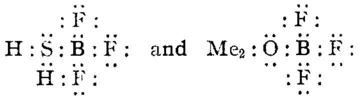
[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Thermal Analysis of the System Argon–Boron Trifluoride. Compounds with the Inert Gases of the Atmosphere[1,2]

BY HAROLD SIMMONS BOOTH AND KARL STUART WILLSON

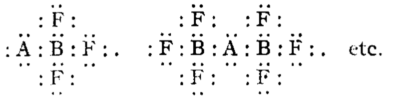
Although numerous attempts have been made to prepare compounds of the rare gases, practically all investigations have served only to show the inertness of these elements. Villard,[3] however, in 1896, reported a very unstable hydrate of argon, and since then hydrates of krypton and xenon[4] have been reported.

For some time this Laboratory has been studying compounds formed by boron trifluoride in which boron acts as acceptor for electrons from an element in another compound, usually an element with a completed octet such as oxygen in methyl ether and sulfur in hydrogen sulfide,[5] *i. e.*



$$\begin{array}{lcl} \qquad\quad :\ddot{\mathrm{F}}: & & \qquad\qquad\quad :\ddot{\mathrm{F}}: \\ \mathrm{H}:\ddot{\mathrm{S}}:\ddot{\mathrm{B}}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: & \text{and} & \mathrm{Me_2}:\underset{\cdot\cdot}{\ddot{\mathrm{O}}}:\ddot{\mathrm{B}}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: \\ \quad\;\; \mathrm{H}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}: & & \qquad\qquad\quad :\underset{\cdot\cdot}{\mathrm{F}}: \end{array}$$

It seemed reasonable to expect therefore that under the right conditions boron trifluoride could likewise accept electrons from elements such as argon which have self-contained octets, *i. e.*



$$\begin{array}{lll} \qquad :\ddot{\mathrm{F}}: & \qquad\quad :\ddot{\mathrm{F}}:\;\; :\ddot{\mathrm{F}}: & \\ :\underset{\cdot\cdot}{\ddot{\mathrm{A}}}:\underset{\cdot\cdot}{\ddot{\mathrm{B}}}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:. & :\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:\underset{\cdot\cdot}{\ddot{\mathrm{B}}}:\underset{\cdot\cdot}{\ddot{\mathrm{A}}}:\underset{\cdot\cdot}{\ddot{\mathrm{B}}}:\underset{\cdot\cdot}{\ddot{\mathrm{F}}}:. & \text{etc.} \\ \qquad :\underset{\cdot\cdot}{\mathrm{F}}: & \qquad\quad :\underset{\cdot\cdot}{\mathrm{F}}:\;\; :\underset{\cdot\cdot}{\mathrm{F}}: & \end{array}$$

Preliminary Study.[6]—Preliminary experiments were made with an apparatus similar to that used for thermal analysis of the systems mentioned above, save that the freezing points were measured by a two-junction copper–constantan thermocouple recorded by a special Leeds and Northrup Micromax potentiometer.

The first appearance of crystals on cooling was established in three ways: by the appearance of points of light in the field when the cell was placed between crossed Nicols, by the inflection in the cooling curves recorded on the potentiometer, and visually. It was found that the three methods of observation checked. Freezing point curves, one of which is shown in Fig. 1, revealed maxima and minima indicating compound formation corresponding to $A\cdot 8BF_3$ and $A\cdot 16BF_3$. However, the relatively large volume in the gas space above the liquid mixture permitted some segregation of the mixture, thus displacing the curve.

This was finally overcome by adopting the basic design of the Cailletet apparatus, using a fine capillary connecting tube and a relatively large cell similar to that used earlier in this Laboratory for determining the critical phenomena of pure gases[7] and gas mixtures.[8]

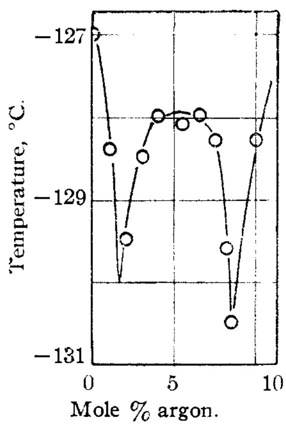


Fig. 1.—Preliminary freezing points.

Apparatus.—The all glass apparatus for preparing the samples is shown in Fig. 2. Cailletet sample tubes of Pyrex glass were joined to the system by the ground glass conical joints (J). The sample tube (L) had a volume of about 100 cc. and the cell itself where the phenomena were to be observed had a volume from 0.1 to 0.5 cc. depending on the composition of the mixture being studied. If the cells were too large, the mercury would freeze in the capillary above the cell before many points had been determined, and if the cells were too small, liquid would rise into the capillary, adequate stirring could not be obtained and erroneous results would be secured.

The mixture in the cell was stirred by the glass enclosed iron wire actuated by the electromagnets shown in Fig. 3. The lower magnet was found helpful in securing positive stirring action at the freezing point and at other points where the liquid became viscous.

Pressure was measured by a differential dead-weight gage used by Booth and Swinehart[7] which under the conditions of this investigation was observed to ±0.1 atm.

Temperature was recorded by a special high speed, high precision Leeds and Northrup Micromax potentiometer using copper–constantan thermocouples described later.

Ordinary stopcock grease is attacked by boron trifluoride but a mixture of four parts of white vaseline and one

---

(1) From a part of a thesis submitted by K. S. Willson to the Graduate Faculty of Western Reserve University, May, 1935, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) On the advice of the Editor we withheld publication of a preliminary note submitted July 17, 1932.

(3) Villard, *Compt. rend.*, **123**, 377 (1896).

(4) DeForcrand, *ibid.*, **176**, 355 (1923); **181**, 15 (1925).

(5) Germann and Cleaveland, *Science*, [2] **53**, 582 (1922); Germann and Booth, *J. Phys. Chem.*, **30**, 369 (1926).

(6) During the preliminary part of this investigation, we enjoyed the collaboration of Mr. M. J. Bahnsen of this Laboratory.

(7) Booth and Carter, *J. Phys. Chem.*, **36**, 1359 (1932); Booth and Swinehart, THIS JOURNAL, **57**, 1337 (1935).

(8) Booth and Carter, *J. Phys. Chem.*, **34**, 2801 (1930).

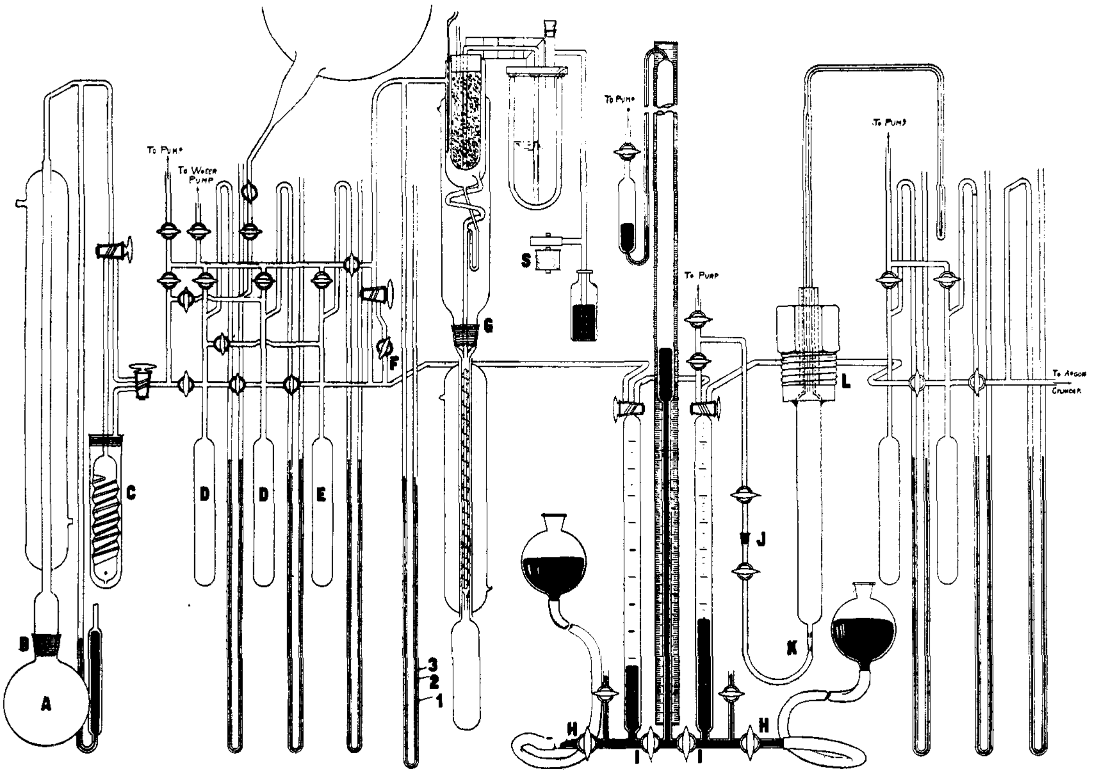


Fig. 2.

part of paraffin, saturated with boron trifluoride at 140°, then evacuated and 5% beeswax added, was found to be satisfactory.

Preparation of the Samples.—The boron trifluoride was prepared from sodium fluoborate (300 g.), boric oxide (50 g.) and sulfuric acid (300 cc.). The solid chemicals were mixed, placed in the flask (A) (Fig. 2), the acid added and the liquid mass thoroughly mixed. The flask was joined to the system by the greased conical joint (B). A rubber sleeve was placed over the joint and water circulated around it in an inverted bottle with bottom removed. The water prevented melting of the grease with subsequent sticking or leaking at the joint.

Since any silicon tetrafluoride, formed from impurities in the sodium fluoborate, was evolved at room temperature and boron trifluoride was not, the tetrafluoride was largely removed along with air, by pumping the flask with the stopcocks turned to by-pass the wash-bottle (C). After rinsing the entire system, except the generating unit and wash-bottle (C), twenty times with dry, carbon dioxide-free air, the stopcocks were reversed to include the wash-bottle, and the charged flask heated, gently at first, to avoid frothing. The boron trifluoride generated passed through the water-cooled condenser, the wash-bottle filled with sulfuric acid saturated with boric oxide to remove water and hydrogen fluoride and, after discarding the first part of the generation product through the water pump, was condensed in the ampoules (D) by means of liquid nitrogen. This method gave little silicon tetrafluoride, and by distilling to (E) and then to the still pot at a low pressure and discarding the tailings, little of the tetrafluoride was carried into the still.

The boron trifluoride was purified in the distilling column (G) described by Booth and Stillwell.[9] By distilling at about 10 cm. pressure, the temperature was such that the vapor pressure of silicon tetrafluoride, the most probable impurity, was very small and the absence of this substance in the purified gas was doubly assured. The gas, after a single distillation in the column using great care to rinse the lines with the pure gas before collecting in the ampoule, was shown to be spectroscopically pure by Mr. H. M. Strong of the Physics Department at Ohio State University.

At the beginning of series D the still head cracked and a new head of simpler design[10] was used with satisfactory results.

In operation, the boron trifluoride was permitted to reflux about fifteen minutes after any air blocks had been removed. The gas was then bled off very slowly by "cracking" the stopcock at (F), being sure that a high reflux ratio was maintained. After discarding the first few cc. of the solid distillate, about one-fifth of the gas was condensed in the nearest ampoule (D), then the middle three-fifths in the ampoule (E) where it was held until used to rinse the mixing apparatus and sample tubes, and to prepare the samples.

The argon, 99.9 + pure, was condensed from the cylinder into ampoules and then further purified by ampoule to ampoule distillation with generous discarding of first and last portions. After this treatment it was found to be spectroscopically free from nitrogen by Mr. Strong.

The purified gases were introduced into their respective

---

[9] Booth and Stillwell, THIS JOURNAL, **56**, 1529 (1934).

[10] To be described shortly by Booth and Bozarth.

burets of the baro-buret which had been previously dried and rinsed with the pure gases, and the pressures and volumes recorded as described by Booth and Carter.[8]

After measuring each gas, thorough mixing was assured by forcing the gases alternately from one buret to the other.

Meanwhile, the sample tubes were rinsed twenty times with dry, carbon dioxide-free, air, being flamed while pumping, and were then rinsed twenty more times with pure boron trifluoride and argon, allowing the gases to remain in the tubes some time before pumping.

The gas mixture was introduced into a sample tube to a pressure a centimeter or two less than one atmosphere. Stopcocks above and below the conical joint (J) were closed, the sample tube removed from the apparatus, and the tube broken off under dry mercury at the constriction (K). The inner seal prevented bits of glass from rising into the body of the tube. The sample tube was then placed in the steel well as shown in Fig. 3, keeping the lower end under mercury, and screwed down onto the fiber gasket. After connecting the pump line, pressure was increased to test for leaks and weakness in the glass. After releasing the pressure, the bath was raised to surround the cell.

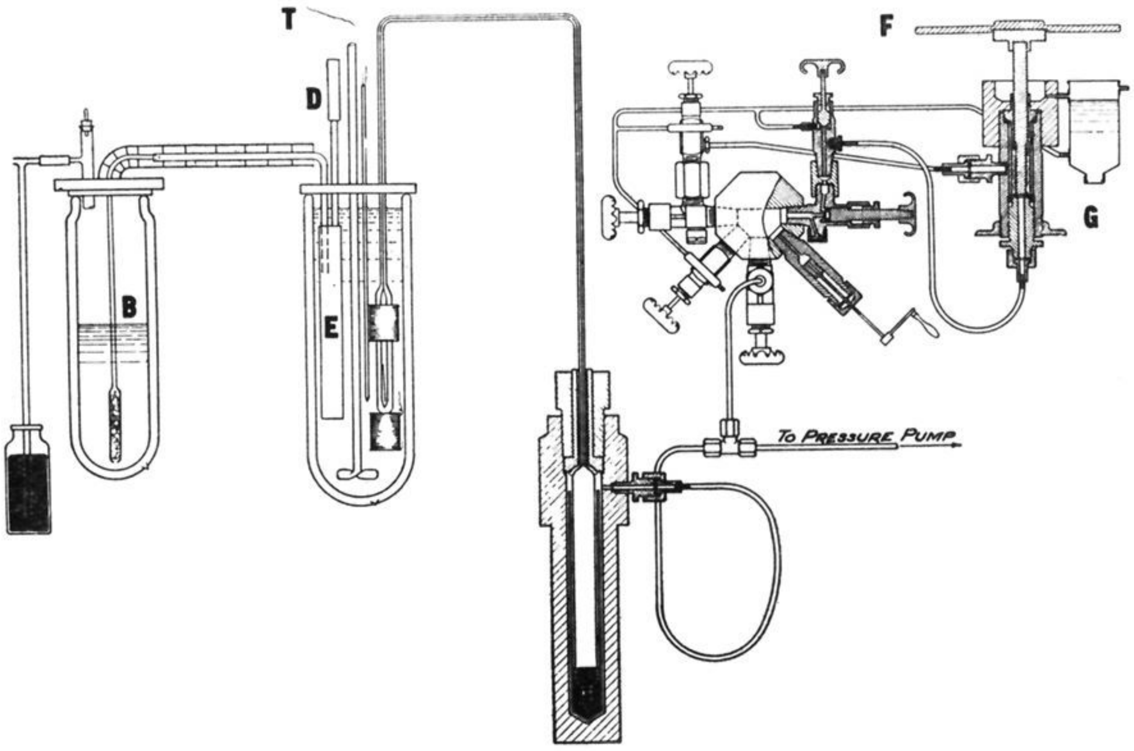


Fig. 3.

Experimental Procedure

For the freezing point determinations weights were placed on the piston of the dead weight gage and the pressure equilibrium established while the liquid butane bath was cooling. Liquid nitrogen was forced into the evaporator (E) (Fig. 3), rapidly at first, then slowly as the freezing point was approached. By adjusting a screw clamp at (D), cooling could be secured at less than 0.3° per minute, this having been found a sufficiently slow rate to prevent error due to lag in the cell, thermocouples or recorder. In the first determinations, a current was passed through a heater coil in the bath to adjust the rate of cooling, but this was later found unnecessary.

When the first crystals appeared, the temperature was noted. Since warming the sample after obtaining a freezing point would cause argon to boil off, giving rise to segregation, care was taken to raise the temperature as little above the freezing point as possible, usually not more than 3°. While the temperature was rising, more weights were placed on the piston, thus decreasing the volume of the gas and preventing segregation due to expansion. Pressure was increased and freezing points determined until the liquid rose into the capillary, preventing mixing, or until the mercury froze in the capillary.

The freezing point determinations were made in five different series.

Series A covered the preliminary work shown in Fig. 1, while series B, C, D and E were made with the Cailletet apparatus.

Series B includes all points measured by a two-junction thermocouple which had a total maximum error of ±0.4°. Ice served as the reference point. In series C, D and E greater precision was obtained by using a five-junction thermocouple with carbon dioxide snow as the reference point. The snow point was found to remain constant for long periods and was checked against an ice-bath by an identical five-junction thermocouple several times during a set of freezing point determinations. By this method a maximum error of ±0.2° in the differential temperature was secured although considerably greater accuracy was obtained since the final freezing point was the average of many values. The two and five-junction couples were also checked against each other.

The absolute temperature in the region of the freezing points was secured by comparing the couples with a platinum resistance thermometer, and by extrapolating from −123.3°, the freezing point of ether. The absolute temperature of the freezing points therefore probably shows the same order of error as the differential temperature.

After completing series C the entire purification apparatus was rebuilt to eliminate stopcock grease which had contaminated the lines. A new stopcock grease was made and new drying tubes installed. The five-junction thermocouple was recalibrated, found to check its previous value and series D and E undertaken. In series B and C, liquid nitrogen was forced into the evaporator (E) at a rapid cooling rate, adjusted by controlling the heat input of the heater. In series D and E the liquid nitrogen input was considerably slower and was adjusted to give the desired cooling rate without using the heater. The agreement between the values for the different series indicates the constancy of temperature maintained in the bath by means of the propeller, which was driven at 3600 r. p. m.

Before beginning series E every possible source of error was considered and all precautions for purity of the samples were redoubled. The cells were rinsed and flamed even more thoroughly, and the mercury used for the Cailletet well was run through a nitric acid tower and dried instead of merely washed and dried before each run.

To eliminate silicon tetrafluoride as much as possible even from the crude generation product which might contaminate the lines, fresh boron trifluoride was made using ammonium instead of sodium fluoborate. The ammonium fluoborate was recrystallized by cooling with agitation from a hot solution to give only a 50% yield, thus leaving the more soluble fluosilicates in the mother liquor.

In series D and E, before making up the samples the boron trifluoride was distilled in the column to a constant melting point measured in a cell similar to that used in the preliminary runs and stored under a mercury seal out of contact with stopcocks (not shown in Fig. 2).

TABLE I

FREEZING POINTS

Series B—Two-Junction Thermocouple

Mole % argon	Pressure, atm.	T., °C.
1.0	2.8	−130.6
2.0	3.8	131.2
3.0	2.3	130.6
	2.8	130.6
	4.0	130.4
	4.8	130.4
5.0	7.9	129.4
	9.8	129.4
	12.0	129.2
	14.1	129.2
18.5	27.9	129.2
	29.0	129.4
	33.0	129.2
	33.0	129.0
	36.7	128.8
	40.5	129.0
20.2	13.8	131.9
	30.6	130.0
	38.2	129.9
30.0 A	10.2	133.5 A
30.0 B	15.3	133.5 B
	25.5	132.3 A
	27.9	132.5 B
	39.3	131.7 A
	55.6	131.6 A
40.1 A	10.7	133.3 A
39.9 B	11.8	133.1 B
	11.9	133.1 A
	18.8	131.7 B
	20.3	131.9 A
	29.2	131.7 A
	31.1	131.7 A
	39.3	131.7 A
59.9	22.2	131.4
	24.5	131.4
	36.3	131.2

TABLE II

FREEZING POINTS

Series C—Five-Junction Thermocouple

Pressure, atm.	Temp., °C.
17.0 Mole % argon	
8.7	−131.2
14.0	130.1
19.4	129.5
21.3	129.4
26.7	129.0
29.5	128.6
33.0	128.6
52.5	128.3
18.5 Mole %	
9.6	131.8
12.3	131.1
19.0	129.9
32.3	129.3
19.9 Mole %	
12.9	131.3
15.6	130.9
19.4	130.5
22.8	130.3
24.5	130.3
28.2	130.1
32.3	129.8
34.0	129.6
21.3 Mole %	
8.9	131.5
11.6	131.2
15.4	130.3
15.4	130.1
18.9	129.3
19.7	129.3
20.6	129.1
22.7	129.0
22.9	129.3
24.6	129.0
25.5	129.0
27.0	129.2
28.7	129.0
29.2	129.0
32.3	129.1
32.3	128.6
34.7	129.0
34.7	128.5
22.9 Mole % argon	
9.0	−131.0
10.8	130.7
17.8	130.2
18.0	130.1
21.5	129.2
21.5	129.1
23.7	129.3
30.0	129.0
32.8	128.7
36.5	128.6
38.2	128.4
40.6	128.6
25.0 Mole %	
12.3	129.6
15.4	129.3
19.0	129.1
21.1	129.0
24.8	128.7
28.3	128.2
30.3	128.3
36.9	128.4
33.3 Mole %	
11.6	129.0
15.4	128.6
19.0	128.3
24.5	128.0
28.5	127.4
31.8	127.6
34.1	127.4
37.7	127.1
41.7	127.2
43.1	127.3
50.0 Mole %	
13.0	130.3
16.7	129.6
19.0	129.2
22.6	129.1
24.9	128.6
28.5	128.4
30.4	128.4
34.1	128.7
37.7	128.6

Results.—The freezing points are found to increase with increase in pressure at first and then become independent of further increase in pressure within the experimental limits. This is exactly what would be expected with unstable compounds. Thus, at low pressures, the compound formed will be appreciably dissociated, shifting the equilibrium

$$A + xBF_3 \rightleftharpoons A \cdot xBF_3$$

to the left. The A and BF_3 units acting as impurities in the compound A·$x$$BF_3$, will lower its freezing point as shown in region A, Figs. 4–6. As the pressure is increased, the equilibrium will shift to the right and less A and BF_3 units will be present, hence the freezing point will be lowered to a lesser extent.

As more and more pressure is applied, the equilibrium will shift farther and farther to the right and the freezing point will be raised until the separate A and BF_3 particles are present in too small quantities to lower the freezing point appreciably. The freezing point will then, of course, become independent of further increase in pressure as shown in region B, Figs. 4–6. The normal effect of increase in pressure tending to change the melting point in the direction of decreasing vol-

TABLE III

FREEZING POINTS

Series D—Five-Junction Thermocouple

Press., atm.	Temp., °C.
1.3 Mole % argon	
3.2	−131.0
4.9	130.9
5.9	131.0
2.5 Mole %	
3.2	130.9
6.5 Mole %	
9.2	130.0
10.5	130.9
11.2	130.2
7.5 Mole %	
3.2	130.2
5.1	130.3
8.5 Mole %	
10.8	131.7
12.6	131.8
12.6	131.5
10.9 Mole %	
5.1	129.6
8.9	129.5
10.6	129.6
12.6	129.3
15.1	128.8
16.7	128.5
18.1	128.4
19.4	128.4
26.0 Mole %	
8.9	129.6
11.6	129.2
17.0	128.4
19.0	128.2
21.8	128.1
26.1	128.2
28.3	128.1
32.4	128.2[a]
36.0	128.2
42.9 Mole %	
17.4	130.6
19.5	130.2
21.2	130.1
26.6	130.1
28.9	130.0
30.5	130.0
34.5	129.5[a]
38.0	129.1
39.8	129.1
46.1 Mole %	
9.3	−131.3
15.4	130.3
17.1	130.2
19.5	129.7
21.2	129.7
24.3	129.6
27.7	129.3
29.6	129.4
30.5	129.0
34.1	129.0
34.8	129.0
35.5	128.8
38.1	128.8[a]
39.7	128.8
50.0 Mole %	
11.6	130.9
15.4	130.1
19.5	130.0
21.2	129.7
25.3	129.4
28.9	128.9
30.4	128.8
34.1	128.8
38.0	128.6[a]
57.2 Mole %	
8.9	131.4
11.6	130.8
17.1	130.5
19.5	129.8
22.9	129.5
27.0	129.4
34.6	129.0
38.0	128.4[a]

TABLE IV

FREEZING POINTS

Series E—Five-Junction Thermocouple

Press., atm.	Temp., °C.
12.5[b] Mole % argon	
7.3	−130.5
8.7	130.4
11.0	130.2
15.6	129.5
19.2	129.1
20.8	128.8
22.7	128.8
13.5[b] Mole %	
8.7	130.7
9.9	130.9
13.0	130.3
15.5	129.7
25	128.8
15.0[b] Mole %	
5.6	129.8
7.3	129.7
9.3	129.7
11.0	129.7
13.3	129.5
15.7	129.1
21.0	128.7
25.0	128.3
28.2	128.3
28.0 Mole %	
11.6	130.5
13.3	130.1
15.4	129.8
19.0	129.3
21.2	129.0
24.8	128.7
28.3	128.2
30.0	128.2
31.0	128.2
34.0	128.0
35.6	127.9[a]
37.0	127.8
37.7	127.8
38.2	127.9
31.4 Mole % argon	
11.6	−131.6
13.3	130.9
15.3	130.5
19.0	129.8
21.1	129.3
22.8	129.2
24.4	129.0
26.1	128.6
28.3	128.3
30.0	128.3
31.6	128.2
33.9	128.3
36.0	128.2[a]
38.3	128.2
39.0	128.3
35.8 Mole %	
11.6	131.2
13.3	130.7
15.7	130.5
17.4	129.7
19.4	129.7
25.5	129.6
27.9	129.4
32.5	129.7
34.4	129.4[a]
37.9	129.3
36.9 Mole %	
11.6	132.4
13.3	132.2
22.9	131.1
25.2	130.6
28.7	130.2
30.4	130.2
34.0	129.9
36.0	129.7
36.6	129.9
37.3	129.9[a]
37.7	129.9

[a] At this and higher pressures a second liquid layer immiscible with the first was noted.

[b] This sample under-cooled considerably but the results are believed accurate to better than ±0.3° since melting points as well as freezing points could be obtained.

ume, is too slight to be measurable with the present method.

One would expect the freezing points to approach some final value asymptotically as the pressure increases. The exact curve, however, is difficult to predict and would not differ to any great extent from the straight lines shown in the figures. No significance is attached to the inflection point as drawn.

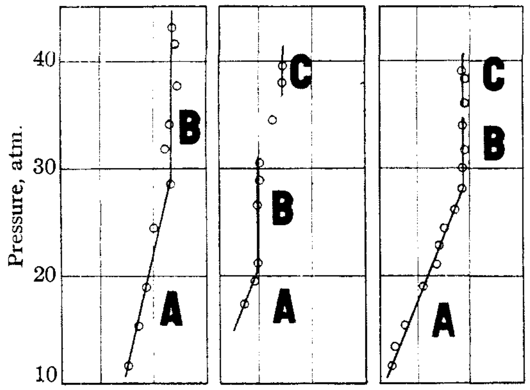


Fig. 4.—33.3 Mole % argon. Fig. 5.—42.9 Mole % argon. Fig. 6.—31.4 Mole % argon.

For the samples of less than 5% argon, the liquid fills the cells after only one or two readings are taken, and hence an extended pressure range cannot be studied. However, these compositions seem to be stabilized at low pressures, and the points secured are probably for pressures above the decomposition pressure.

The freezing of the samples occurred differently depending on the composition and consequently the place on the curve. For compositions not at maxima or minima a few crystals appeared at first followed by more and more if the temperature was allowed to decrease further. However, stirring could be continued for some time before the stirrer became frozen, indicating freezing over a temperature range. At points near the maxima or minima of the curves, however, the mass tended to freeze solid immediately after the appearance of the first crystals. This phenomenon is characteristic of systems in which compounds are formed.

The possibility of under-cooling was recognized at the beginning of the work and was found to be absent or very slight for samples except those near maxima and particularly those containing 12.5, 13.5 and 15.0% argon. The 12.5, 13.5 and 15% samples showed under-cooling by as much as 2°. Fortunately, the mass did not freeze solid and by careful manipulation, *melting points* were secured although such determinations are less accurate than are the freezing points.

Since under-cooling causes the volume to decrease and subsequent warming causes expansion, fewer points could be determined if segregation was to be avoided. Furthermore, since the decomposition pressure is relatively high and mercury freezes in the capillary at a relatively low pressure, the exact decomposition pressure is less certain than in other parts of the system. However, the isobaric graphs show maxima at about 11 and 15% argon and the points plotted in Fig. 7 in this region are probably correct in relation to each other although it is possible they should be located at a slightly higher temperature.

When the isobaric freezing points are plotted *versus* composition, maxima and minima appear, indicating compound formation. Isobars cannot be plotted over the whole range since only low pressures can be measured for the low argon samples, while low pressure measurements for higher argon percentages are somewhat erratic and of little importance.

Figure 7 shows what might be termed a temperature *versus* composition plot of the "stabilized system." The pressure at which the temperatures are taken is such that it is above the decomposition pressure shown on the freezing point curves. Since the temperature was found to remain constant with increase in pressure within the experimental limits, Fig. 7 may be considered as drawn from the data by extrapolating the temperature upward to a pressure sufficiently high to be above the decomposition pressure for all of the compounds. This seems a reasonable method of drawing the diagram and should introduce only a small error due to the actual slope of the line drawn as vertical. This diagram is probably more truly representative of the system than are isobaric graphs since in the former graph, the only constituents present in appreciable quantities are $A\cdot xBF_3$ and $A\cdot x'BF_3$. In the isobaric graphs, below the inflection points, complexities are certain to be introduced due to unpredictable pressure effects on the complex equilibrium

$$A\cdot xBF_3 \rightleftharpoons A + nBF_3 \rightleftharpoons A\cdot x'BF_3$$

The stabilized diagram, together with the isobaric diagrams, shows that maxima are found corresponding to the ratios $A\cdot BF_3$, $A\cdot 2BF_3$, $A\cdot 3BF_3$, $A\cdot 6BF_3$, $A\cdot 8\ BF_3$ and $A\cdot 16BF_3$, indicating compound formation. While the range in melting points exhibited is small similar short excursions between maxima and minima are known in other systems yielding compound formation.

In the case of certain samples, as the pressure increased, a phenomenon occurred which seems best described as retrograde immiscibility. A second liquid layer, immiscible with the first, appeared as in region C, Figs. 5–6, near 35 atmospheres. Although complete miscibility would probably again be secured if the pressure were increased sufficiently, this could not be determined due to experimental difficulties. That it is not inhomogeneity of the sample, prior to the appearance of the second layer, is evidenced by the fact that while the second layer increases in volume, the first layer also increases in volume, to a comparable extent. Second liquid layers probably formed in all samples where the pressure was sufficiently high (about 35 atmospheres) although their presence was not realized since they were hidden by the electromagnet.

This explains the break in several of the freezing point curves. The first vertical line is the normal freezing point. The second line occurs after the second liquid layer has appeared. That the freezing point should change seems entirely reasonable since formation of a second immiscible layer might change the composition of the first liquid. Since a very slight pressure change caused all the vapor to liquefy, a close study of this region could not be made.

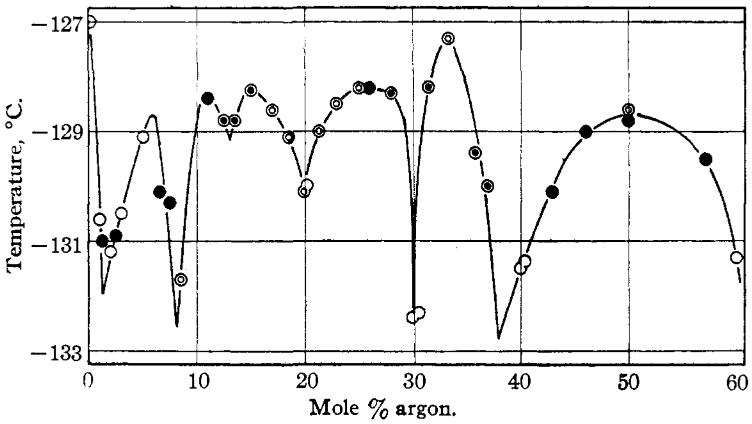
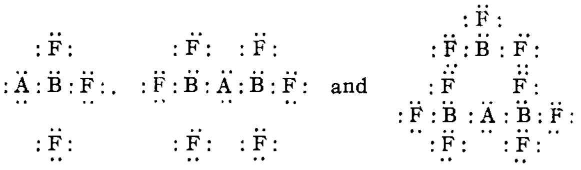


Fig. 7.—Freezing points of the stabilized system: B, ○; C, ◎; D, ●; E, ◉.

Furthermore, from about 30 to 37 atmospheres, erratic points were found in some cases indicating a metastable state in which the system was undergoing some decided change. For some samples in this pressure region, a light foam appeared on the surface of the liquid on stirring. When the second meniscus appeared the foam disappeared.

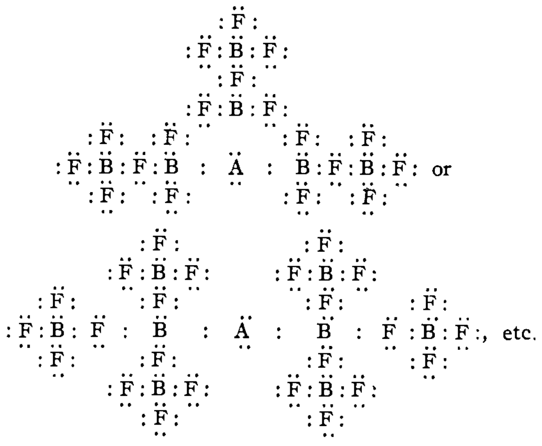
The absence of a maximum at 20% argon (Fig. 7) is surprising at first thought but may possibly be due to steric hindrance or may exist but require closer detailed study in this region to reveal it.

The compounds $A \cdot BF_3$, $A \cdot 2BF_3$ and $A \cdot 3BF_3$ doubtless are formed by coördinate links in which the argon donates electrons to complete the boron octet



$$\begin{array}{c} :F: \\ :A:B:F: \\ :F: \end{array}, \quad \begin{array}{ccc} :F: & & :F: \\ :F:B & :A: & B:F: \\ :F: & & :F: \end{array} \quad \text{and} \quad \begin{array}{ccc} & :F: & \\ & :F:B:F: & \\ :F & & F: \\ :F:B & :A: & B:F: \\ :F: & & :F: \end{array}$$

In this and other investigations in this Laboratory it has been noticed that liquid boron trifluoride at vapor pressures between five and ten atmospheres becomes viscous, indicating association. The compounds $A \cdot 6BF_3$, $A \cdot 8BF_3$ and $A \cdot 16BF_3$ doubtless contain boron trifluoride molecules linked directly to the argon atom as above and the rest of the boron trifluoride linked to these inner boron trifluoride molecules *via* their fluorine atoms,[11] *i. e.*



$$\begin{array}{ccccc} & & :F: & & \\ & & :F:B:F: & & \\ & & :F: & & \\ & & :F:B:F: & & \\ :F: \; :F: & & & & :F: \; :F: \\ :F:B:F:B & : & A & : & B:F:B:F: \\ :F: \; :F: & & & & :F: \; :F: \end{array} \quad \text{or}$$

$$\begin{array}{ccccccccc} & & :F: & & & & :F: & & \\ & & :F:B:F: & & & & :F:B:F: & & \\ :F: & & :F: & & & & :F: & & :F: \\ :F:B: & F: & B & : & A & : & B & :F: & :B:F: \\ :F: & & :F: & & & & :F: & & :F: \\ & & :F:B:F: & & & & :F:B:F: & & \\ & & :F: & & & & :F: & & \end{array}, \text{ etc.}$$

Another explanation of the compounds $A \cdot 6BF_3$, $A \cdot 8BF_3$, $A \cdot 16BF_3$ is that the "excess" BF_3 groups are merely located in the crystal lattice in more or less symmetrical arrangements.[12] The writers

---

[11] Lewis, "Valence and the Structure of Atoms and Molecules," The Chemical Catalog Co., New York City, 1923, page 99.

[12] Sidgwick "The Electronic Theory of Valency," Oxford University Press, London, 1929, pp. 186–187 and 199.

feel, however, that the evidence points to the first explanation analogous to that of Sidgwick (*loc. cit.*, p. 199) for excessive hydration by polymerized water molecules.

Undoubtedly the system krypton–boron trifluoride will show stabler compounds and the system xenon–boron trifluoride still stabler. Investigations of these systems are already under way and will be reported as soon as possible.

Summary

Study of the system boron trifluoride–argon has shown that:

1. The freezing point of any mixture increases with increase in pressure up to a certain value and is in general little affected by any further pressure increase, indicating an equilibrium $A + xBF_3 \rightleftharpoons A{\cdot}xBF_3$ or $A{\cdot}xBF_3 + yBF_3 \rightleftharpoons A{\cdot}(x + y)BF_3$.

2. A graph of the freezing points *versus* composition exhibits maxima and minima, the maxima corresponding to the ratios $A{\cdot}BF_3$, $A{\cdot}2BF_3$, $A{\cdot}3BF_3$, $A{\cdot}6BF_3$, $A{\cdot}8BF_3$ and $A{\cdot}16BF_3$, indicating compound formation. These compounds are unstable and dissociate above their melting points. From the shape of the curve the ratio $A{\cdot}2BF_3$ appears to be the stablest.

3. The freezing points of the argon–boron trifluoride mixtures of compositions approximating that of the maxima and minima were sharp and immediately complete while intermediate compositions melted over a range of temperatures. This is typical of systems in which compounds are formed.

4. At pressures in the neighborhood of 35 atmospheres, a second liquid layer appears which is probably best explained as retrograde immiscibility.

CLEVELAND, OHIO RECEIVED JUNE 19, 1935

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

Critical Phenomena of the System Argon–Boron Trifluoride[1]

BY HAROLD SIMMONS BOOTH AND KARL STUART WILLSON

In view of the fact that thermal analysis of the system argon–boron trifluoride[2] showed maxima indicating compound formation, it was thought interesting to see whether or not this tendency would result in abnormalities in the critical phenomena.

The gases were purified and samples prepared as previously described.[2] Temperatures were measured by the Leeds and Northrup Micromax potentiometer using a two-junction copper–constantan thermocouple with ice as reference point. The couple was calibrated at the ice and carbon dioxide snow point and the calibration curve drawn through these points guided by the theoretical curve. Temperatures are subject to a maximum error of ±0.4°.

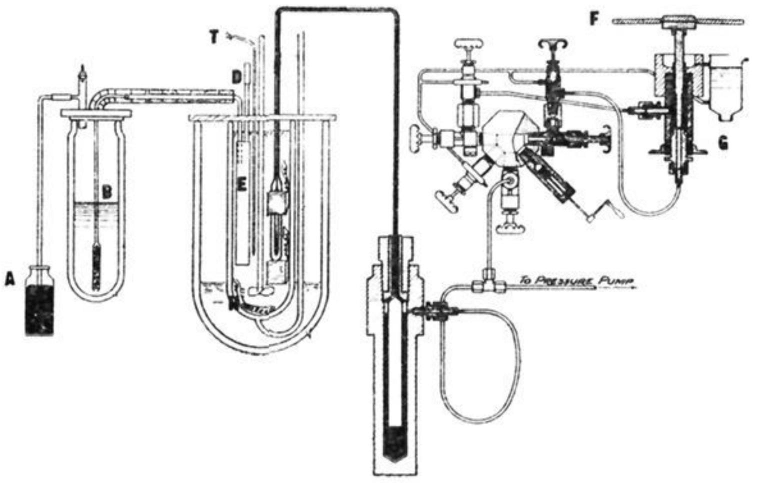


Fig. 1.—Critical apparatus.

The thermostat (Fig. 1) consisted of a pint Dewar flask set in a gallon Dewar. The temperature of the thermostat was controlled in either of two ways. For temperatures down to −85°, alcohol was used as the bath liquid and cooling was effected by placing liquid nitrogen in the outer Dewar. The rate of cooling of the bath was controlled by the depth of the liquid nitrogen in the outer bath and also by adjustment of the vacuum of the inner Dewar. The control contacts on the recording potentiometer were adjusted to close the relay heating circuit and warm the bath by means of the coil (H) when the bath cooled below the desired temperature. By adjusting the rate of cooling and the heating circuit, the bath temperature could be held within the limits of sensitivity of the recorder (±0.2°) for determination of the critical constants of the mixtures. For critical constants of pure boron trifluoride, manual control and observation of a calibrated mercury thermometer permitted an accuracy of ±0.05°.

---

[1] From a part of a thesis submitted by K. S. Willson to the Graduate Faculty of Western Reserve University, May, 1935, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Booth and Willson, THIS JOURNAL, **57**, 2273 (1935).