of boron trifluoride.

The System Nitrous Oxide–Boron Trifluoride

Over one hundred years ago, Kuhlmann[13] noted a reaction between the oxides of nitrogen and their respective acids with boron trifluoride, with the exception of nitrous oxide which he reported did not react. Germann and Booth[2] mention a reaction between nitric oxide and boron trifluoride. One would expect a reaction between nitrous oxide and boron trifluoride in the light of the addition compounds to which each of its constituents

(11) Graff, Compt. rend., 197, 754 (1933).
(12) Wiberg and Sütterlin, Z. anorg. allgem. Chem., 202, 37 (1931).
(13) Kuhlmann, Ann. chim. phys., [3] 2, 116 (1841); Ann., 39, 319 (1841).

give rise in their respective compounds. The nitrogen atom and the oxygen atom in their respective compounds have been found to donate to the boron atom of boron trifluoride to form addition compounds. Therefore, it was of interest to study the system nitrous oxide–boron trifluoride.

Anhydrous nitrous oxide, of anesthesia quality, from the Ohio Chemical Company, was dried over barium oxide before being fractionally distilled.

In order to fractionate this gas, because of the narrow liquidus range of 2.3°,[14] it was necessary to distil at a pressure of one and one-half atmospheres.

Due to the short liquidus range of nitrous oxide, the freezing point procedure was modified slightly. With pure nitrous oxide or with mixtures on that side of the system, the technique for melting the solid was modified. It was found best to warm gently the wall of the freezing point cell with acetone from the top of the cell to the bottom until it was certain that there was a very small space between the solid and the wall of the freezing point cell. Then the bottom of the cell was warmed rapidly by raising a small bottle of acetone around the bottom. In this manner, the solid at the bottom of the cell was all melted before the liquid on top had acquired too high a vapor pressure. Also, the stirrer was freed more rapidly and could

stir the liquid, which prevented an excessive pressure building up due to the liquid on top vaporizing.

The freezing point of the pure nitrous oxide was found to be −91.05° and that of the pure boron trifluoride −126.8 ± 0.25°. The phase rule diagram was a smooth curve with the eutectic occurring at 76.6 mole per cent. boron trifluoride and at a temperature of −138.0 ± 0.25° (see Table III and Fig. 6).
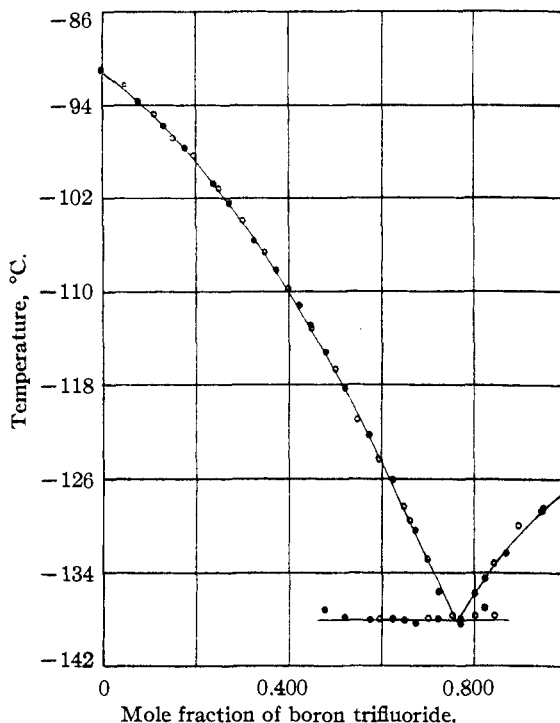

Fig. 6.—The system nitrous oxide–boron trifluoride: O, first analysis; ●, second analysis.

The investigation of this system confirmed the report of Kuhlmann[18] that nitrous oxide and boron trifluoride do not react. The explanation for this is not clear.

The System Sulfur Dioxide–Boron Trifluoride

The sulfur atom and the oxygen atom in their respective compounds have been found to donate to the boron atom of boron trifluoride to form coördination compounds. A compound made up of these two atoms would be expected to coördinate with boron trifluoride. Therefore, the system sulfur dioxide–boron trifluoride was investigated.

The anhydrous sulfur dioxide was obtained from the Ohio Chemical Company, dried over phosphorus pentoxide, and fractionally distilled. The freezing point of the pure sulfur dioxide was

TABLE III

DATA FOR SYSTEM NITROUS OXIDE–BORON TRIFLUORIDE

Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.
0.000	− 91.0		0.501	−116.7	
.000	91.1		.522	118.3	−137.9
.050	92.3		.550	121.0	
.079	93.7		.576	122.3	138.1
.111	94.8		.598	124.4	138.0
.131	95.8		.626	126.1	138.0
.151	96.9		.650	128.4	138.1
.178	97.7		.664	129.5	
.197	98.4		.675	130.4	138.3
.240	100.8		.701	132.9	137.9
.251	101.2		.724	135.6	138.0
.273	102.5		.754	137.7	
.303	104.0		.771	137.9	138.4
.327	105.7		.802	135.8	137.7
.350	106.7		.826	134.5	137.0
.375	108.2		.847	133.2	137.7
.400	109.8		.871	132.3	
.425	111.3		.898	130.0	
.450	113.0		.949	128.7	
.451	113.3		.950	128.5	
.480	115.3	−137.2	1.000	126.8	
			1.000	126.8	

(14) Blue and Giauque, THIS JOURNAL, 57, 991 (1935).

found to be $-73.5°$ and that of the pure boron trifluoride to be $-126.75 \pm 0.25°$. A maximum was found at 50 mole per cent. of boron trifluoride, indicating a one to one addition compound between sulfur dioxide and boron trifluoride, whose freezing point was found to be $-96.0 \pm 0.25°$. Eutectic points were found on each side of this maximum. One was found to exist at 38.0 mole per cent. boron trifluoride and at a temperature of $-97.15 \pm 0.25°$, while the other eutectic point was found at 95.2 mole per cent. of boron trifluoride and $-128.6 \pm 0.25°$ (see Table IV and Fig. 7).
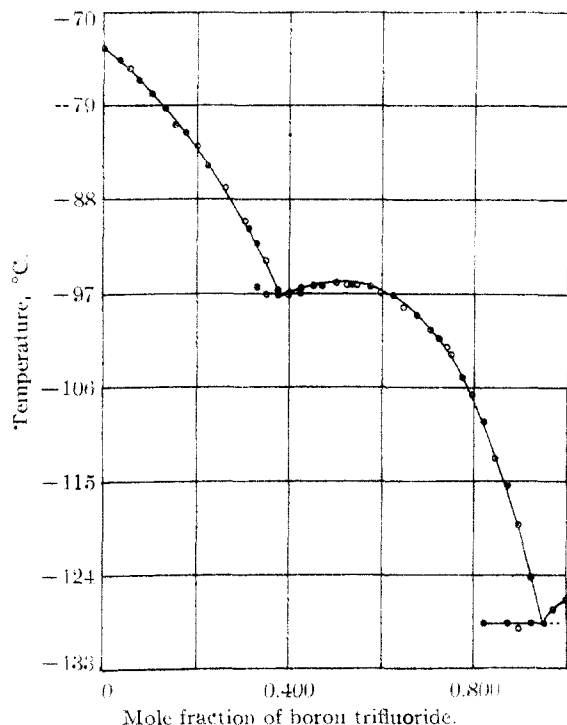

Fig. 7.—The system sulfur dioxide–boron trifluoride: O, first analysis; ●, second analysis.

From the flatness of the maximum obtained it is obvious that the compound is somewhat dissociated above the melting point.

Liquid sulfur dioxide has been found to be a solvent analogous to water and liquid ammonia. Extensive work has been done in this field since 1936 by Jander and his co-workers.[15] Liquid sulfur dioxide is a good solvent for organic and inorganic substances, the solutions being good electrical conductors, while sulfur dioxide itself is a poor conductor. The solutes have been found to be more or less dissociated. The results of their

(15) Jander and Wickert, *Z. physik. Chem.*, **A178**, 57 (1936), is the first article of a series. The last to appear is Part 10. Jander and Mesech, *ibid.*, **A183**, 277 (1939).

TABLE IV

DATA FOR SYSTEM SULFUR DIOXIDE–BORON TRIFLUORIDE

Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.	Mole fraction BF₃	Freezing point, °C.	Eutectic temp., °C.
0.000	−73.5		0.524	−96.2	
.000	73.5		.535	96.2	
.034	74.6		.547	96.2	
.055	75.4		.576	96.4	
.077	76.5		.598	97.0	
.105	77.8		.625	97.2	
.132	79.2		.648	98.4	
.154	80.8		.676	99.2	
.177	81.5		.705	100.5	
.201	82.8		.725	101.4	
.223	84.7		.742	102.2	
.261	86.9		.750	102.9	
.303	90.1		.774	105.0	
.311	90.8		.798	106.8	
.331	92.3	−96.4	.823	109.3	−128.6
.350	93.9	97.1	.847	112.8	
.378	96.7	97.1	.874	115.4	128.6
.400	97.0	97.2	.898	119.2	129.2
.426	96.5	97.1	.926	124.2	128.6
.453	96.2		.952	128.6	
.473	96.3		.972	127.3	
.500	96.0		1.000	126.8	
.501	96.0		1.000	126.7	

experiments have been explained on the assumption of the following types of dissociation of other solvents

$$2 H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$2 NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$
$$2 SO_2 \rightleftharpoons SO^{++} + SO_3^{--}$$
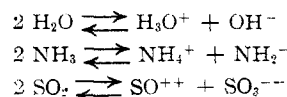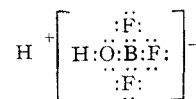
Wickert,[16] who also has been working with liquid sulfur dioxide, suggested that the dissociation of sulfur dioxide might also be written

$$SO_2 \rightleftharpoons SO^{++} + O^{--}$$

The structure of this compound with boron trifluoride might be

$$S:O]^{++} \left[\begin{array}{c} :F: \\ :O:B:F: \\ :F: \end{array} \right]^{--}$$
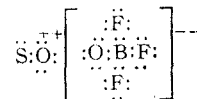
analogous to the monohydrate of boron trifluoride

$$H^+ \left[\begin{array}{c} :F: \\ H:O:B:F: \\ :F: \end{array} \right]^-$$

It is this dissociation which would have to take place in order to form the above addition compound with boron trifluoride. This addition compound would fit into the "sulfito" system of acids, bases and salts as developed by Jander.[15] The boron trifluoride addition compound would
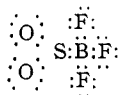
(16) Wickert, *Z. Elektrochem.*, **44**, 410 (1938).

be an acid in the sulfur dioxide system just as it is an acid in the water system.

Hägg[17] has explained the ease of oxidation of sulfur dioxide up to sulfur trioxide as being due to the electron pair on the sulfur. Thus

$$:\ddot{O}:\ddot{S}:\ddot{O}: + :\ddot{O}: = :\ddot{O}:\ddot{S}:\ddot{O}:$$
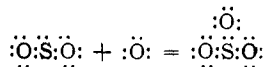
Thus, we could write the one to one addition compound with boron trifluoride

$$\begin{matrix} :\ddot{O}: & :\ddot{F}: \\ & S:\ddot{B}:\ddot{F}: \\ :\ddot{O}: & :\ddot{F}: \end{matrix}$$

The fact that hydrogen sulfide formed the compound $H_2S \cdot BF_3$,[2] where only the sulfur can be the donor, would permit this latter mechanism.

Regardless of which structural formula represents sulfur dioxide, it is possible to account for

(17) Hägg, Z. physik. Chem., **B18**, 199 (1932).

the addition compound between the given structure and boron trifluoride.

Summary

In the present investigation it has been found that hydrogen chloride and methyl chloride give eutectics and no compounds with boron trifluoride, showing that, at least in these two compounds, chlorine does not act as a donor to boron trifluoride, thus refuting the existence of the reported compound $BF_3 \cdot 3HCl$.

It has been found further that nitrous oxide also will form no compound with boron trifluoride although it has been reported that nitric oxide does. Sulfur dioxide, just as the other parent solvents, water and ammonia, forms a one to one compound with boron trifluoride and two eutectics.
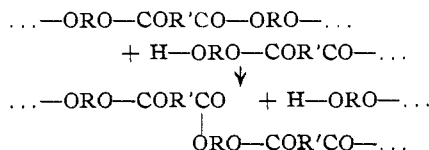

Random Reorganization of Molecular Weight Distribution in Linear Condensation Polymers[1]

BY PAUL J. FLORY

In a recent publication[2] concerned with the viscosities of molten polyesters, it was observed that the viscosity of a mixture of two polyesters decreases when heated. This decrease was attributed tentatively to a change in the distribution of molecular species in the mixture, brought about by the occurrence of ester interchange between terminal hydroxyl groups and ester groups of the polymer chains

$$\ldots -ORO-COR'CO-ORO- \ldots$$
$$+ H-ORO-COR'CO- \ldots$$
$$\downarrow$$
$$\ldots -ORO-COR'CO \quad + H-ORO- \ldots$$
$$|$$
$$ORO-COR'CO- \ldots$$

where —ORO— and —COR'CO— represent, respectively, the glycol and the dibasic acid residues of a linear polyester formed through polycondensation of a glycol and a dibasic acid. As the result of such an interchange process, an x-mer may react with a y-mer to yield a $(y + z)$-mer and an $(x - z)$-mer. There is no net change in the number of molecules; hence, the number

(1) A portion of this work has been discussed briefly by H. Mark and R. Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, 1941, p. 147.

(2) P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

average molecular weight will be unaffected by reorganization processes of this sort. On the other hand, the distribution of species may be altered, and changes in distribution will produce corresponding changes in the weight average molecular weight. Since the viscosity of the molten polyester, composed of a mixture of polymeric species, depends directly on the weight average molecular weight,[2] the viscosity will be sensitive to changes in distribution caused by ester interchange, and these changes can be observed conveniently through viscosity measurements.

Investigations of rates of formation of polyesters and of their degradation[3] by monomeric alcohols have shown that the rate constant for alcoholysis, though somewhat smaller, is similar in magnitude to that for esterification under the same conditions. The two reactions are similarly affected by catalysts and temperature. After polyesterification has proceeded to the point where the average molecular weight is large, the free carboxyls are so overwhelmingly outnumbered by ester groups that the rate of reaction of the free hydroxyls with ester groups will exceed their rate

(3) P. J. Flory, ibid., **62**, 2255, 2261 (1940).